ISSN 0021-9673

VOL. 710 NO. 1 25 AUGUST 1995

Chromatography and Electrophoresis in Environmental Analysis: Air Pollution

JOURNAL OF CHROMATOGRAPHY A

INCLUDING ELECTROPHORESIS AND OTHER SEPARATION METHODS

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JOURNAL OF CHROMATOGRAPHY A

INCLUDING ELECTROPHORESIS AND OTHER SEPARATION METHODS

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Publication information. *Journal of Chromatography A* (ISSN 0021-9673): for 1995 Vols. 683–714 are scheduled for publication. *Journal of Chromatography B: Biomedical Applications* (ISSN 0378-4347): for 1995 Vols. 663–674 are scheduled for publication. Subscription prices for *Journal of Chromatography A*, *Journal of Chromatography B: Biomedical Applications* or a combined subscription are available upon request from the publisher. Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by surface mail except to the following countries where air delivery via SAL is ensured: Argentina, Australia, Brazil, Canada, China, Hong Kong, India, Israel, Japan, Malaysia, Mexico, New Zealand, Pakistan, Singapore, South Africa, South Korea, Taiwan, Thailand, USA. For all other countries airmail rates are available upon request. Claims for missing issues must be made within six months of our publication (mailing) date. Please address all your requests regarding orders and subscription queries to: Elsevier Science B.V., Journal Department, P.O. Box 211, 1000 AE Amsterdam, Netherlands. Tel.: (+31-20) 485 3642; Fax: (+31-20) 485 3598. Customers in the USA and Canada wishing information on this and other Elsevier journals, please contact Journal Information Center, Elsevier Science Inc., 655 Avenue of the Americas, New York, NY 10010, USA, Tel. (+1-212) 633 3750, Telefax (+1-212) 633 3764.

Abstracts/Contents Lists published in Analytical Abstracts, Biochemical Abstracts, Biological Abstracts, Chemical Abstracts, Chemical Titles, Chromatography Abstracts, Current Awareness in Biological Sciences (CABS), Current Contents/Life Sciences, Current Contents/Physical, Chemical & Earth Sciences, Deep-Sea Research/Part B: Oceanographic Literature Review, Excerpta Medica, Index Medicus, Mass Spectrometry Bulletin, PASCAL-CNRS, Referativnyi Zhurnal, Research Alert and Science Citation Index.

US Mailing Notice. *Journal of Chromatography A* (ISSN 0021-9673) is published weekly (total 52 issues) by Elsevier Science B.V., (Sara Burgerhartstraat 25, P.O. Box 211, 1000 AE Amsterdam, Netherlands). Annual subscription price in the USA US$ 5389.00 (US$ price valid in North, Central and South America only) including air speed delivery. Second class postage paid at Jamaica, NY 11431. **USA POSTMASTERS**: Send address changes to *Journal of Chromatography A*, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003. Airfreight and mailing in the USA by Publications Expediting.

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0021-9673/95/$09.50

Printed in the Netherlands

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JOURNAL OF CHROMATOGRAPHY A

VOL. 710 (1995)

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INCLUDING ELECTROPHORESIS AND OTHER SEPARATION METHODS

ELSEVIER

Amsterdam – Lausanne – New York – Oxford – Shannon – Tokyo

0021-9673/95/$09.50

Printed in the Netherlands

SPECIAL ISSUE

CHROMATOGRAPHY AND ELECTROPHORESIS IN ENVIRONMENTAL ANALYSIS

AIR POLLUTION

VOL. 710, NO. 1 JOURNAL OF CHROMATOGRAPHY A 25 AUGUST 1995

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(Abstracts/Contents Lists published in Analytical Abstracts, Biochemical Abstracts, Biological Abstracts, Chemical Abstracts, Chemical Titles, Chromatography Abstracts, Current Awareness in Biological Sciences (CABS), Current Contents/Life Sciences, Current Contents/Physical, Chemical & Earth Sciences, Deep-Sea Research/Part B: Oceanographic Literature Review, Excerpta Medica, Index Medicus, Mass Spectrometry Bulletin, PASCAL-CNRS, Referativnyi Zhurnal, Research Alert and Science Citation Index)

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JOURNAL OF CHROMATOGRAPHY A

Foreword

The warm reception which greeted our Special Issue on "Chomatography in Environmental Analysis" [*Journal of Chromatography*, Vols. 642 and 643 (1993)] has prompted us to invite some of the leaders in that field to present a closer look at its individual branches. This issue deals with air pollution, the next one will cover water pollution, and so on.

Having lived in Pasadena, California, a town which practically invented smog, in the sixties, I derive a personal satisfaction from this contribution to the fight against a scourge which has caused so much misery. It was then and there that the scientific attack on this problem started. Ronald Reagan, then governor of California, had appointed the eminent biochemist A.J. Haagen-Smit at the California Institute of Technology to head a group of scientists in an investigation of the causes of smog with the object of recommending remedial legislation. Haagy, whom we at Caltech dubbed the "Czar of the Smog", indeed identified automobile exhaust as the main culprit and elucidated the mechanism of atmospheric interactions, but legislation to curb the emission of noxious fumes was still a long way off under Governor Reagan.

Much has happened in atmospheric research and pollution abatement since the sixties, and this issue focuses on the current analytical methods, which now form the basis of governmental regulations. The most common and most dangerous pollutants, the polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are treated separately, followed by exhaust fumes from automobiles, incinerators, and various industrial operations. These two sections are preceded and followed by sections on theoretical and technical aspects of environmental analysis. Armed with such methods of determining the nature and extent of air pollution, government authorities will now only need to set and enforce air quality standards to ensure a healthier atmosphere.

Orinda, CA, USA Erich Heftmann

SSDI 0021-9673(95)00462-9

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Review

Trace enrichment methods for the determination of organic pollutants in ambient air

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Abstract

The sampling and analysis of organic compounds in air remain a challenge. Air is a matrix very difficult to handle. In addition, the pollutants are usually present at very low concentrations; so, their detection and quantitation require a preconcentration step. This paper describes the enrichment methods that may be used for the accurate monitoring of pollutants in ambient air.

Many techniques can be used to collect air samples. The simplest way is to use special containers, but this procedure is expensive and time-consuming. The adsorption of pollutants on adsorbents faces a growing interest, despite the difficulty to choose the appropriate support in order to obtain quantitative yields. To overcome this problem, two or three types of adsorbents may be used in series for collecting a wide range of analytes. In addition, the miniaturization of these techniques (i.e. microtraps and solid-phase microextraction) is also very promising: easy to handle, low cost, no solvent required, detection limits at the ppt level when sensitive detectors are used.

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1. Introduction

For several years, there has been a growing interest in the protection of our atmosphere. As a consequence, air pollution needs to be strictly and carefully controlled. This requires accurate analytical procedures.

As a matter of fact, air is probably the most difficult environmental matrix to sample. It is a heterogeneous system of gases, liquids (aerosols) and solid particles. Besides, its composition continuously evolves. Pollutants not only diffuse and move, but they also chemically react in the atmosphere; this eventually can lead to secondary pollutants much more toxic than the initially emitted compounds. Consequently, air pollution is very difficult to control.

A monitoring device of air pollution should fulfil at least three conditions: (1) the air sampled needs to be representative; (2) the procedure should be very simple to be performed in any region (even when no electric power supply is available); (3) no degradation or losses between sampling and analysis may occur.

Also, due to the low concentrations of pollutants in the atmosphere, an enrichment step is often required in order to reach acceptable detection limits.

2. Whole-air sampling

The simplest way to collect air samples is to use special containers. The samples are later analysed by gas chromatography (GC), either by direct injection, or in combination with a preconcentration step. The latter method offers a better sensitivity, which is very useful when dealing with trace components.

The most widely used sampling vessels are plastic bags and glass or stainless-steel containers.

2.1. Plastic bags

Polymer bags (usually Teflon, Tedlar or aluminised Tedlar) are very simple to use and can allow 10 to 100 l of air to be sampled. However, filling the bags requires the air sample to be pumped in, which may add a potential source of contamination.

2.2. Glass or stainless-steel containers

A simple glass container can be used for sampling air. As an example, a 1-l glass bottle sealed with a poly(tetrafluoroethylene) (PTFE) plug equipped with a PTFE stopcock was used for sample collection of car exhausts (prior to sampling, air within the bottle was evacuated with a vacuum pump) [1]. Trace volatile aldehydes were further determined by GC, after their derivatization to thiazolidine derivatives [1].

Stainless-steel containers have also been frequently used. These recipients (called "canisters") entail less contamination problems than polymer bags, but they are more expensive. Prior to their use, the canisters have to be carefully pretreated and conditioned, in order to avoid contamination or surface losses. Besides, minimising of the active surface area is also essential [2]; this can be achieved by electropolishing.

The volume of containers is limited to a few litres, unless the samples are pressurised to allow larger amounts of air to be collected [3].

A passivated canister is an ideal container for volatile and apolar species. Accurate representation of the air under investigation can be obtained, provided it can be effectively cleaned. For example, the United States Environmental Protection Agency canister method TO-14 coupled with gas chromatography–mass spectrometry (GC–MS) analysis, allowed the monitoring of volatile organic compounds (VOCs) in urban air [4]. The samplers were operated in a passive mode (i.e. vacuum filling) to eliminate the pump as a potential source of contamination or air leaks.

These samplers offer several advantages that make them attractive in air analysis. The actual air sample is collected without any breakthrough; in addition, no degradation of the trapping materials takes place, and moisture has no effect upon the sampling. Finally, several analyses of the sample can be performed.

However, they present major drawbacks: they require complex sampling apparatus, severe clean-up procedures between samples, and they are expensive to transport. In addition, to achieve acceptable sensitivity, air contained within canisters needs to be preconcentrated (using either a cold trap or a cryofocussing device) if trace components have to be monitored [5,6]. The trapped analytes are then thermally desorbed and transferred into the GC column, as illustrated in Fig. 1 [5]. In some particular cases, a second cryogenic system can be added, to provide narrower bands before the capillary column [3,7].

3. Collection in a solvent or on impregnated surfaces

3.1. Collection in a solvent

For solvation-based sampling, the sample is bubbled (using a pump) through a volume of solvent in a recipient (called an "impinger" or a "bubbler") where the analyte is dissolved. To enhance the liquid transfer of the solutes, the air bubbles have to be as small as possible. For that reason, several types of bubblers have been designed [8,9]. To protect the pump against the solvent vapours inside the impinger, a trap filled with methanol–dry ice can be used [10,11].

This technique is very simple to perform and allows large volumes of air to be sampled. To avoid losses, the solvent needs to have a high boiling point. Besides, collection can be performed by using two bubblers in series. Using this system and further GC analysis, determination of trace amounts of epichlorohydrin in workplace atmospheres could be achieved with a high sensitivity (0.05 $\mu g\ ml^{-1}$) [12].

By adding a specific reactant to the collection solvent, chemisorption takes place. This proved to be effective for the direct detection of low-molecular-mass aldehydes in automobile exhaust gas [13]. In that example, 2,4-dinitrophenylhydrazine (2,4-DNPH) and an acidic catalyst were added to the solvent. Simultaneous sample collection and derivatization took place within the impinger. An aliquot of the solution was then injected into a liquid chromatograph (LC), without any extraction or concentration step; 2,4-

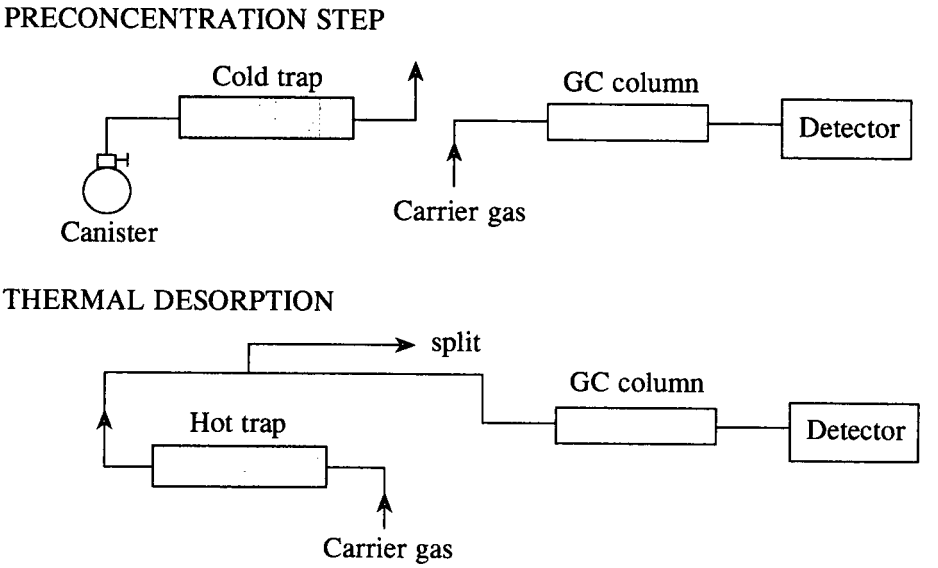

Fig. 1. Schematic representation of the transfer of canister-air samples to the gas chromatograph, using a preconcentration step and a thermal desorption. From Ref. [5].

DNPH and its derivatives were identified by ultraviolet (UV) and mass spectrometric detection.

3.2. Collection on impregnated surfaces

Glass tubes can be used to fix a sorptive agent (they are called "wet denuders") [14]. The inner wall of the tube has to be treated to maintain a compact film of liquid. Before sampling, the tube is placed vertically to assure correct operation. Then, a film of absorbing liquid flows continuously down the inner wall of the denuder, while gas passes counter-currently and, in this way, a continuous stream of concentrated analytes is obtained at the bottom of the tube. The concentrate can be analysed directly.

This system was employed for the monitoring of 2,4,5-trichlorophenol [14]. A 50-cm length tube, with water as the liquid, allowed a collection efficiency greater than 99% for an air flow-rate of 0.5 l min^{-1}. A similar system gave 40–60% collection efficiencies (flow-rate of 0.6–0.7 l min^{-1}) for airborne cocaine and heroin [15].

Annular denuders have also been designed: they consist of an outer and an inner glass tube, held in coaxial position. Such a sampler, coated with 2,4-DNPH, was investigated for the collection of C_1–C_3 aldehydes in air and exhaust gas [16].

In practice, wet denuders offer a continuously renewed collection surface, a rapidly obtainable concentrate of solutes, and the possibility of direct analysis. They are especially useful in detecting and quantitating compounds that cannot be analysed by conventional preconcentration with GC (i.e. polar or highly reactive analytes).

4. Cryotrapping

Cryotrapping (or cryogenic concentration) is the technique of choice in several studies of air samples [17]. Most of the time, no adsorbents

are used in cryotraps, which allows desorption at moderate temperatures (40–70°C), thus avoiding interferences arising from solutes thermal degradation [18]. Addition of a second cryotrap, just at the entry of the chromatographic column, is necessary to give narrow chromatographic bands, compatible with a capillary analytical column.

A possible cryogenic trap consists of a U-shaped borosilicate glass tube immersed in liquid argon. The lower portion of the tube is packed with quartz wool to increase the contact surface. Ambient air samples are collected by connecting the trap to a portable pump. Air volumes of 1 to 10 l were drawn through the trap at flow-rates of 0.15–0.30 l min^{-1}. For instance, volatile sulphur compounds were preconcentrated with this system, then desorbed at 60–70°C, and finally cryofocussed in a second trap immersed in liquid argon, and injected in a GC [17]. Detection limits less than or equal to 10 pg of sulphur per litre of air were achieved for individual compounds.

Another reported trap consisted of a U-shaped stainless-steel tube packed with 60–80 mesh untreated glass beads [7]. Frits (1 μm) and silanized glass-wool were placed at both ends of the tube to keep the glass beads in place. Again, liquid argon (− 186°C) was used to cool the trap. After sampling air, the tube was heated to 100°C and the sample was swept with helium in a cryofocussing device prior to the GC. With this system, urban measurements of hydrocarbons (C_2–C_{10}) could be made (concentrations ranging from several ppt to 100 ppb by volume in air samples). The resulting chromatogram is presented in Fig. 2 [7].

In practice, high water content in air causes a lot of problems when using cryotrapping. For example, plugging frequently occurs; also, when the trap is heated, water collected on the trap may be transferred to the GC column, which affects the analytes separation. They can be eliminated by placing a drying tube before the cryogenic trap to remove air humidity [6,18].

As a consequence, most of the time, cryotrapping serves as a cryofocussing mechanism, in conjunction with solid adsorption–thermal desorption.

5. Collection onto adsorbents

Sampling on adsorbents allows larger volumes than with canisters to be collected [19]; besides, adsorbents are easier to handle than canisters.

This technique can be applied using two distinct modes: passive or active [2,8]. Whatever the mode, the concentrated analytes may be recovered with either thermal desorption or liquid extraction. Each method will be briefly discussed below, after which the main characteristics of common solid sorbents will be detailed.

Usually, a cryofocussing trap is needed before the GC analysis, to entail narrow bands entering the capillary columns, and thus good resolutions [20].

5.1. Nature of the adsorbents

Usually, porous polymers are the best choice. However, when a higher capacity is needed, activated carbon and graphitized carbon blacks should be used.

5.1.1. Activated carbon, graphitized carbon blacks and carbon molecular sieves

5.1.1.1. Activated carbon

Activated carbon is prepared by low-temperature oxidation of vegetable charcoal. This material has a large specific surface area (300–2000 $m^2 g^{-1}$), a high thermal stability (up to 700°C), and a heterogeneous surface containing active functional groups (including phenolic, carboxylic, quinone and lactone groups). It was firstly used to trap volatile organic compounds in ambient air [21]. Anyway, its use failed because of several problems encountered: adsorption of water, irreversible adsorption and/or degradation of the analytes, high desorption temperature required (the latter can be overcome by using solvent extraction instead of thermal desorption). When dealing with trace components,

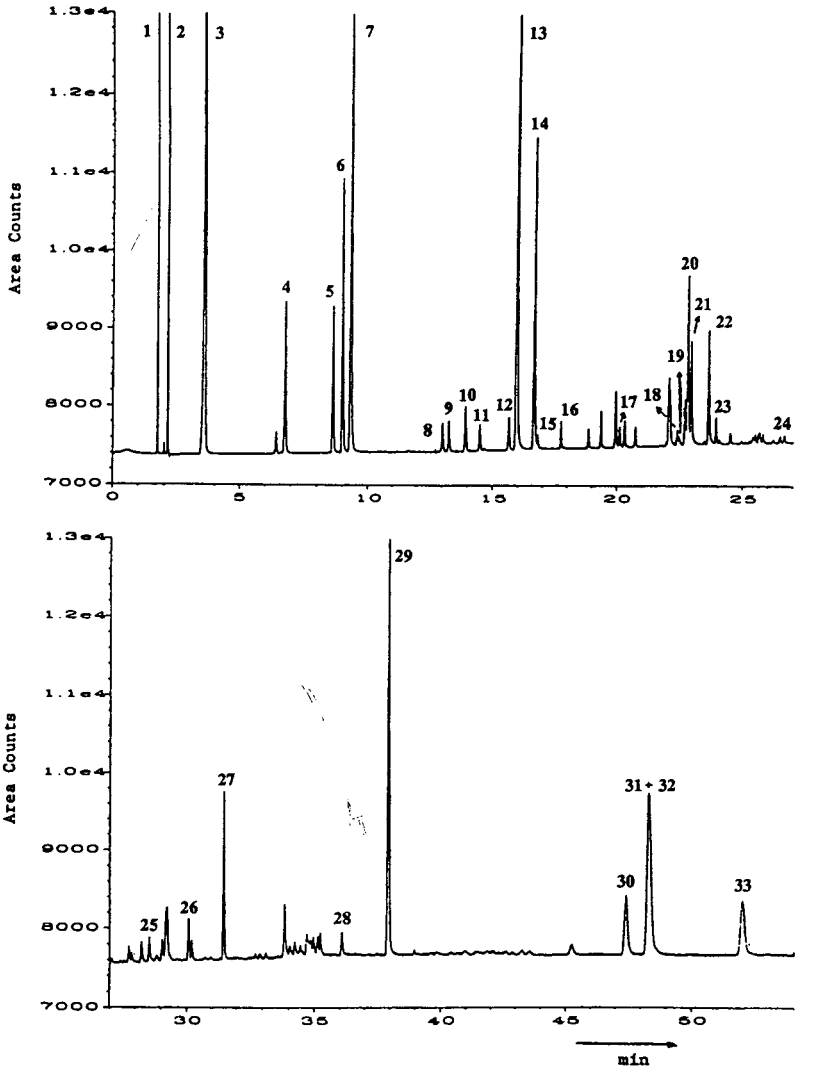

Fig. 2. Separation of urban air pollutants (sampling site Toronto, Bay street; sampling volume 640 ml). Peaks: 1 = ethane; 2 = ethylene; 3 = propane; 4 = propene; 5 = isobutane; 6 = acetylene; 7 = *n*-butane; 8 = *trans*-2-butene; 9 = 1-butene; 10 = isobutene; 11 = *cis*-2-butene; 12 = cyclopentane; 13 = isopentane; 14 = *n*-pentane; 15 = propyne; 16 = 1,3-butadiene; 17 = 1-pentene; 18 = cyclohexane; 19 = butyne; 20 = 2-methylpentane; 21 = 3-methylpentane; 22 = *n*-hexane; 23 = isoprene; 24 = 1-hexene; 25 = methylcyclohexane; 26 = *n*-heptane; 27 = benzene; 28 = *n*-octane; 29 = toluene; 30 = ethylbenzene; 31 = *m*-xylene; 32 = *p*-xylene; 33 = *o*-xylene. GC conditions: Al_2O_3-KCl porous-layer open tubular (PLOT) column (50 m × 0.32 mm I.D., 5-μm film thickness); temperature programme 35°C (2 min), increased at 5°C min^{-1} to 200°C, 22 min isothermal; carrier gas (helium) linear velocity 56.84 cm s^{-1}. From Ref. [7].

these drawbacks are accentuated, leading to low recovery and artefacts.

To minimize these problems, graphitized carbon blacks may be used [22].

5.1.1.2. Graphitized carbon blacks

These are non-specific, non-porous adsorbents, with a high surface homogeneity and hydrophobic properties. Indeed, the graphitiza-

tion process eliminates the specific adsorption sites and hinders the formation of hydrogen bonds. As a consequence, very polar and small molecules (like water) are not strongly adsorbed. These materials differ in their surface area and the extent of graphitization: the larger the graphitization, the smaller the surface area, which ranges between 6 and 100 $m^2 g^{-1}$.

Carbotrap and Carbotrap C graphitized carbon blacks are ideal adsorbents for trapping a wide range of airborne organic compounds (from C_4–C_5 hydrocarbons to polychlorinated biphenyls, polynuclear aromatics and other large molecules). Due to their hydrophobic nature, they enable accurate samples to be obtained, despite a high relative humidity. Because of its higher surface area (100 $m^2 g^{-1}$), Carbotrap can be used to trap many C_4–C_8 compounds, while Carbotrap C (10 $m^2 g^{-1}$) is preferred for trapping larger airborne organic compounds.

Carbopack B and C are the same adsorbents as Carbotrap and Carbotrap C, respectively, but in the 60–80 mesh size instead of 20–40 mesh. Carbopack graphitized carbon blacks can be used for C_1 to C_{10} compounds, including alcohols, free acids, amines, ketones, phenols and aliphatic hydrocarbons.

Table 1
Main characteristics of graphitized carbon blacks and carbon molecular sieves used for preconcentration of trace organic volatiles (from Ref. [23])

Sorbent	Surface area ($m^2 g^{-1}$)	Temperature limit (°C)
Activated carbon		
Activated coconut charcoal	1070	220
Graphitized carbon blacks		
Carbotrap		
Carbotrap	100	400
Carbotrap C	10	400
Carbopack		
Carbopack B	100	>400
Carbopack C	10	>400
Carbopack F	5	
Carbon molecular sieves		
Carbosieve		
Carbosieve G	910	225
Carbosieve S-III	820	400
Carboxen		
Carboxen 563	510	400
Carboxen 564	400	400
Carboxen 569	485	400
Carboxen 1000	1200	400
Carboxen 1004	1100	225

5.1.1.3. Carbon molecular sieves

Carbon molecular sieves are designed for the analysis of permanent gases and light hydrocarbons. For instance, Carbosieve S-III is well suited to the trapping of small airborne molecules such as C_2 hydrocarbons. Carboxen 563 and 564 allow the monitoring of many C_2–C_5 volatile organic compounds (Carboxen 563 having a lower capacity than Carboxen 564); Carboxen 569 has the highest capacity for organic molecules and the lowest capacity for water.

The main features of these sorbents are reported in Table 1 [23].

5.1.2. Porous polymers

The most commonly used porous polymers are reported below; their characteristics are summarized in Table 2 [23].

5.1.2.1. Tenax

Tenax GC has been widely used, in spite of its limited specific surface area (19–30 $m^2 g^{-1}$), because of its high temperature limit (450°C). This adsorbent is well suited to the collection of high-to-intermediate volatility organic compounds. Thus, it is efficient for C_6–C_{14} hydrocarbons (at room temperature). Selected monoterpenes could be monitored using this material [24]. It presents the advantage of not retaining water. But it can undergo chemical decomposition in highly oxidizing atmospheres (i.e. in the presence of reactive gases such as O_3 and NO_2), generating benzaldehyde and other oxygenated components which can interfere with the GC determination. Besides, degradation of reactive analytes during sampling may be a serious inconvenient [25].

Tenax TA differs from Tenax GC only in

Table 2
Main characteristics of porous polymers used for preconcentration of trace organic volatiles (from Ref. [23])

Sorbent	Composition	Surface area ($m^2 g^{-1}$)	Temperature limit (°C)
Tenax			
Tenax GC	Poly (2,6-diphenyl-*p*-phenylene oxide)	19–30	450
Tenax TA	Poly (2,6-diphenyl-*p*-phenylene oxide)	35	300
Tenax GR	Poly (2,6-diphenyl-*p*-phenylene oxide) with 23% graphitized carbon		350
Chromosorb			
Chromosorb 101	Styrene-divinylbenzene copolymer	350	275
Chromosorb 102	Styrene-divinylbenzene copolymer	350	250
Chromosorb 103	Cross-linked polystyrene	350	275
Chromosorb 104	Acrylonitrile-divinylbenzene copolymer	100–200	250
Chromosorb 105	Polyaromatic type	600–700	250
Chromosorb 106	Polystyrene	700–800	225
Chromosorb 107	Polyacrylic ester	400–500	225
Chromosorb 108	Cross-linked acrylic ester	100–200	225
Porapak			
Porapak N	Polyvinylpyrrolidone	225–350	190
Porapak P	Styrene-divinylbenzene copolymer	100–200	250
Porapak Q	Ethylvinylbenzene-divinylbenzene copolymer	500–600	250
Porapak R	Polyvinylpyrrolidone	450–600	250
Porapak S	Polyvinylpyridine	300–450	250
Porapak T	Ethylene glycol dimethyl adipate	250–350	190
HayeSep			
HayeSep A	Divinylbenzene-ethylene glycol dimethacrylate copolymer	526	165
HayeSep D	Divinylbenzene polymer	795	290
HayeSep N	Divinylbenzene-ethylene glycol dimethacrylate copolymer	405	165
HayeSep P	Styrene-divinylbenzene copolymer	165	250
HayeSep Q	Divinylbenzene polymer	582	275
HayeSep R	Divinylbenzene-N-vinyl-2-pyrrolidone copolymer	344	250
HayeSep S	Divinylbenzene-4-vinyl-pyridine copolymer	583	250
Amberlite resins			
XAD-2	Styrene-divinylbenzene copolymer	300	200
XAD-4	Styrene-divinylbenzene copolymer	750	150
XAD-7	Polymethacrylate resin	450	150
XAD-8	Polymethyl-methacrylate resin	140	150

reduced column bleeding [26]. It has very low levels of potentially interfering substances such as aromatic hydrocarbons. It is also suitable for use with highly volatile compounds [27,28]. For example, C_2–C_4 halocarbons [29] and C_6–C_9 hydrocarbons [30] were retained on Tenax TA. Also, chlordane, an insecticide, was determined in ambient air using sampling tubes packed with Tenax TA [31].

Tenax GR is a recent adsorbent for trapping low-molecular-mass organic solutes. It consists of a Tenax matrix having 23% graphitized carbon.

Sampling volumes are greater than with Tenax GC or Tenax TA (values about twice higher) [32].

5.1.2.2. Chromosorb series

Eight types of Chromosorb porous polymers are commercially available, as indicated in Table 2 (Chromosorb 101–108).

5.1.2.3. Porapak series

In the series, Porapak Q has the highest specific surface area. Several applications of this polymer have been reported [20,33–35].

5.1.2.4. HayeSep series

These are porous polymers. HayeSep N, P, Q, R, S, T are interchangeable with the corresponding Porapak polymers for separating low-molecular-mass mixtures containing halogenated or sulphur-containing compounds, water, alcohols, glycols, free fatty acids, esters, ketones, or aldehydes.

HayeSep A should be used at ambient temperature for permanent gases (hydrogen, nitrogen, oxygen, argon, carbon monoxide, nitric oxide), and at higher temperatures for C_2 hydrocarbons, hydrogen sulphide, or water.

HayeSep D is a new polymer, with a very high purity. Its specific surface area is very large (795 $m^2 g^{-1}$) and its maximal operating temperature is high (290°C).

5.1.2.5. Amberlite XAD resins

Amberlite XAD resins are non-ionic macroreticular resins. They adsorb and release species based on hydrophobic or hydrophilic interactions. As with other polymers such as Porapaks and Chromosorbs, only adsorption on the surface occurs.

Amberlite XAD-2 and XAD-4 resins are aromatic in character, very hydrophobic and possess no ion-exchange capacity. For example, Amberlite XAD-4 is particularly effective in adsorbing relatively low-molecular-mass hydrophobic organic compounds.

Amberlite XAD-7 and XAD-8 are acrylic esters resins with a very low ion-exchange capacity. They are more hydrophilic than the other two resins; as a consequence, they show a higher adsorptive capacity for polar solutes.

Due to their instability on heating, desorption is usually performed by liquid extraction.

5.1.2.6. Polyurethane foam

This sorbent is well suited to the collection of non-volatile analytes using high sampling flow-rates [25]. For example, it was used for the sampling of airborne pesticides and polychlorinated biphenyls [25,36–40]. It is convenient to handle and inexpensive, but exhibits breakthrough of semivolatile and volatile compounds [41].

The choice of the appropriate material is not easy, as it strongly depends on the sample and on the components to be collected. For non-volatile and strongly adsorbed compounds, sample recovery remains the limiting step; on the opposite, very volatile solutes may pass through the sorbent bed without being trapped. Also, the adsorbent must avoid irreproducible results, as well as contamination.

Activated carbon is generally too strong and causes lots of problems; thus, its use should be avoided. Tenax matrices and porous polymers have been successful for a broad range of applications. They have a characteristically low capacity for water, but oxidizing atmospheres should be avoided while working at elevated temperatures. When dealing with very volatile compounds, graphitized carbon blacks or carbon molecular sieves should be preferred, because they show a far better performance than other sorbents such as activated carbon and porous polymers (however they have the drawback of retaining water).

5.2. Sampling mode

5.2.1. Passive sampling (or diffusive sampling)

The tube containing the adsorbent is exposed to the atmosphere, usually in the vertical position; the adsorption process is controlled by the adsorption properties of the sorbent and diffusion processes. This way of sampling is simpler and cheaper than active sampling. In fact, the major disadvantage of this system is that un-

stable flow-rates may be obtained during the sampling period.

Passive samplers are mainly used for the monitoring of workplace atmospheres and the control of industrial areas with potentially very high pollution levels. As an example, they have been used to quantify the exposure of operating room personal to isoflurane, an anaesthesic agent [42]. Sample tubes were packed with different sorbents: Tenax TA, Chromosorb 102 and Chromosorb 106, the latter being the strongest adsorbent in that case. The retained solute was thermally desorbed, preconcentrated in a cool trap, and GC analysed. It was found that Chromosorb 106 was a suitable adsorbent for isoflurane, as it allows a constant sampling rate independent of both time and concentration; no effect of humidity was observed.

In fact, diffusive sampling offers several advantages [43], mainly simplicity, low running costs, and the possibility to make large surveys of air pollution.

However, passive samplers face a major limitation of their use for monitoring trace components in the atmosphere. This is related to the problems of contamination and artefact formation. They are more pronounced than for active samplers because long sampling periods are required with passive samplers, due to the very low uptake rates. Besides, artefacts may form during storage.

To solve these problems, the sampling period needs to be reduced. This could be achieved by using a high-sensitivity detector (a mercuric oxide reduction gas detector) [44]. In this study, passive sampling tubes, packed with different adsorbents (Tenax TA, Tenax GR, Carbotrap or Chromosorb 106), were placed vertically and exposed for about 15 h. They were thermally desorbed and the analytes retrapped cryogenically before their GC analysis. This sensitive detector allowed the determination of VOCs in ambient air, while significantly reducing the sampling periods (8 times lower) compared with those necessary using a flame ionization detector. As an example, Fig. 3 shows representative chromatograms of samples collected onto these adsorbents [44]; concentrations vary from 0.03 ppb to 1 ppb.

5.2.2. Active sampling

Here, a defined volume of air is pumped through the adsorbent at a specific controlled flow-rate.

Care has to be taken to select the correct sorbent, in order to eliminate the risks of breakthrough during sampling as well as artefacts formation. For instance, maximum sample volumes ("breakthrough volumes") of low-molecular-mass compounds were found to be greater on Tenax GR than on Tenax TA or Tenax GC [32]. The breakthrough volumes can be very useful for estimating the amount of adsorbent required to quantitatively trap the solutes of interest for any size air sample.

By selecting sorbents having a large loadability, relatively large air volumes (< 10 l) can be sampled onto the tubes, which enables detection limits as low as 100 ppt. Hence, several adsorbents (including activated charcoals, carbon molecular sieves, porous polymers and graphitized carbons) have been investigated for the trapping of some halocarbons and hydrohalocarbons at ambient temperature [45]. While the activated carbons were too strong adsorbents, the porous polymers appeared to be the less effective for trapping these compounds. In fact, no single adsorbent was suitable. As a consequence, a combination of adsorbents was required. So, a triple-stage trap was designed, containing a porous polymer (HayeSep D) and two carbon molecular sieves (Carboxen 1000 and Carbosieve S-II). Using this system, all of the target analytes were collected from a 5-l air sample at 25°C and efficiently recovered at 200°C [45].

Multiple-packed sorbent tubes are very practical as they afford the opportunity to collect compounds of a wide volatility range. Low-volatility solutes can be retained on a moderate adsorbent, while the more volatile ones go through it; they are subsequently trapped on a stronger adsorbent. This system avoids the irreversible adsorption of low-volatility analytes on the latter sorbent. Several applications have been reported.

Using an organic polymer (Tenax TA) and graphitized carbon black (Carbosphere S), the whole C_2–C_8 fraction of hydrocarbons and

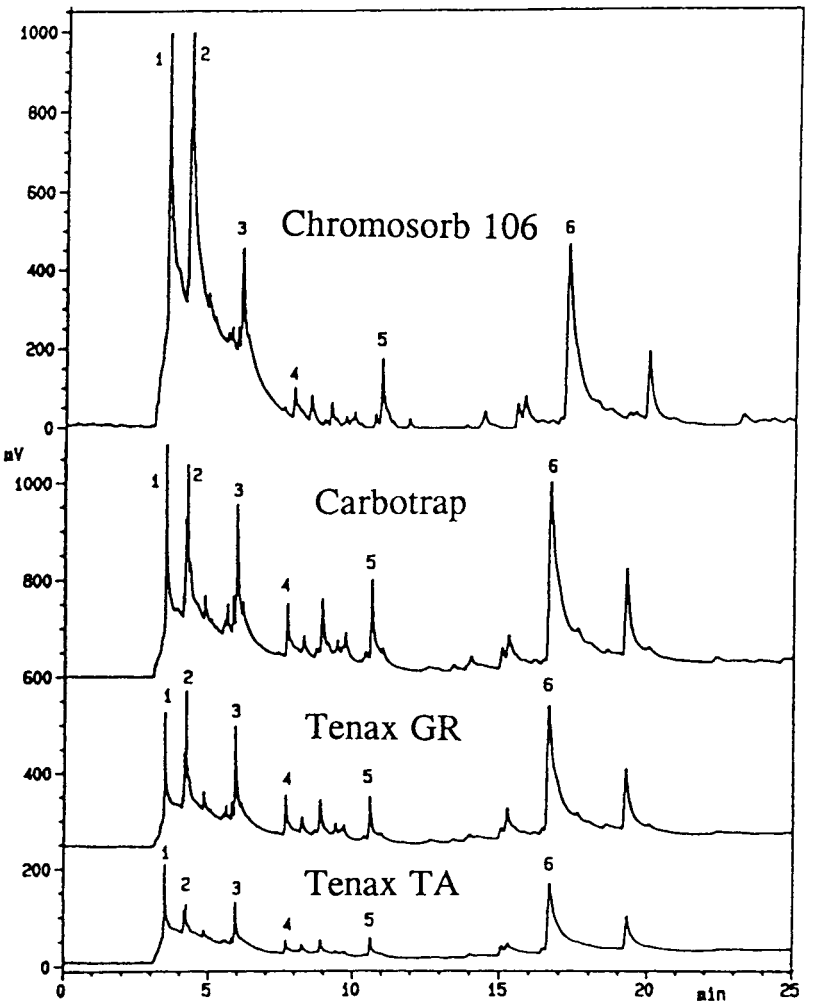

Fig. 3. Chromatograms of passive sampling of VOCs in ambient air (for about 15 h) onto different adsorbents. Peaks: 1 = propylene; 2 = 1-butene; 3 = 1-pentene; 4 = isoprene; 5 = 1-hexene; 6 = benzene. GC conditions: Al_2O_3-KCl porous-layer open tubular (PLOT) column (50 m × 0.32 mm I.D.); temperature programme 160°C (8 min), increased at 3°C min^{-1} to 180°C; carrier gas helium; mercuric oxide reduction gas detector. From Ref. [44].

halocarbons in ambient air could be collected [19]. With this combination, low-volatility solutes were adsorbed on the Tenax, while the more volatile ones were subsequently trapped on the Carbosphere S. When only C_2–C_8 hydrocarbons are of interest, triple-layer cartridges (packed with Tenax TA, Carbotrap and Carbosieve S-III) may be used. With this trapping system, tobacco smoke and vehicle-polluted urban air could be analysed [46].

The combination of carbon adsorbents of different surface area (Carbotrap C, Carbotrap and Carbosieve S-III) was employed to sample non-polar C_4–C_{14} hydrocarbons from polluted and unpolluted areas [47]. Carbotrap C (with the smallest surface area: 10 $m^2 g^{-1}$) was placed in front to retain high-boiling components and make possible their quantitative recovery without the use of high temperatures during desorption. An ambient relative humidity higher than 50% was found to entail plugging in the system, due to enrichment of water on Carbosieve S-III.

Two-stage traps containing Carbotrap C and Carbotrap particles allowed the monitoring of VOCs in ambient air [48]. A triple-packed adsorbent tube using successively carbon black and molecular sieve sorbents has also been successful for the collection of VOCs in air samples [49].

Chlorophenols could be retained on adsorbent traps containing Tenax GC sandwiched between two polyurethane foam plugs [50].

In addition, adsorbents may be cryogenically cooled during the sampling, to enable the collection of volatile analytes. As an example, −100°C appeared as the optimal trapping temperature of hydrocarbons on Porapak Q [20].

Active sampling is best suited to general environment monitoring. Numerous applications have been reported. Hence, natural VOCs (dimethyl sulphide, bromoform, isoprene and its reaction products) were monitored in the atmosphere by GC–MS, using an adsorption on Tenax TA followed by thermal desorption [51]. An excellent detection limit could be achieved: 1 to 2.4 ppt, with a sampling volume of 0.2 l.

Tenax TA was also investigated as a sorbent for the determination of an insecticide (chlordane) [31] and two herbicides (trifluralin and triallate) [52] in air samples.

5.3. Desorption mode

5.3.1. Thermal desorption

Most of the time, thermal desorption (followed by GC) is preferred. Nevertheless, this step is usually too slow for effective capillary GC, so a preconcentration step at the entry of the chromatographic column is required. As a consequence, this results in a two-stage thermal desorption process, as illustrated in Fig. 4 [8]. Most of the time, good resolution has been achieved [53].

When the analytes are too strongly adsorbed (this frequently occurs with polar solutes and strong adsorbents such as activated carbon), thermal desorption is useless to recover the compounds due to the very high temperature needed (too high a value will entail the thermal degradation of the solutes or/and the sorbent bed). In that case, it is very convenient to use liquid extraction.

5.3.2. Liquid extraction

The adsorbent is extracted with a low-boiling solvent (such as carbon disulphide, dichloromethane, benzene or pentane), mostly with Soxhlet-type extraction procedures.

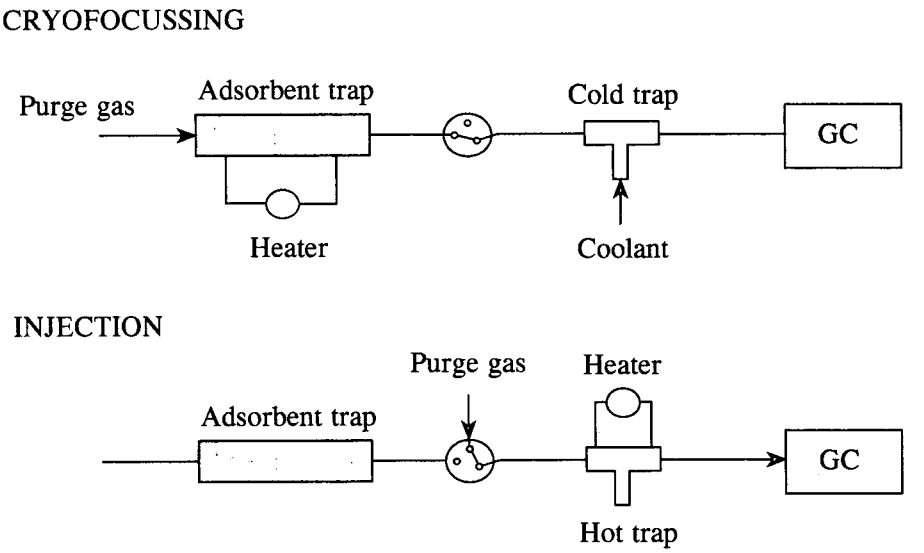

Fig. 4. Schematic representation of the two-stage thermal desorption process following passive or active sampling. From Ref. [8].

Solvent extraction allows longer sorbent beds, as well as higher flow-rates and larger total sample volumes than thermal desorption. Besides, the sample obtained can be analysed using different techniques, leading to more accurate results.

However, trace analysis requires the evaporation of part of the solvent in order to concentrate the analytes. This procedure can lead to several problems: artefacts may be introduced, either by the glassware or by the solvent; losses of volatiles can occur during the evaporation; the solvent peak in the chromatogram can mask the peaks of volatile solutes.

Sorbent tubes offer great flexibility in terms of compatibility with a wide component volatility and polarity range. Recently, automated systems have been developed [54,55]. Nevertheless, collection onto adsorbents presents its own drawbacks also. The sorbent bed may be overloaded, resulting in losses during sampling; interfering compounds may cause problems (like water). Particulates initially present in the sample may clog the system, unless a prefilter is used to remove them. Retained analytes can decompose when using thermal desorption. Finally, a cryofocussing step is required to maintain the resolution during the analysis. An alternative is to use miniaturised traps (also called "microtraps") [56–62].

5.4. Microtraps

A microtrap consists of a small-diameter tubing packed with an adsorbent. Due to their small size (about 5-cm length, with an internal diameter corresponding to the capillary analytical column: 320 to 530 μm), microtraps are well suited to GC. They can be thermally desorbed at the GC flow-rate, which minimises dilution and entails sharp peaks without any cryotrapping or cryofocussing step. Also, they can be extracted with a low volume of solvent, allowing transfer of the whole concentrated sample to the GC.

A very strong adsorbent needs to be chosen, otherwise breakthrough of the analytes will occur. For example, charcoal has been used for the GC analysis of trichloroethylene, tetrachloroethylene, benzene and toluene in 20-ml air samples [57]. Detection limits ranged between 0.05 and 3 ng l^{-1}. To retain hydrofluorocarbons (HFCs) and hydrochloro-fluorocarbons (HCFCs), a carbon molecular sieve sorbent (Carboxen) has been used [61].

Breakthrough volumes, desorption temperature and number of theoretical plates have been evaluated for microtraps containing various sorbents (Chromosorb 102, HayeSep D, Graphtrap 5, Charcoal SK4 and Carbosphere) for C_1 and C_2-halocarbons [58]. Air samples (60 ml) could be analysed by GC with a microtrap packed with HayeSep D at ambient temperature.

In addition, sampling of analytes with wide-range boiling points can be achieved using a composite microtrap, packed with two or more sorbents. Hence, a microtrap containing Carboxen 1003 (6 mg) and Carboxen 1000 (5 mg) allowed the quantitative trapping of the very volatile HFCs and HCFCs at −50°C [59].

Microtraps have a short heating–cooling cycle, which makes them attractive for on-line analysis. For example, continuous monitoring of a gaseous stream containing ppb (v/v) levels of benzene, toluene and xylene could be achieved, using a 6.5-cm long fused-silica microtrap (packed with Carbotrap C) at 22°C [62].

6. Collection onto filters

6.1. Glass-fibre filters (or quartz-fibre filters)

Such filters allow the collection of high-molecular-mass organics associated with air particulates or aerosol particles [63]. Retained analytes can be recovered by Soxhlet extraction, ultrasonic treatment or supercritical fluid extraction.

As an example, more than 140 organic compounds were determined in aeolian particulates from a coastal urban area [64]. These included *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), *n*-alkanals, 2-alkanones, *n*-alkanols and alkanoic acids. The filter had a collection efficiency higher than 99% for particulates with radius larger than 0.3 μm at 90 m^3 h^{-1}. Before

the analysis, acids were first separated by using a LC column containing silica gel, and then the neutral compounds were fractionated by flash chromatography on a silica gel column.

These filters may also be used in conjunction with other trapping materials such as solid sorbents. Hence, a sampling apparatus combined a quartz-fibre filter and two polyurethane foam plugs (PUFPs), as illustrated in Fig. 5 [65]. Ambient air was sampled at 0.6–0.7 $m^3 min^{-1}$ for 24 h. The filter and the PUFPs were each extracted with acetone in a Soxhlet extractor. After washing the recovered sample with sulphuric acid and purifying it by silica gel and alumina column chromatography, a GC–MS analysis was performed. This method has been successfully used for monitoring polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the atmosphere at ground levels [65].

In another study, a glass-fibre filter followed by a XAD-2 resin was successful in sampling chlorophenols [66].

Also, the collection and quantitation of these analytes in ambient air could be achieved using a glass-fibre filter followed by a silica gel cartridge, and further GC–MS analysis [67].

Another system was applied to the collection of organotin compounds in air [68]. Air was sampled through two quartz-fibre filters and through an activated carbon-fibre filter at 5 $l min^{-1}$ for 24 h. Each filter was then ultrasonically extracted, and the concentrated solutes analysed using GC.

These filter–sorbent systems have disadvantages. Artefacts may form, due to the adsorption of analytes on the filter or on the collected particles, and to the volatilisation of solutes from particles.

6.2. PTFE filters

These filters have been effective in sampling atmospheric aerosols [69]. Using X-ray fluorescence, the elemental composition of the sample could be determined, while ion chromatography allowed the characterization of the chemical form of the compounds.

6.3. Coated filters

A diffusive sampler has been specially designed for the collection of reactive compounds. It primarily consists of a reagent-coated filter (Fig. 6) [70]. The filter part under the holes is used as a sampling filter, the other half as a blank filter. Once retained on the filters, the solutes were extracted with acetonitrile and analysed by LC.

This sampler has already been validated for formaldehyde with a 2,4-DNPH-coated filter [71], and for diethylamine with a 1-naphthyl isothio cyanate-impregnated filter [72]. Recently, it has also been successfully used for the determination of amines in air (methylamine, isopropylamine, *n*-butylamine, alkylamine and dimethylamine) with the latter reagent [70]. Short-time sampling (30 min) was possible with detection limits below 1 $\mu g l^{-1}$. The influence of concentration, sampling time and relative humidity on uptake rates was low.

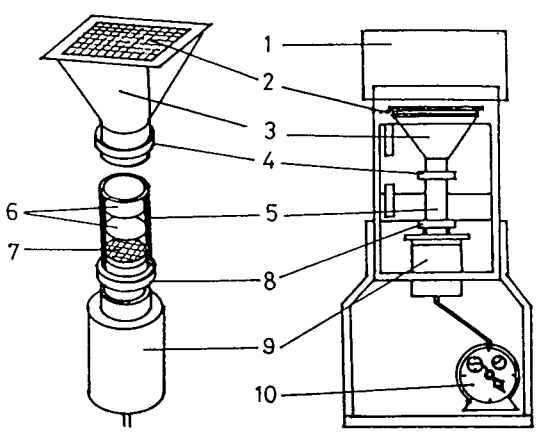

Fig. 5. Design of a sampling apparatus that combines a quartz-fibre filter and two polyurethane foam plugs (PUFPs): 1 = shelter; 2 = filter and stainless-steel wire net; 3 = filter holder; 4 = screw clasp with PTFE packing; 5 = PUFP holder; 6 = two PUF plugs; 7 = stainless-steel wire net; 8 = screw clasp with PTFE packing; 9 = high-volume air-suction pump; 10 = integrating gas flow-meter. From Ref. [65].

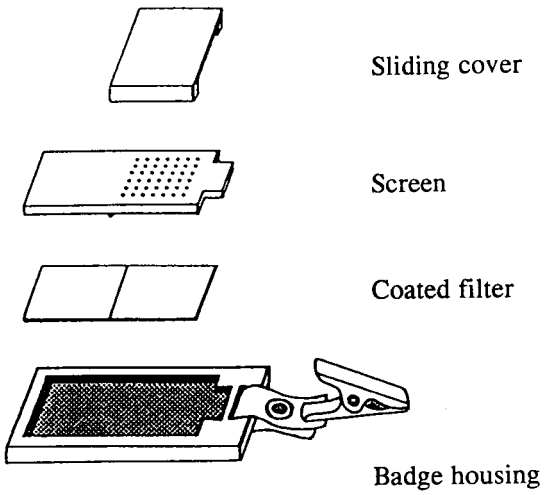

Fig. 6. Diffusive sampler for the collection of reactive compounds. From Ref. [70].

7. Collection onto fibres

7.1. Solid-phase microextraction

Solid-phase microextraction (SPME) is a very useful technique for air sampling. It is portable, inexpensive, requires no solvent, and can be used with any type of gas chromatograph.

The SPME device, illustrated in Fig. 7 [73], is easy to transport: a fused-silica fibre coated with a polymeric organic liquid is contained in a syringe. The fibre is placed in the atmosphere and the analytes partition into it. Once equilibrium has been reached, the fibre containing the concentrated solutes is transferred to the injector of a GC, where the compounds are thermally desorbed (they may be cryofocussed at the head of the chromatographic column during the desorption, because the desorption time can be longer than the elution time of a chromatographic band in a capillary column).

This technique has been used to determine volatile chlorinated organic compounds in air [73]. Samples were taken by exposing the fibre for 35–45 min.

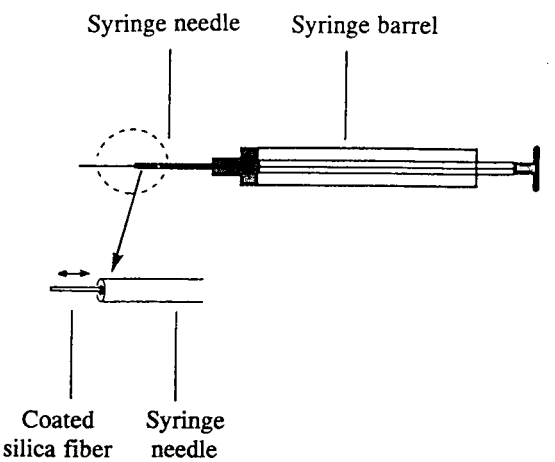

Fig. 7. Solid-phase microextraction device. From Ref. [73].

7.2. Membrane extraction with a sorbent interface

A new analytical method has been recently reported [74]. It combines membrane extraction, cryofocussing and thermal desorption. Fig. 8 shows the schematic representation of the system; the membrane probe consists of a hollow silicone fibre. Extracted compounds were indeed cryogenically focused at the head of the capillary column. After a certain time, an electrical pulse was applied to thermally desorb the solutes into the carrier gas stream for GC analysis.

Membrane extraction with a sorbent interface (MESI) has been used as a simple and effective VOCs monitoring station [74]. Unlike the common methods for air sampling, it eliminates the

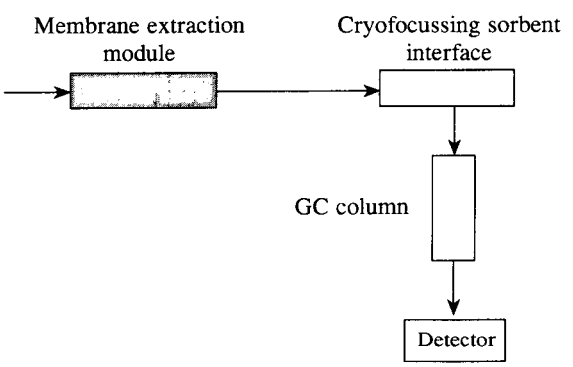

Fig. 8. Schematic representation of the membrane extraction with a sorbent interface system. From Ref. [74].

need for a sorbent cartridge, organic solvents, and a drying step.

8. Conclusions

Numerous preconcentration procedures now exist. However, collection on adsorbents has probably become one of the most popular methods, and it is often proposed as a method of choice by official organisations. Most of the time, volatile organic compounds are transferred from the sorbent tube to the analytical column using rapid thermal desorption; in some cases, a cryofocussing step may be required if insufficient resolution is obtained.

The development of microtraps should allow the continuous monitoring of air pollution, once the sorbent has been correctly chosen.

Nevertheless, the choice of the adsorbent nature is very difficult and often two or three types of adsorbents must be used in series to collect a broad range of solutes.

A recent technique, solid-phase microextraction, is also very promising. It offers many advantages over the other methods: easy to transport, low cost, no solvent needed. Therefore, it should face a growing interest in the next few years.

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Journal of Chromatography A, 710 (1995) 21–37

JOURNAL OF CHROMATOGRAPHY A

Review

Application of chromatographic studies of air pollution in China

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Abstract

A review of chromatographic studies on air pollution in China is presented. Gas chromatography and high-performance liquid chromatography are two of the techniques most commonly used. Various aspects of investigations of environmental potential carcinogens, such as polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons, are discussed. In addition, studies on greenhouse effect trace gases and other hazardous or toxic pollutants on air particulates from or in the vapour phase (gaseous phase) in many cities in China have also been carried out.

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0021-9673/95/$29.00
SSDI 0021-9673(95)00173-5

1. Introduction

Coal accounts for more than 70% of the fuels used in China. Serious pollution by polycyclic aromatic hydrocarbons (PAHs) from coal combustion, especially during winter in northern cities, has been found by chromatographic analysis in many studies. Other pollutants, such as aldehydes, phthalates and alkanes, and also greenhouse effect trace gases are present in ambient air or in workplaces. Analytical investigations will serve as the basis for the assessment of air quality source identification and the evaluation of secondary reaction. Based on the data obtained, pollution abatement measures can be suggested.

2. Chromatographic methods used for studies on air pollution in China

Various chromatographic methods have been developed in China for the determination of many pollutants in the ambient atmosphere or in emission sources. Among them, gas chromatography (GC) with both capillary and packed columns, and various detection methods, including thermal conductivity (TCD), electron-capture (ECD), flame ionization (FID), flame photometric (FPD) and mass spectrometric (MS) detection, accounts for more than 70% of the analytical studies, while the growing use of high-performance liquid chromatography (HPLC) with UV and fluorescence detection, etc., is evident, especially because of its sensitivity and the possible avoidance of decomposition during the analysis. In addition, photodiode-array detection (DAD) has been proved useful, especially for some advanced studies [1–4].

Ion chromatography (IC) has been widely used in recent years, especially in studies of anions and organic acids relating to acid precipitation investigations. Supercritical fluid chromatography (SFC) possesses the advantages of both GC and HPLC. Studies on SFC methods of analysis are in progress.

3. Target compound analyses

3.1. Polycyclic aromatic hydrocarbons (PAHs)

Suspended particulate matter, consisting of both adsorbed organic and inorganic substances, is one of the most important atmospheric pollutants of nationwide concern in China. The concentrations of total suspended particles (TSP) are comparatively high all year round, with higher values in northern than in southern cities. Owing to the increased amount of coal burning for heating in winter, the level is generally higher than in summer. Many large cities located in northern China are heavily contaminated by PAHs, e.g., the well known carcinogen benzo[*a*]pyrene [B(a)P], adsorbed on dense air particulates.

GC, GC–MS and especially HPLC methods have been applied to the systematic study of the distribution of 10–17 PAHs in atmospheric suspended particulates from many cities [5–19]. In the early 1980s, the concentration of B(a)P in residential areas in the urban districts of Beijing ranged from 4 (summer) to 74 ng/m^3 (winter), and in some industrial sites where coal was used as the main fuel, the concentration of B(a)P may be as high as 500 ng/m^3. Near some petrochemical complexes, however, the value of 1–14 ng/m^3 was close to those in clean areas (0.6–6.7 ng/m^3) [5]. In general, the B(a)P concentration accounts for less than 10% of the total PAHs studied. Over 120 PAH compounds were identified by GC–MS in a sample collected from an area near a steel works, including thirteen sulfur-containing, fifteen nitrogen-containing and ten oxygenated heterocyclic compounds [6].

Regular seasonal and diurnal variations of PAH have been observed [5]. Excessive concentrations in the winter are related to the increased use of coal for heating purposes. Two maxima in PAH concentration have been detected during the day, as summarized briefly in Ref. [2]. The maximum concentration that occurred at 5–9 a.m. is coincident with rush-hour traffic and morning cooking. Some degradation by sunlight and higher wind velocities might be

the cause of the minimum concentration observed after 9 a.m. The second maximum occurred in the evening, probably corresponding to the traffic at the end of the day and also to cooking. Fig. 1 shows the monthly variation of B(a)P in air particulates collected from three typical locations in Beijing [8]: (1) is a heavily polluted area where each institution has its own boilers or heating devices, (2) is a location where a central heating facility was established and (3) is a rural clean site [8].

Some correlations between different PAHs have been observed, and in most places samples collected at noon are higher in PAHs with three and fewer rings than those collected in the morning, while the reverse holds for compounds with four and more rings [5,14].

Systematic data indicating the concentration of B(a)P and PAHs on very fine particles [5,14] and the mutagenicity results confirmed the regularity that mutagenic compounds are mainly adsorbed on fine inhalable particles (see Figs. 2, 3 and 4) [5].

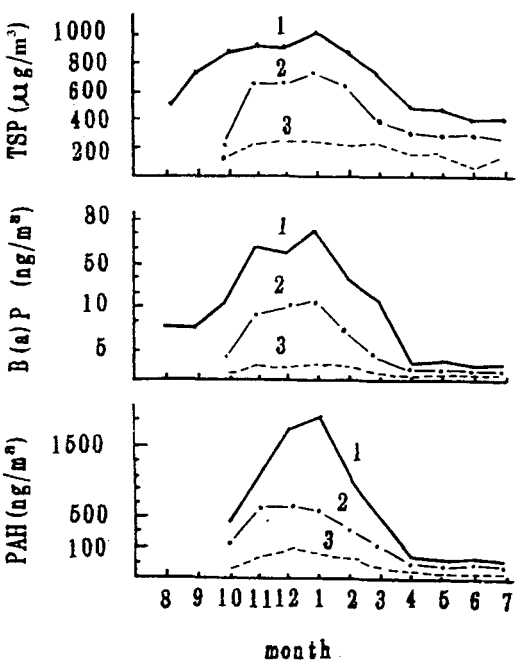

Fig. 1. Monthly changes in the concentrations of TSP, B(a)P and PAH pollutants at different sites [8]: 1 = Zhong-guan-cun; 2 = Qing-hua University; 3 = Shi-san-ling Reservoir.

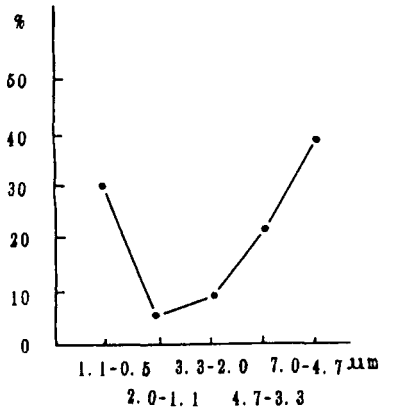

Fig. 2. Percentages (w/w) of air particulates of different sizes (from coke plant, Dec. 1983) [5].

It is very interesting that several PAHs, such as perylene, B(a)P, benzo[*ghi*]perylene and coronene, are very similar even quantitatively in their size-based percentage concentrations.

Cocaine (whether from tobacco leaves processing or from cigarette smoking) was detected for the first time [9] in Chengdu city.

In a Chinese–Japanese cooperative study (1981–84) on elements, organic constituents,

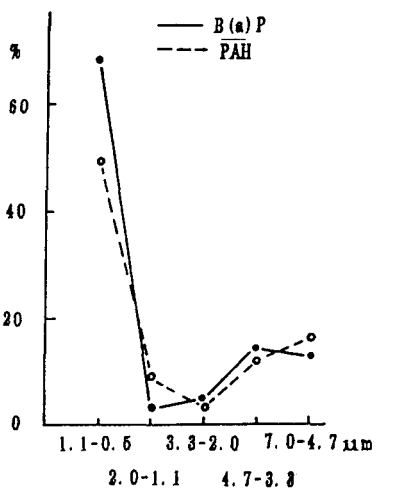

Fig. 3. Percentages of B(a)P and PAHs in air particulates of different sizes (from coke plant) [5].

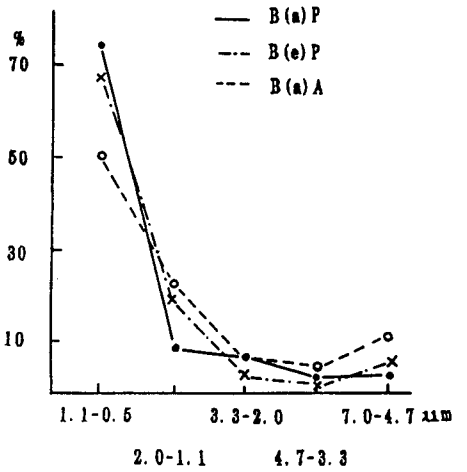

Fig. 4. Percentages of PAHs in air particulates of different sizes (from Yan-shan area) [5]. B(e)p = Benzo[*e*]pyrene; B(a)A = benz[*a*]anthracene.

TSP, SO_2, NO_2 of atmospheric pollutants in Beijing, PAHs in airborne particles were determined by HPLC and GC–MS in both summer and winter [10]. The major components found were fluoranthene, B(a)P, benzofluoranthenes (sum of [*b*,*j*,*k*] isomers), indeno[1,2,3-*cd*] pyrene, benzo[*ghi*]perylene and dibenzo [*a*,*c*]pyrene. Chlorine and sulfur compounds were also found at the sampling sites. The concentrations in the industrial, urban and rural areas generally decreased in that order, and those in winter were 2–5 times higher than those in summer.

The concentrations of B(a)P and benzo [*ghi*]perylene in ambient air in Tokyo (urban site) were slightly lower [10] than those at the rural area in Beijing and as low as 10–20% of those at the urban area in Beijing.

The data obtained were used for the study of source identification. For example, samples of suspended particulate matter were collected during the period of 26 October–4 November 1982 and 27 January–2 February 1983 in five sampling locations of Beijing. Non-polar, moderately polar, polar and strongly polar fractions of particulate organic matter (POM) were sequentially extracted with cyclohexane, dichloromethane, acetone and methanol for chemical analysis. Atmospheric concentrations of total POM were used in factor analysis to identify emission sources. The results of multiple regression analysis indicated that the contribution of coal combustion was almost three times those of oil-burning and motor vehicles [11].

Many studies have also been carried out on the evaluation of alternative fuels and emissions from different stoves and furnaces as PAH pollution sources [20–26].

Modified US EPA Methods 5 and 17 were used for stack sampling. More than 110 organic compounds (including PAHs and alkanes) have been identified by capillary GC–MS from stack samples [25]. An HPLC method with dual detection (UV at 254 nm and fluorescence at 296/427 nm) was developed [20] in order to obtain higher sensitivities for all different PAHs (see Fig. 5).

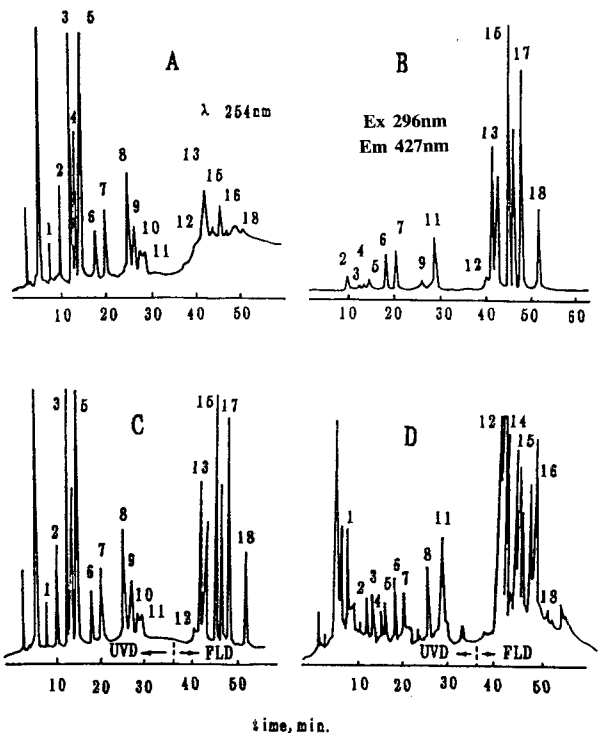

Fig. 5. HPLC of PAHs. (A) Mixture of 18 standard PAHs with UV detection (UVD); (B) mixture of 18 standard PAHs with fluorescence detection (FLD); (C) mixture of 18 standard PAHs with dual UVD–FLD; (D) extract of emission sample from coal-burning boiler with dual UVD–FLD [20].

Eighteen PAHs in different stack samples were quantified by this HPLC method. Fluorescence spectra of PAHs in real samples could be recorded by the stopped-flow method and compared with those in standard mixtures for identification. However, during routine analysis the retention values of peaks were checked under control of the same chromatographic conditions.

Differences of several orders of magnitude in the emission concentration factor of B(a)P in different cases were observed (see Table 1) [25]. It is evident that small domestic stoves give rise to much more B(a)P pollution than other combustion sources. In order to protect the environment, city coal gasification systems are being developed and some interim measures, such as using coal briquettes instead of raw coal, have been suggested.

3.2. Nitro-PAHs

HRGC–electron impact (EI) MS and HRGC–negative ion chemical ionization (NICI) MS have been used for the detection of nitro-PAHs such as 9-nitroanthracene, 1-nitropyrene and nitrofluoranthene in air particulate samples collected from the Beijing area [3,27]. The results were checked by HPLC with fluorescence detection after reduction of nitroarenes to the corresponding amino-PAHs, and 6-nitrochrysene was also found [28–30].

Different reducing agents for the reduction–HPLC–fluorescence detection method have been carefully compared and $NaBH_4$ was found to be better than Zn–HCl with regard to extent of reduction of compounds with higher numbers of rings and their stability during storage. In addition, this method has been applied for the quantification of nitro-PAHs in various air samples. Table 2 shows some of our results in comparison with data from other workers [29,31–35].

With proper selection of wavelengths of excitation and emission, minimum detectable amounts of most amino-PAHs are 0.02–0.2 ng. However, with derivatization of amino compounds with heptafluorobutyric anhydride, the detection limits may be as low as 0.25–11 pg [35]. Nitro-PAHs were also detected in the vapour phase (Table 3). However, further work is required to identify many undefined peaks on the chromatograms after reduction when more standard chemicals are available.

3.3. n-Alkanes and vapour-phase organics

Analyses of vapour-phase organics in air were carried out by capillary GC–FID and GC–MS [36–56]. The compounds tentatively identified included alkanes, cyclic hydrocarbons, alkenes, aromatics, acids, alcohols, aldehydes, ketones, esters and halocarbons.

In a study [7] with GC–ion trap detection (ITD) and GC–FID, C_{19}–C_{34} *n*-alkanes were found at concentrations in the range of 2.0–92 ng/m^3 (higher in winter than in summer). For *n*-alkanes it has been reported that the CPI value [carbon preference index = sum (content of odd carbon number *n*-alkanes)/sum (content of even carbon number *n*-alkanes)] of *n*-alkanes from anthropogenic activities such as combustion of fossil fuels is close to 1, whereas those origina-

Table 1
Emission coefficients of B(a)P from various coal-fired boilers and stoves [25]

Boiler type or stove	Emission coefficient (mg/ton coal)	B(a)P concentration (μg/m^3)
Power plant, 35 t/h	0.2–0.4	0.14–0.16
Industry, 10 t/h	0.2–0.35	
Industry, 4 t/h	2.1–9.7	0.3–0.8
Industry, 2 t/h	1.4–5.9	0.2–0.4
Tea boiler, 0.2 t/h	20–677	1.7–96
Household stoves	350–20000	

Table 2
Concentrations of nitro-PAHs in air particulates (pg/m^3) [29,32–35]

Sample source	4-NBP	2-NF	3-NFL	1-NP	6-NCH	6-NB(a)P	Ref.
Beijing							[33]
S-2	–	57.7	420	117	55.7		
S-3	–	10.4	342	29.8	8.5		
S-4	14.9	1.9	259	77.1	12.1		
S-5	21.5	16.5	318	99	7.1		
W-2	162	23.3	38.7	299	393		
W-3	305	–	31.7	293	334		
W-4	101	8.8	8.7	132	269		
W-5	234	12.3	83	265	93		
Shandong (A)				110			[34]
Shandong (B)				55			
Tunnel				1400			[29]
PC, China				162			[35]
Warren				20		35–65	[32,34]
Detroit				19–30		100–280	
Washington			1.1 ppm				
Japan				21			
Copenhagen			<100			<100	
Columbus			5–200				

4-NBP = 4-Nitrobiphenyl; 2-NF = 2-nitrofluorene; 3-NFL = 3-nitrofluoranthene; 1-NP = 1-nitropyrene; 6-NCH = 6-nitrochrysene; 6-NB(a)P = 6-nitrobenzo[*a*]pyrene.

ting from natural sources are >5. Alkanes in atmospheric aerosols were studied by different workers [36,47,55]. It has been found that different values and different seasonal changes of *n*-alkane CPI are characteristics of aerosols from different cities in China, e.g., Guangzhou and Beijing. Also, the *n*-alkane CPI decreases with increasing particulate size. This means that the smaller the particulate, the larger is the contribution of *n*-alkanes from anthropogenic sources. The *n*-alkane CPI is useful for identifying their sources in aerosol particulates.

For other hydrocarbons in air, a method was developed for the simultaneous determination of low- and high-molecular-mass hydrocarbons in the atmosphere by means of preconcentration with cyrogenic trapping (liquid nitrogen), splitless injection and capillary column GC–MS [36]. Using this method, 45 out of about 100 chromatographic peaks were identified for atmospheric samples collected from a petrochemical production area in Beijing. Table 4 shows the analytical results for this sample obtained with GC–FID and GC–MS. In a separate study the

Table 3
Concentration of nitro-PAHs in gaseous phase of ambient atmosphere (Beijing) (ng/m^3) [28]

Season	1-NO_2-naphthalene/ 2-NO_2-naphthalene[a]	2-NO_2-fluorene[b]	1-NO_2 pyrene[b]
Winter	2.25	2.84	0.39
Summer	0.44	0.35	8.4×10^{-3}

[a] Calculated as 1-NO_2-naphthalene.
[b] According to retention time.

Table 4
Analytical results for an air sample from a petrochemical complex district in Beijing [36]

Peak No.	Retention time (min)	Compound	Identification method	Concentration (mg/m^3)
11	21.50	1-Butene	MS	0.353
14	22.58	2-Methylbutane	MS	0.500
21	26.94	Ethylcyclobutane	MS	0.151
22	27.33	2-Methyltetrahydrofuran	MS	0.341
23	28.55	3-Methylpentane	MS	1.054
26	30.19	Hexane	MS	0.596
27	37.72	2-Methyl-1-pentene	MS	0.934
29	35.26	Benzene[a]	GC–MS	0.805
31	36.33	Cyclohexane	MS	0.853
32	37.52	3-Methylhexane	MS	0.078
33	38.46	1,3-Dimethylcyclopentane	MS	0.083
35	41.34	*n*-Heptane[a]	GC–MS	5.725
36	43.33	Methylcyclohexane	MS	1.313
37	44.64	Ethylcyclopentane	MS	0.082
39	45.14	2,4-Dimethylhexane	MS	1.451
43	47.15	Toluene[a]	GC–MS	2.065
44	48.00	2-Methyl-3-ethylpentane	MS	0.182
46	48.84	4-Methylheptane	MS	1.364
47	49.45	2,5-Dimethylhexane	MS	0.105
49	50.58	2,5-Dimethyl-1-hexene	MS	0.075
53	52.20	*n*-Octane[a]	GC, MS	0.175
54	53.86	2,3,5-Trimethylhexane	MS	1.223
56	54.64	2,3,4-Trimethylhexane	MS	3.571
58	55.10	3-Ethylheptane	MS	0.026
59	55.55	2-Methyl-2-hepten-4-one	MS	0.063
61	56.20	2,6-Dimethyl-3-heptene	MS	2.964
62	56.77	Xylene	MS	0.039
63	57.06	Styrene[a]	GC–MS	0.078
64	57.38	Xylene	MS	0.104
67	58.39	Trimethylhexane	MS	0.521
69	59.66	3-Methyloctane	MS	0.084
70	59.57	1-Nonene	MS	0.043
72	60.93	Dimethyloctene	MS	0.102
73	61.45	*n*-Nonane[a]	GC–MS	0.070
76	63.09	5-Methylnonane	MS	0.185
78	64.12	Camphene	MS	0.455
79	64.39	3-Methylnonane	MS	0.371
80	64.83	2,6-Dimethyloctane	MS	0.067
84	66.07	Methylnonane	MS	0.069
85	66.59	4-Methylnonane	MS	0.045
86	66.82	Isodecane	MS	0.061
87	67.36		MS	0.123
88	67.90	5-Methyldecane	MS	0.109
89	68.08	Isoundecane	MS	0.553
96	72.39	Methyldecane	MS	0.111

[a] Checked with standard compounds.

analytical results for the main components of exhaust from a rubber tire refining factory were reported [57].

It is important to point out that many compounds having comparatively high vapour pressures under ambient conditions are present both in the gaseous phase (or vapour phase) and on particulates, such as PAHs and phthalates, when both filters and adsorbents such as XAD resin or polyurethane foam (PUF) were used for air sampling. Higher concentrations of four-ring and smaller PAHs were found in the vapour phase of the atmosphere (see Table 5) [39].

The quantitative relationship suggested by Yamasaki [40] is recommended for comparison with real measurements [38]:

$$\log\left(\frac{PAH_v}{PAH_p/TSP}\right) = -A/T + B$$

where PAH_v = concentration of PAH in vapour phase (ng/m^3), PAH_p = concentration of PAH on particulate (ng/m^3), TSP = concentration of total suspended particles (mg/m^3), T = absolute temperature (K) and A and B are constants.

HPLC determinations of separated PAHs were carried out both in the vapour phase and on particulates from residential areas and clean meadow areas in winter and summer. The results also showed that over half of the PAHs with four and fewer rings were found in the vapour phase, and most of the PAHs with five rings were found in particulates. Moreover, the distribution of PAHs in clean meadow samples was different from those in the residential area [42].

Both vapour phase and particulate phthalate esters in atmospheric samples collected from a city in Inner Mongolia were studied and compared with those from a clean meadow [44]. After extraction and preseparation, dibutyl *o*-phthalate and di(2-ethylhexyl) *o*-phthalate (DEHP) were detected and analysed by GC–FID. In the samples from this city, where small domestic stoves were used for heating purposes, very high concentrations of both phthalates (up to 1.3–1.9 $\mu g/m^3$) were found in particulates in winter and in the vapour phase in summer, and a high TSP (up to 1.65 mg/m^3) was found in winter. However, in the clean meadow samples, total phthalates in both the vapour phase and particulates were as low as 0.2–0.4 $\mu g/m^3$. The results suggest that the phthalates are derived mostly from anthropogenic or industrial sources.

An automatic and continuous analysis device for aromatic compounds in ambient air has been developed [45]. This device is composed of a GC–FID system, a six-way valve and a vacuum pump, which is controlled by a microprocessor. Air samples from Huhehot have been analysed qualitatively and quantitatively with this device and sixteen kinds of compounds, such as C_6–C_9 *n*-alkanes, benzene and eleven C_1–C_4 alkylbenzenes were detected and the trend of the changes in their concentrations was observed. Many other papers have dealt with analyses for benzene and alkylbenzenes [48–50,53–56].

Table 5
Atmospheric polycyclic aromatic hydrocarbons in vapour phase

PAH	VPO/POM	Reference VPO/POM
Naphthalene	40:1	
Biphenyl	40:1	
Phenanthrene	100:1	Phenanthrene + anthracene
Anthracene	40:1	245:1
Methylphenanthrene	20:1	Methyphenanthrene + methyanthracene
Methylanthracene	20:1	64:1
Fluoranthene	4:1	20:1
Pyrene	4:1	12:1

Comparison of PAH samples adsorbed on polyurethane (VPO) with PAHs on particulates (POM) [39].

3.4. PCBs, PCDDs, chlorinated PAHs and pesticides

Systematic determinations of PCBs began in the late 1970s and early 1980s [57,58–60]. Two commercial products, PCBs No. 1 (41% Cl) and 2 (53% Cl) were analysed and confirmed with different methods: elemental analysis, GC–microconductivity detection, GC–ECD and GC–MS. They were recommended to be used as reference standards [58]. With computerized multi-ion monitoring techniques, quantification of PCBs and organochlorine pesticides became possible without preseparation [59].

Dimethylformamide solution was used to absorb PCBs and, after extraction with petroleum, GC–FID was used to determine PCBs in air with recoveries of 89–106% and a detection limit of 20–30 ng/m^3 (sampling volume 60 l) [60,61]. In most cases, preseparation is not necessary.

A two-dimensional separation system of GC (SE-54 column)–GC (FFAP column) with dual parallel FID–ECD [62] was developed for fractionating and analysing complex mixtures as in the case of trace analyses for PCDD and PCB toxins in environmental samples. Fractions cut from the SE-54 column were separated instantly by the FFAP column without the necessity for using cold trapping. Other papers [63,64] were concerned with the ubiquitous pollutants PCDDs and PCDFs.

Polychloronaphthalene (PCN) congeners were found to induce enzymes such as AHH (aryl hydrocarbon hydroxylase) in a similar way as dioxins and therefore have received considerable attention. An improved packed column GC method [65] for determining PCNs in fly ash from municipal incinerators was proposed. Using a short packed column, 1-chloronaphthalene can be well separated from 2-chloronaphthalene at column temperatures as low as 110°C.

Hexachlorocyclohexane (HCH) and DDT in rain and snow were determined with packed column GC–ECD [66]. Organophosphorus pesticides in exhaust samples or in the workplace air of a pesticide factory were determined by packed column GC–FPD after enrichment with a solid adsorbent. The adsorption tube was first desorbed with acetone and the eluate was concentrated with a Kuderna–Danish concentrator. The detection limit was as low as 0.04 μg/m^3 when a 250-l air sample was analysed [67,68].

3.5. Malodorous sulfur compounds

Combined techniques for sampling and determination of the main malodorous compounds in air have been developed [69–72]. With CH_3SH and $(CH_3)_2S_2$ as typical pollutants, the complete set of apparatus, including adsorbent sampling tube, constant-flow sampling pump, thermodesorption device and gas mixer for the preparation of calibration gas mixtures has been established. Commercial GDX-105 was found to be suitable for the collection of these compounds at the room temperature. The methods afford recoveries between 60 and 100%, a detection limit of 0.2 ng and an accuracy of ±3%.

In a case study of an emergency (which lasted for several days and affected 400 000 individuals) that occurred in November 1988 in a city in Jiangxi Province, GC–FID and GC–MS were used to determine the organic pollutants in the effluent waste water from a refinery factory. Concentrations of 29 ppm of C_2H_5SH in waste water and 800 ppm of $(CH_3)_2S_2$ in original oil and 0.001 ppm in air (sampling volume 0.6 m^3) were detected and identified. The threshold values of odor were 0.00019 ppm (water) and 0.0037 ppm (air), respectively [71,72].

GC–photoionization detection (PID) [10] was used to analyse low-pressure gas and exhaust samples. Concentrations of 14 ppm of C_2H_5SH and 19 ppm of $(CH_3)_2S$ were found in the latter. With the application of PID, the pretreatments of samples can be simplified. Other malodorous compounds, such as indole and butyric acid, have also been determined [73].

3.6. Aldehydes, etc.

A simplified method was used to evaluate the amounts of aldehydes emitted from an oil-fuelled boiler and a gasoline engine under different operating conditions [74]. Low-molecular-mass aldehydes in the sample were directly collected

and derivatized with a catalyst in a bubbler containing a methanol or acetonitrile solution of 2,4-nitrophenylhydrazine (2,4-DNPH), HPLC being used for further separation and determination. The recoveries achieved for formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde all exceeded 85%, with detection limits of 0.6, 1.3, 0.4 and 0.5 ng, respectively. Table 6 shows the emission concentrations of aldehydes in automobile exhaust gas. A similar method has been applied to determine formaldehyde in air [75].

With a commercial preconcentration and derivatization tube (with 2,4-DNPH), concentrations of C_1–C_3 aldehydes as low as 2–13 ppb in ambient air of Guiyang have been detected [76]. Ambient C_2–C_5 aldehydes can also be determined by GC [77].

Methyl nitrite (MeONO) and methyl nitrate ($MeONO_2$) concentrations in exhaust gas from an engine fuelled with methanol were measured by GC, with detection limits of 20 and 50 ppb, respectively (sample volume 1 ml). The exhaust from a Santana M100 engine contained 5–250 ppm of MeONO and less than 50 ppb of $MeONO_2$ [78].

Analysis using GC–FID also provided data on CH_3OH concentration in the assessment of the effects of exhaust from methanol–gasoline combustion and catalytic purification of exhaust from a methanol-fuelled vehicle [79–81].

3.7. Greenhouse effect and trace gases

Carbon dioxide, CH_4, chlorofluorocarbons (CFCs), N_2O, etc., are now considered to be responsible for global climatic changes and ozone layer depletion. These are two of the main environmental problems currently of concern all over the world. Many international research projects have examined reliable monitoring methods, mechanisms and extents of emissions and reduction measures. In this respect, China has also played an important role in the monitoring and study of greenhouse gases.

After examination of the data for year-round temperature and precipitation in China at 160 observation stations during 1951–1989, a rise of about 0.23°C in the annual temperature was deduced [82].

CO_2 is present in much higher concentrations in the atmosphere than other trace gases. Among the prevailing methods for CO_2 measurement, the non-dispersive IR absorption (NDIR) method tends to be the most precise continuous method, with precision up to 0.1 ml/m^3, and GC is still the most popular and readily available methodology. Both FID and

Table 6
Concentrations of aldehydes in automobile exhaust [74]

Aldehyde	Operating conditions			
	Low speed (25–30 km/h)		High speed (70–80 km/h)	
	Emitted concentration (ppm, v/v)	Emitted amount (μg/h)	Emitted concentration (ppm, v/v)	Emitted amount (μg/h)
Formaldehyde	6.7	52.1	14.1	164.5
Acetaldehyde	6.3	72.4	1.2	20.5
Acrolein	7.2	103.9	1.3	27.8
Propionaldehyde	1.1	16.4	n.d.[a]	n.d.
Butyraldehyde	0.8	15.5	n.d.	n.d.
Benzaldehyde	–	–	n.d.	n.d.

[a] Not detected.

TCD can be used, but prior conversion of CO_2 into CH_4 is required in the former case. Using this approach, other hydrocarbons in air may also be measured simultaneously [83]. Thus it has been applied for the multi-component determination of a few samples collected from the troposphere.

Both IR and GC are now used in China to determine N_2O. Mass spectrometry and volumetric analysis (pressure method) for the determination of N_2O have recently been reported, but few data are available [84–86].

Many detection methods, such as TCD and FID, were used for N_2O monitoring in the early years. However, GC–ECD is now the simplest and most accurate and precise method. In March–July 1992 a study [84] of ground level N_2O concentrations (in ppb, v/v) in some typical environments found that the mean concentration was 349 in a campus, 352 in a rice field and 345 in a forest, and higher (362) in an organic source (manure). Various combustion processes are also sources of air N_2O. Improvements in the continuous injection of two consecutive samples led to a 30% decrease in analysis time [84].

Nitrous oxide flux has been studied in a typical winter wheat field in Northern China [85]. Gaseous samples were collected from a sampling chamber of $1 \times 1 \times 1$ m^3 located in the field and analysed by GC–ECD. With similar (soil) conditions, the fluxes on winter wheat field and alfalfa farm land did not show obvious differences. The effects of fertilization, irrigation, soil temperature, etc., are conducive to the emission.

The emission factors of nitrous oxide have also been determined during the combustion of rice straws, wheat stalks and maize stalks in an enclosed combustion system [86]. They were 84.4 g/t for rice straws, 132 g/t for maize stalks and 27.3 g/t for wheat. The N_2O-N (nitrogen in nitrous oxide emission) accounts for 0.59% and 0.87% of the total nitrogen in rice straws and maize stalks, respectively.

GC–ECD with ambient temperature injection and a freezing technique was successfully used to determine the concentrations of halocarbons in ambient atmospheric samples collected in the suburbs of the Beijing area [87]. The stainless-steel columns used were (1) 25% DC-200 Chromosorb W AW DCMS (60–80 mesh) (3 m × 3 mm I.D.) and (2) gas–solid Carbopack CHT (80–100 mesh) (2 m × 3 mm I.D.). The detection limit can be as low as 0.04–0.3 pg.

The measured concentrations of CFC-11, CFC-12, $CHCl_3$, CH_3CCl_3, CCl_4, $CHCl=CCl_2$ and CCl_2CCl_2 were 127 ± 24, 275 ± 12, 49 ± 32, 80 ± 27, 60 ± 18, 8 ± 2, and 30 ± 17 ppt, v/v, respectively. These values are lower than those of global concentrations, but the relative concentrations of CCl_4 are close.

No. 407 macroreticular resin adsorbent (made in China) has also been used as a stationary phase to separate CFC-12 (CCl_2F_2) from $CHCl_3$, CCl_4, C_2H_6, CH_4 and CFC-11 by GC-FID with direction injection of a 1-ml sample from a workplace. The detection limit was 5 ppm [88].

Direct measurement of trace isoprene monoterpenes in the atmosphere has been made possible by using GC–PID. The experiments showed that the rate of release of α- and β-pinene from some oriental pine trees is faster during the day than at night [89].

The contribution of volatile organic acids has also been taken into consideration in studies on acid rain. A rapid GC procedure consisting of (1) collection by adsorption on Amberlite XAD-2 resin, (2) esterification with benzyl bromide in the presence of silver oxide as catalyst and (3) derivatizing followed by determination of volatile organic acid by GC–FID was suggested [90]. The experimental results indicated that C_1–C_4 (even up to C_6) organic acids can be effectively separated and determined. Concentrations of formic acid, acetic acid and propionic acid were found in the ranges 0.005–0.234, 0.023–0.542 and 0.030–1.60 mg/m^3, respectively, in air samples collected from six different locations. However, C_4 and higher organic acids were not detected in these samples. Other references are given in Section 4.

3.8. Miscellaneous compounds

Packed column GC with a liquid crystal stationary phase was used to determine phenol,

cresol, dimethylphenol, etc., after adsorption on GDX-502 macrorecticular resin. The detection limit was 0.01 mg/m^3 with R.S.D. 10% [91]. *p*-Chlorophenol in workplace air was desorbed from a resin adsorption tube with CS_2 solvent and determined by GC–FID. A detection limit of ca. 6 mg/l [92] can be achieved.

Derivatization followed by GC was used for the determination of hydrazine and unsymmetrical dimethylhydrazine after collection in a tube containing the special solid adsorbent SG-2 coated with sulfuric acid and then extraction with water [93]. An FFAP conventional column was used to separate isopropyl alcohol after extraction from air with active carbon [94].

Benzoyl methyl ester (BME) and substituted PTME in air as the by-products of terephthalic acid methyl ester (PTME) production were determined by GC [95]. After CS_2 elution from the active carbon adsorption tube, 10% silicone elastomer on a silanized carrier 101 packed column was used satisfactorily with detection limits down to 1 ng. Other pollutants such as acrolein, vinylchlorobutadiene and cyclooxypropane were determined using similar procedures [96–98].

GC coupled with an element-specific detector now has wide application in the speciation analysis of organometallic compounds. Among them, GC–atomic absorption spectrometry is the most popular [99].

3.9. Urinary 1-hydroxypyrene as a possible biomarker for human exposure to ambient PAHs

Jongeneelen et al. [100] suggested that urinary 1-hydroxypyrene, a major metabolite of pyrene, was a sensitive and specific marker for detection of occupational exposure to genotoxic PAHs from tar products. Since 1987, Zhao and coworkers have carried out a series of investigations on this metabolite [41,101–103]. 1-Hydroxypyrene in urine was determined using HPLC with synchronous fluorescence detection after hydrolysis of urine in the presence of β-glucuronidase/aryl sulphatase and preseparation on a Sep-Pak column. Samples of urinary 1-hydroxypyene from residents in several cities, workers at two coke plants, a steel plant and an aluminium factory, groups of people with different occupations, including traffic policemen and bankers, and persons in several control groups were determined in parallel at the same time when PAHs of airborne particulate to which they were exposed were determined using GC–MS. The ratio of pyrene to B(a)P in PAHs samples was fairly constant in certain environments or from similar emission sources. Statistical analysis showed a significant correlation of urinary 1-hydroxypyrene with the concentration of pyrene and B(a)P with correlation coefficients of 0.978 and 0.959, respectively. It is therefore suggested that urinary 1-hydroxypyrene can be used as a biological monitoring index for human exposure to PAHs.

4. Ion chromatography and supercritical fluid chromatography

Ion chromatography (IC) is an increasingly popular analytical technique. The good separations of many chemically similar species, the provision of reliable information on the presence or absence of a wide variety of ions, its speed and simplicity of operation, the readily availability of reagents together with its versatility and high sensitivity make this technique attractive for the monitoring of atmospheric pollution and acid precipitation and analyses of soil, food and biota samples [104,105].

In China, large-area monitoring of acid precipitation has already been carried out. Although precipitation samples have been collected and analysed for acidity and chemical composition since the late 1970s, extensive research and sample monitoring only began after IC had become more popular [106–112]. Major water-soluble chemical constituents of airborne particulates collected in different cities were analysed by IC and are found to be related to the particle size.

It was reported that acid precipitation with pH values lower than 5.6 occurred in some southern parts of China, especially in Sichuan, Guizhou

and Jiangxi Provinces. In two major cities, Chongqing and Guiyang, the annual mean pH value of precipitation is only 4.1.

IC is now accepted as the optimum procedure for the study of acid rain. Both cations (such as K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, NO_3^- and SO_4^{2-}) can be determined by IC using a single IC column with dimethyl phthalate as eluent and conductivity detection [113].

In addition to inorganic ions, some organic acids, including formic, acetic, maleic, chloroacetic, benzoic and ascorbic acid, can also be determined by IC [112].

IC was used in the early 1980s to determine SO_2 and NO_2 in ambient air [106]. A simple portable sampler with a solid absorption tube containing molecular sieve 13X soaked with triethylanolamine was used and dilute $NaHCO_3$ solution was used for extraction (NO_2 as NO_2^-, NO_3^- and SO_2 as SO_4^{2-} after oxidation with H_2O_2). Later it was used for the simultaneous determination of F^-, Cl^-, NO_2 and SO_2, and has now been applied for low-level routine analysis [114]. With Dionex 2120 IC, ammonia in air can be determined with a detection limit of 0.01 ppm, and hydrazine in air from a pesticide factory was determined with a detection limit of 0.001 mg/m^3 when the sampling volume was 60 l [110].

Regarding supercritical fluid chromatography (SFC), work is continuing with promising results. The various advantages of SFC should provide considerable success in the future [115].

5. Some regulation information

Air pollution, like water pollution, is very much of concern to both the public and the government in China. Great efforts have been made to minimize the pollution level accompanying the extraordinarily rapid recent economic growth. A national air quality monitoring network, consisting of 103 monitoring stations selected from 2131 stations, has been organized, engaging in regular monitoring of nation-wide air quality, but since China is a developing country, most of the current regulations on air pollution are focused mainly on the inhalable total suspended particle (TSP), SO_2, NO_2, CO and a few others, including some cations and anions of wet precipitations.

Methods so far available for air quality determination are limited. However, in accordance with our obligation to global environmental protection, concerns for public health and integrity of the ecosystem, more regulatory controls and stricter standards will be promulgated. Table 7 shows a revised draft of concentration limits in an ambient air quality standard [116].

6. Discussion and conclusion

Ambient air samples and stack samples as pollution sources, like other environmental samples, are very complex in nature and composition. They usually consist of hundreds of trace potential carcinogens, such as PAHs, heavy metals and various organic components of different polarities. Various types of chromatography, including coupled techniques (e.g., HRGC–MS, HPLC–FT-IR), have been shown to be efficient for detection and quantification as discussed, and have wide applications in the characterization and determination of these pollutants in China, as briefly reviewed in this paper.

The analytical data obtained are usually the requisite basis for many environmental studies. They indicate not only the environmental quality, but also the transformation, transport and fate of pollutants. Further, they suggest directions for solving problems and the possible impact on the ecosystem and human health. The quality of analytical data affects to a significant extent the success of various types of pollution studies undertaken.

Air pollution is closely related to energy consumption. Traditional coal combustion results in serious pollution problems in China. Modernization also increases vehicle emissions. Great efforts have been made to keep contamination levels of the ambient atmosphere stable or lower, in spite of extremely rapid progress in

Table 7
Concentration limts in "Ambient Air Quality Standard", revision draft [116]

Pollutant	Sampling time[a]	Concentration limit (mg/STP m^3)			
		Class 1	Class 2	Class 3	Remarks
Sulfur dioxide	Yearly av.	0.02	0.06	0.10	
	Daily av.	0.05	0.15	0.25	[b]
	Hourly av.	0.15	0.50	0.70	
TSP	Yearly av.	0.10	0.20	0.30	
	Daily av.	0.15	0.30	0.50	[b]
Inhalable particulates	Yearly av.	0.04	0.10	0.15	mg/m^3
	Daily av.	0.05	0.15	0.25	[b]
Nitrogen oxide	Yearly av.	0.05	0.05	0.10	
	Daily av.	0.10	0.10[b]	0.15[b]	
	Hourly av.	0.15	0.15	0.30	
Nitrogen dioxide	Yearly av.	0.04	0.04	0.08	
	Daily av.	0.08	0.08	0.12	
	Hourly av.	0.12	0.12	0.24	
Carbon monoxide	Daily av.	4.00	4.00	6.00	[b]
	Hourly av.	10.00	10.00	20.00	
Ozone	Hourly av.	0.12	0.16	0.20	[b]
Lead	Season av.		1.50		
	Yearly av.		1.00		
Benzo[*a*]pyrene	Daily av.		0.01		$\mu g/m^3$
Fluoride	Daily av.		7		
	Hourly av.		20		

[a] av. = Average.
[b] Same value as those in GB 3095-82 "Ambient Air Quality Standards" (analytical standard method in China) now used.

the national economy and the continuous increase in energy consumption. A network of over 1000 air monitoring stations has been established. New methods of analyses and standards will be developed. Based on the results of scientific investigations, including chromatographic studies, measures are being taken to reduce pollution, such as coal gasification, use of natural gas, centralization of power plants and some interim measures, e.g., using coal briquettes. China is also participating in many projects of global interest such as studies of acid rain, ozone depletion and climatic changes.

China is now developing its own environmental protection industry. Various materials, equipment and instruments are produced in either local or internationally collaborating factories to support environmental studies. These will greatly speed up the progress of environmental science in China.

Acknowledgements

The authors acknowledge the support of the National Natural Science Foundation of China. Professor Qihui Zhai is thanked for her advice on the English manuscript.

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ELSEVIER

Journal of Chromatography A, 710 (1995) 39–50

JOURNAL OF CHROMATOGRAPHY A

Review

Detection methods for the analysis of biogenic non-methane hydrocarbons in air

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Abstract

Volatile organic compounds in air, especially the reactive biogenic hydrocarbons (e.g., isoprene and monoterpenes), play important roles in the chemistry of the troposphere even at very low concentrations. Sensitive and reliable detection methods are required in order to determine their low concentrations in air and to estimate their emission fluxes from sources. The flame ionization detector and the mass spectrometer have been widely used for the quantitative and qualitative analysis of biogenic non-methane hydrocarbons in air but other detection systems are available. Both the sampling and analytical methods used for these measurements are summarized in this review. The possible applications of several potential detection methods and recent developments in the use of new methods are also discussed.

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0021-9673/95/$29.00
SSDI 0021-9673(95)00427-0

1. Introduction

Although there are considerable uncertainties [1,2] in estimates of the emission rates of volatile organic compounds (VOCs) from the biosphere, it is believed that the majority of global VOC emissions are from biogenic, and not anthropogenic, sources [3]. The emission of VOCs from plant foliage to the atmosphere accounts for about half of the estimated total VOC emissions in the USA [4] and two-thirds of global VOC emissions [2]. Although they comprise less than 50% of the total VOC mass emitted from vegetation [3], the non-methane hydrocarbons (NMHCs), especially isoprene and monoterpenes, have received much more attention than other VOC species during the past two or three decades. The concentrations of NMHCs in ambient air, especially of the more reactive compounds, are very low, and their measurement is therefore difficult. However, even at low concentrations they play an important role in atmospheric chemistry at global, regional and local scales (i) by reacting rapidly with hydroxyl radicals and ozone, forming, among other products, carbon monoxide and thereby impacting directly on the oxidizing capacity of the atmosphere, (ii) by influencing the formation and removal of ozone, depending on the ambient hydrocarbon and nitrogen oxides mixing ratios, and hence influencing the photochemical oxidant loading of the troposphere, (iii) by contributing to the global carbon budget, (iv) by the production of organic acids, contributing to the deposition of acidity in remote areas. Thus, more and better measurements of their concentrations in air and of their rates of emission into the atmosphere are required in order to fully understand their role in tropospheric chemistry and in order to estimate their contributions to the global atmospheric carbon budget.

The low concentrations of hydrocarbons in ambient air and the lack of adequately sensitive detection methods means that preconcentration is required during the sampling of ambient air. This may result in artifact formation, possible destruction of analytes by reaction with O_3 and other oxidants, and loss (or gain) on contact with surfaces. By developing more sensitive detection methods, not only can these problems be minimized, but also development of automatic sampling and analytical systems may be possible.

Although many other gas chromatographic (GC) detection systems are available, only flame ionization detection (FID) and mass spectrometry (MS) have been used widely for the quantitative and qualitative analysis of biogenic NMHCs in air. In this paper, the sampling and analytical methods used for these measurements are summarised. The possible application of several potential detection methods in this area and recent developments of new methods are also discussed.

2. Measurements of hydrocarbons in air

2.1. Sampling methods

Several different sampling methods are available [5,6], each method has its own range of application, and suitable sampling techniques should be used in order to carry out accurate and reliable sampling. The most widely used methods for the sampling of NMHCs at low concentrations in air are grab sampling with Teflon bags or stainless-steel canisters, and the adsorptive sampling method.

2.1.1. Grab sampling

Grab sampling, which is also called whole-air sampling, involves the direct collection and isolation of the test atmosphere in an impermeable container, and generally requires relatively simple equipment. This technique is ideal for the light hydrocarbons, and has been widely used for the measurements of C_2–C_6 hydrocarbon concentrations in rural, remote and maritime atmospheres [7–14]. Although it is in general not applicable to less volatile compounds due to their possible adsorptive losses on the walls of the sample containers, this method has also been used occasionally for the measurements of biogenic hydrocarbons in air [15,16]. Because the concentrations of NMHCs in air are very low and the sensitivity of present detection methods

is not adequate, large volumes of sample, which must be preconcentrated prior to analysis, are required for analysis. Samples can be preconcentrated cryogenically on adsorbents, followed by thermal desorption [14], or by cryogenic on-column enrichment [12]. As the volume of sample containers is, for practical reasons, limited to a few litres, the total amount of air available for analysis is very low. Larger amounts of air can be collected by pressurizing the samples cryogenically, e.g., by immersing the container in liquid nitrogen.

2.1.2. Adsorptive sampling

Sampling by pumping air through an adsorption tube packed with adsorbent(s), followed by thermal desorption, is the most widely used method for the sampling of less volatile NMHCs (C_5 and above) at low concentrations in air. Several different adsorbents can be used for this purpose, such as Tenax-TA, Tenax-GR, Carbotrap, Chromsorb, activated carbon, etc. Suitable adsorbents should be used for the sampling of different hydrocarbons to ensure not only the representative collection of the hydrocarbons of interests, but also their subsequent complete desorption for analysis. It has been found that some monoterpene compounds (e.g., α- and β-pinene) can be partly or completely decomposed, or transformed to other isomers, during thermal desorption on some adsorbents [17,18]. The most commonly used adsorbent for the sampling of monoterpenes is Tenax (GC or TA). Although it has the desired property of not retaining significant amounts of water, its adsorption capacity for the more volatile hydrocarbons is poor, and it also has the problem of artifact formation by reaction with oxidizing gases (e.g., O_3) in air. It has been observed that several new compounds appeared after Tenax polymer was exposed to the air containing ozone, with benzaldehyde and acetophenone being the most significant [19,20].

2.2. Analytical methods

Because of the complexity of the mixture of hydrocarbon compounds present in air, an analytical method that can resolve one compound from another is required. GC, particularly combined with the use of a high-resolution capillary column, offers excellent possibilities of speciation while the commonly used FID gives good sensitivity. However, there are also several other potential detection methods, some offering advantages over FID.

2.2.1. Flame ionization detection

FID is traditionally considered as a highly non-selective detector, and can respond to almost all VOCs. It has therefore been widely used for the determination of volatile organic compounds in air [7–17,21–33], and has undergone little change in the last two decades. Table 1 gives examples of the use of FID for the detection of biogenically-derived VOCs in ambient air.

Measurements of air concentrations of biogenic hydrocarbons (isoprene and monoterpenes) and their diurnal variations have been made at different forest and agricultural sites since the late 1970s [e.g., 16,21,25–27,30]. Different diurnal patterns have been observed for isoprene and monoterpenes. Generally, isoprene concentrations increase sharply in the early morning after sunrise with a maximum in the afternoon, while the air concentrations of monoterpenes during the diurnal cycle are the inverse of those observed for isoprene. This is due to the fact that emission of isoprene from vegetation is highly dependent on both temperature and light intensity, and is almost nil during the night. Monoterpenes are still emitted during the nighttime, since their emissions depend mainly on temperature, and are not very sensitive to light intensity. In a polluted area, isoprene and monoterpenes can be destroyed by reactions with ozone and the OH radical during the day, and during the night they can react with the NO_3 radical, in addition to ozone. Since some monoterpenes, especially α-pinene, can react more quickly with ozone and NO_3 than does isoprene, their concentrations during the day may reach a minimum even though their emissions are at maximum.

Concentrations of light hydrocarbons (C_2–C_6)

Table 1
Sampling and analytical methods for the analysis of natural NMHCs in air

Ref.	Sampling methods	Analytical methods	Detection limit	Compounds	Sampling location	Concentration (average/range) (ppbv)	
14	Stainless-steel canisters	Cryogenic preconcentration on Tenax GC (−120°C) Thermal desorption GC–FID	1 l 2 pptv (6 pg)	Ethyne	Rural area France	1.674	
				Ethene		2.039	
				Ethane		2.418	
				Propane		2.302	
				Propene		0.535	
				1-Butene		0.055	
				n-Butane		0.352	
				Isoprene		0.088	
				1-Pentene		0.014	
				1-Hexene		0.011	
10	Stainless-steel canisters	On-column enrichment (−80°C) GC–FID	0.5 l 5–10 pptv (5–10 pg)	Ethyne	Antarctic troposphere	0.011 (0.01–0.024)	
				Ethene		0.36 (0.20–0.90)	
				Ethane		0.37 (0.30–0.45)	
				Propene		0.21 (0.01–0.05)	
				Propane		0.04–0.09	
12	Stainless-steel canisters	On-column enrichment (−80°C) GC–FID	0.5 l 30 pptv (30 pg)	Ethyne	North Atlantic	0.19 (0.08–0.40)	
				Ethene		0.18 (0.04–0.51)	
				Ethane		1.56 (1.0–3.3)	
				Propene		0.11 (0.04–0.20)	
				Propane		0.48 (0.13–2.5)	
				n-Butane		0.30 (0.03–1.3)	
				n-Pentane		0.22 (0.03–1.3)	
16	Stainless-steel canisters	GC–FID	1 l 2.5 pptv (14 pg)	Isoprene	Tropical atmosphere: Brazil	2.40 (1.00–5.24)	
				β-Pinene		0.27 (0.07–0.54)	
				Myrcene		0.19 (0.01–0.32)	
				α-Phellandrene		0.18 (0.11–0.28)	
				α-Terpinene		0.49 (0.12–0.81)	
				Δ^3-Carene		0.24 (0.05–0.62)	
				γ-Terpinene		0.11 (0.03–0.18)	
				α-Terpineol		0.76 (0.04–1.46)	
				Linalool		0.20 (0.11–0.30)	
						Aug./Sept. 1982	Nov. 1982
				Isoprene	Niwot Ridge forest USA	0.63 (0.22–1.76)	0.11 (0.03–0.16)
				α-Pinene		0.14 (0.01–0.66)	0.07 (0.03–0.11)
				β-Pinene		0.08 (0.01–0.39)	0.07 (0.01–0.11)
				Camphene		0.04 (0.01–0.11)	0.05 (0.03–0.11)
				Δ^3-Carene		0.05 (0.01–0.19)	0.03 (0.01–0.04)
				α-Terpinene		0.04 (0.01–0.05)	
26	Adsorption on Tenax GC	Thermal desorption GC–FID GC–MS (SIM mode, for identification)	1 l 1 pptv (6 pg)		Niwot Ridge forest USA	May–Oct. 1981, Jun.–Oct.1982	
				α-Pinene		0.054	
				β-Pinene		0.097	
				Δ^3-Carene		0.051	
				Camphene		0.038	
				Limonene		0.03	
17	Adsorption on Tenax GC or Carbochrome	Thermal desorption GC–MS GC–FID	not available	Σmonoterpenes	Conifer forests USSR	7.25 (0.5–26.8)[b]	
						47.3 (3.0–180.4)[B]	

Table 1 (*continued*)

Ref.	Sampling methods	Analytical methods	Detection limit	Compounds	Sampling location	Concentration (average/range) (ppbv)	
30	Adsorption on Tenax GC	Thermal desorption GC–FID GC–MS (for identification)	0.2 l 10pptv (10 pg)	Isoprene α-Pinene β-Pinene Camphene	Agricultural area Japan	Wet season 0.56 (0.10–4.0)[a] 2.0 (0.10–21.0)[a] 0.82 (0.10–6.1)[a] 0.77 (0.10–4.0)[a]	Dry season 1.9(0.12–4. 3.0(0.23–22 0.73(0.10–4 0.44(0.10–2
15	Teflon bags	GC–FID	1 l 5 pptv (28 pg)	Isoprene Σmonoterpenes Σalkanes Σalkenes Σaromatics	Forests	2.04 (1.14–2.72) 0.23 (0.12–0.34) 7.88 (6.0–15.1) 17.41 (12.6–22.0) 8.43 (3.7–26.2)	
31	Stainless-steel canisters cryogenic	GC–FID GC–PID	0.3 l 20 pptv 1 ml 20 pptv	Isoprene	Forests Amazon basin	1.6 (0.6–2.7)	
32	Adsorption on Tenax TA	Thermal desorption GC–MS (for idetification) GC–FID	not available	α-Pinene β-Pinene Δ^3-Carene Limonene + 1,8-Cineole	Landes forests France	1.3 (0.6–2.5) 1.7 (0.6–3.4) 0.6 (0.2–2.5) 1.1 (0.5–2.0)	
33	Adsorption on Tenax-TA + Carbotrap	Thermal desorption GC–FID GC–MS (SIM mode, for identification)	5 l 2–4 pptv (20 pg)	Isoprene α-Pinene β-Pinene Limonene Myrcene Sabinene	Sitka spruce forests SW Scotland	Fall daytime 0.59 0.027 0.012 0.016 0.021 0.008	Fall nighttii 0.302 0.025 0.015 0.015 0.027 0.008
36	Adsorption on Tenax GC	Thermal desorption GC–MS (SIM mode)	0.1 l 10 pptv (6 pg)	α-Pinene β-Pinene Δ^3-Carene	Forests USA	0.11 (<0.01–0.73) 0.09 (<0.01–0.46) 0.10 (<0.01–0.38)	
37	Adsorption on Tenax GC	Thermal desorption GC–MS (SIM mode)	0.1 ng	α-Pinene β-Pinene Myrcene Δ^3-Carene Limonene	Forests (Pine, Sugi, Hinoki) Japan	0.05–1.30 0.03–0.54 0.01–0.12 0.01–0.04 0.03–0.27	
40	Adsorption on Tenax TA	Thermal desorption GC–MS (ITD)	1 l 10 pptv (60 pg)	α-Pinene Camphene β-Pinene Δ^3-Carene Limonene	Scots pine forests Sweden	0.15–1.2 0.01–0.2 0.01–0.35 0.20–2.2 0.01–0.5	
42	Adsorption on Tenax TA	Thermal desorption GC–MS (ITD, full-scan mode)	30–60 pg	α-Pinene β-Pinene Δ^3-Carene Limonene	Pine forest Netherlands	0.56 (0.12–1.2)[b] 0.43 (0.10–1.0)[b] 0.19 (0.03–0.58)[b] 0.11 (0.03–0.25)[b]	

[a]Data are given as parts per billion carbon (ppbC).
[b]Data are given as $\mu g/m^3$.

have also been measured in different areas (rural area, oceanic atmosphere, etc.) (e.g., Refs. [7–14]). In general, the concentrations of less reactive hydrocarbons (e.g., alkanes) are higher than those of more reactive compounds (e.g., alkenes).

The detection limit for the GC–FID system, depending on the operation mode (split or split-

less) when thermal desorption system is used, generally ranges from 5–50 pg. Although FID has been used for the analysis of hydrocarbons in air at very low concentrations (sub part-per-billion levels) with difficulty, the accuracy and precision of the results at these levels become progressively worse, and further improvements to the sensitivity and detection limits of FID would be extremely beneficial. However, FID still remains by far the most commonly used detection system for the measurement of ambient VOCs.

2.2.2. Mass spectrometry

MS has been used extensively as a GC detection method for the identification of organic compounds, and it has made a significant contribution to the understanding of the emissions of VOCs from vegetation. Although isoprene and monoterpenes are the main compounds emitted from plants, many other oxygenated VOCs have also been observed. Isidorov et al. [17] investigated more than 20 plant species, mainly representatives of the forests of northern Europe and Asia, and about 60 compounds of various classes were identified (see Table 2). They included paraffins and unsaturated hydrocarbons, alcohols, esters and ethers, carbonyl compounds, furans, and halogenated compounds. The main VOC components from deciduous trees were light hydrocarbons and oxygenated compounds, while most of the compounds (80%) emitted from coniferous trees were terpenes. Some of the compounds (e.g., paraffin hydrocarbons) may also be from anthropogenic sources. Many agricultural species can also emit VOCs. In the work of Winer et al. [29], VOC emissions from more than 30 agricultural species (crops and fruits) and a few plants have been investigated, and over 50 individual organic compounds were identified or tentatively identified as emissions from these species (see Table 2). In addition to isoprene and the monoterpenes, a number of alcohols, acetates and other esters, aldehydes, ketones, ethers, alkanes, alkenes and aromatic hydrocarbons were observed. Among the monoterpenes, 2-carene, which has not previously been reported as a biogenic emission, was observed to be a principal emission, along with β-phellandrene, from tomatoes. Sesquiterpenes were also observed from a number of plants species and in some cases the emission rates of the sesquiterpenes exceeded the monoterpene emission rates. Among the oxygenated compounds observed, *cis*-3-hexen-1-ol and *cis*-3-hexenylacetate were the most dominant. In the work of Tanner and Zielinska [34], several oxygenated compounds (see Table 2) were identified in addition to α- and β-pinene and camphene from the tarweed species. It has been reported that 6,6-dimethylbicyclo[3.1.1]heptane-2-one is a major product from the β-pinene oxidation reactions [35].

Although MS is used mainly for the identification of organic compounds, it has also been used occasionally for quantitative analysis [e.g., 36–42]. The detection limits of a GC–MS system depend on the split ratio, when the thermal desorption system is used, and also its operation mode, that is, full-scan mode and selected ion monitoring (SIM) mode. By choosing only a few selected ions, instead of full-scan, that are characteristic of the analyte(s), much lower detection limits (up to 100 times lower) are obtained with SIM, as a result of the increased time spent by the detector on the chosen ions. Generally, the detection limit of a GC–MS system in SIM mode is slightly lower than that of GC–FID.

2.2.3. Photoionization detection

Photoionization detection (PID) can almost be considered as a non-destructive detection system, since the ionization efficiency is about 0.1%. It is highly sensitive to most organic compounds, and the detection limits are typically 10 to 50 times lower than those of FID for the same compounds, due to a larger response and a lower signal noise [43,44]. Since a response is obtained only from compounds which have an ionization potential below the energy of the UV photons generated by the lamp, PID is a highly selective detection system, especially for alkenes, aromatic and other reactive hydrocarbons which have lower ionization potentials. This is very advantageous for atmospheric monitoring pro-

Table 2
Volatile organic compounds identified as emissions from vegetation

Sources						
38 agricultural (crops and fruits) and plant species [29]		22 species of plants [17]		Scots pine Norwegian spruce [41]	Monterey pine [28]	Tarweed species [34]
Isoprene	Bornylacetate	Propylene	Santene	α-Pinene	α-Pinene	6,6-Dimethylbicyclo[3.1.1]-heptane-2-one
Camphene	Butylacetate	Butylene	Cyclofenchene	β-Pinene	β-Pinene	Borneol
2-Carene	*cis*-3-Hexenylacetate	Isoprene	Bornilene	Camphene	Limonene	6,6-Dimethylbicyclo[3.1.1]-heptane-2-carboxaldehyde
Δ^3-Carene	*n*-Hexanal	2-Methylbutane	Tricylene	Sabinene	Myrcene	6-C_5H_{11}-tetrahydro-pyrane-2-one
Limonene	*trans*-2-Hexenal	2,3-Dimethyl butadiene	α-Thujene	Δ^3-Carene	Δ^3-Carene	
Myrcene	2-Heptanone	Methanol	α-Pinene	Myrcene	Camphene	
cis-Ocimene	2-Methyl-6-methylene-1,7-octadien-3-one	Ethanol	δ-Fenchene	β-Phellandrene		
trans-Ocimene	Pinocarvone	3-Hexene-1-ol	ϵ-Fenchene	Limonene		
α-Phellandrene	Verbennone	Propanal	α-Fenchene			
β-Phellandrene	1,8-Cineole	Isobutanal	Camphene			
α-Pinene	*p*-Dimethoxybenzene	Crotonal	Sabinene			
β-Pinene	Estragole	Acetone	β-Pinene			
Sabinene	*p*-Methylanisole	Butanone-2	Myrcene			
α-Terpinene	Methylsalicylate	Methyl vinyl ketone	Δ^3-Carene			
γ-Terpinene	*n*-Hexane	Pentanone-2	α-Phellandrene			
Terpinolene	1-Decene	Pentanone-3	β-Phellandrene			
Tricyclene or α-thujene	1-Dodecene	Furan	α-Terpinene			
β-Caryophyllene	1-Hexadecene	2-Methyl furan	β-Terpinene			
Cyoerene	*p*-Mentha-1,3,8-triene	3-Methyl furan	γ-Terpinene			
α-Humulene	1-Pentadecene	Ethyl furan	Limonene			
p-Cymen-8-ol	1-Tetradecene	Vinyl furan	Terpinolene			
cis-3-Hexen-1-ol	*p*-Cymene	3-Hexene-1-ol acetate	1,8-Cineole			
Linalool		Methyl chloride	Fenchone			
		Chloroform	Thujone			
		Dimethyl sulfide	*p*-Cymene			

grammes focusing on photochemical ozone production in which the priority is the speciation and quantification of the more reactive hydrocarbons. PID may also give a less complex chromatogram than FID, and thus simplify peak identification.

Improvements to the design of PID systems with capillary GC are still in progress [45], and despite its advantages mentioned above, PID has only been used occasionally for the analysis of hydrocarbons in ambient air [46–48]. This may be due partly to its major disadvantage, that its response is compound specific, making its general application tedious. It has been recently used for the determination of trace quantities of isoprene and monoterpenes in the atmosphere [49]. Since it is a highly sensitive and selective detector and is very suitable for the reactive hydrocarbons, it is suggested that efforts should be made in the future to use PID with capillary GC for the determination of low concentrations of reactive hydrocarbons, especially biogenic hydrocarbons, in air.

2.2.4. Electron-capture detection

After FID, electron-capture detection (ECD) is most commonly used for GC. The sensitivity of the detector is extremely high, and the detection limits can be 10^4 times lower than with FID. It is also extremely selective, and it has been widely used for the analysis of organic compounds in the atmosphere having strong electron affinity, such as chlorofluorocarbon (CFC) compounds. Its response to hydrocarbons is very low. However, if highly electronegative atoms, such as halogens, can be added to the hydrocarbon molecule, then use of ECD, with much higher sensitivity than FID, should be possible.

Efforts have been recently made to use the GC–ECD for the analysis of volatile alkenes via on-column bromine addition reactions [50,51]. In the work of Cao and Hewitt [50], pyridinium bromide perbromide (PBPB) was used as the Br_2 source, and the excess Br_2 remaining after bromine addition to alkenes removed by a methanol treated cholesterol–glass bead mixture. This mixture also provides suitable polar conditions for the bromine addition reactions with the alkenes in the gas-phase. The conversion efficiencies of the individual alkenes to their brominated products is very low for ethene, but increase with carbon number, reaching 74% for 1-butene. The sensitivity of ECD to brominated C_3–C_5 alkenes is about 200–300 times higher than conventional FID, but poor peak shapes limits its applicability at present. Further work is planned to improve the chromatograms, and thus the detection limits of the brominated compounds, by using a two-oven system which allows the temperatures for the brominating phase and the GC column to be maintained independently.

In the work of Trigg et al. [51], copper(II) bromide coated onto a solid support was used as the Br_2 source. Because of the low bleed of Br_2 from $CuBr_2$, higher temperatures (up to 140°C) could be used, and a bromine bleed scrubbing phase was not required. In addition, the Cu^{2+} ion in $CuBr_2$ may have a catalytic effect on the bromination of alkenes, but at higher temperatures (above 80°C), substitution reaction may occur. The conversion rates for C_2–C_4 alkenes were normally greater than 80%, and the detection limits of the GC–bromination–ECD system for alkenes (C_2–C_5) less than 5 pg.

2.2.5. Reduction gas detection

Reduction gas detection (RGD) was originally developed for detecting the reducing inorganic gases, particularly CO and H_2 [52,53]. However, since the principle of detection relies only on the reduction of HgO to Hg vapour:

$$HgO(s) + X \rightarrow Hg(vapour) + products \quad (1)$$

any reducing species (X) will, in principle, be detected, including organic molecules containing unsaturated bonds. O'Hara and Singh [54] used RGD to measure acetaldehyde and acetone concentrations in air, and Greenberg et al. have used it to determine isoprene concentrations at sub-ppbv levels in air [55]. The responses of RGD to C_2–C_6 alkenes, C_2–C_6 alkanes, isoprene and benzene have been investigated under different conditions using packed column GC [56]. RGD is considerably (about 200–300 times)

more sensitive to alkenes than is FID, and it has much greater sensitivity to alkenes than to alkanes. Its sensitivity increases with increasing HgO bed temperature, but its selectivity towards alkenes decreases at the same time. An additional positive feature of this detector is that it does not require flammable support gases (hydrogen and oxygen).

Although RGD was engineered for use with packed GC columns, an interfaced capillary GC–RGD system has also been developed, and used for environmental analysis [57,58]. The detection limit of this system for hydrocarbons is still not adequate for this purpose, being about 10 pg, due to peak tailing. It should be possible to improve the detection limit by heating the transfer line between the GC column and the detector. However, the peak tailing problem may be mainly due to the dynamic equilibrium process (adsorption–desorption) between the mercury vapour and the wall of the detection cell. Thus, more inert materials towards mercury should be used to reduce this effect.

2.2.6. Combustion–isotope ratio mass spectrometry

Since the isotopic abundances of carbon may be different according to origin (natural and anthropogenic), it may be possible to establish the origin of a chemical compound in air and to evaluate the relative importance of different sources by measurement of the $^{13}C/^{12}C$ ratio of that compound. Isotopic data may also facilitate an understanding of the mechanisms of the production and consumption of compounds. GC–combustion–isotope ratio mass spectrometry (C–IRMS) has been widely used for the determination of the $^{13}C/^{12}C$ ratios for CO_2 and CH_4 in the atmosphere [59–61]. It has also been recently used for studying the biosynthetic pathway of isoprene by measuring the fractionation between stable carbon isotopes during biosynthesis [62]. At present, GC–C–IRMS has rather high detection limits of about 50 ng for isoprene. Because hydrocarbons eluted from the GC column have to be converted to carbon dioxide prior to MS analysis for carbon isotope measurement by passing through an electrically heated combustion oven containing copper(II) oxide, the detection limits of this method for hydrocarbons are also dependent on the combustion efficiency of each organic compound. These can be improved by increasing the oven temperature. Growing interest in isotopic studies of the biogenic emission of hydrocarbons, for which the present detection limits are a limiting factor, necessitates improvements to the sensitivity of the GC–C–IRMS method.

2.2.7. Ozone chemiluminescence detection

The reactions between alkenes and ozone produce electronically excited formaldehyde which subsequently chemiluminesces:

$$\text{alkenes} + O_3 \rightarrow HCHO^* + \text{products} \quad (2)$$

$$HCHO^* \rightarrow HCHO + h\nu \quad (3)$$

Emission from $HCHO^*$ occurs in the region 450–550 nm, and this light can be measured and related to the concentrations of alkenes.

The chemiluminescence of alkene–ozone reactions was first explored as a possible method of detecting ozone by Nederbragt et al. [63], and as a selective GC detector for hydrocarbon gas analysis by Bruening and Concha [64]. It is selective, owing to the relatively small number of compounds that chemiluminesce upon reaction with a given reactant, and very sensitive since the chemiluminescence appears out of a near zero light background. In principle, a single photon generated from a chemiluminescent reaction can be detected. Its selectivity depends very much on the detector temperature: at lower temperatures (100°C), only alkenes can be detected; at higher temperatures (250°C), alkanes can also be detected. The detection limit is frequently at the nanogram level and is temperature dependent. This detection method has the advantage of being based on a very fast, non-catalytic and flameless reaction, but the foremost advantage is that it is possible to monitor certain atmospheric species in real-time.

Hills and Zimmerman [65] constructed a continuous isoprene monitor, based on its reaction with ozone. It has a response time of 0.1 s, is linear over 3 orders of magnitude, and has a

detection limit of 400 pptv and no baseline drift. Its application resulted in the first continuous measurements of single-leaf isoprene fluxes from white oak, aspen, and cottonwood trees, as well as fluxes from blue spruce. In general, one would expect discrimination between isoprene and other alkenes to be poor since all alkenes react to some extent with ozone to produce $HCHO^*$, but the rapid reaction of isoprene with ozone and the use of selected wavebands does allow discrimination of isoprene. Interference from propene is the major problem as responses to these two compounds are roughly the same, and if comparable amounts of each were present, the chemiluminescent signals could not be distinguished. Fortunately, this is rarely the case since the isoprene–propene ratio in air is usually >10 in regions where biogenic isoprene fluxes are significant. Interferences from monoterpene compounds are also slight. Thus, the instrument has the rapid response necessary to measure isoprene fluxes using the micrometeorological eddy correlation technique.

2.2.8. Other detection methods

Gas chromatography combined with atomic spectroscopic detection methods has been extensively used for the determination of organic species in air, and only a few representative examples are quoted here. Often several organic species based on the same element will co-exist in air, for example tetraethyl lead and tetramethyl lead, and GC–atomic spectroscopic detection offers the advantages of chromatographic separation, element specific detection and excellent sensitivity. Atomic absorption, with prior GC separation, has been used to determine individual tetraalkyl lead and ionic alkyllead species in air, with detection limits as low as 20 pg (Pb) [66,67]. Flame photometry has been used with GC separation to determine organosulfur species in air including dimethylsulfide, produced by marine phytoplankton [68]. Atomic fluorescence has been used for a range of organometallic compounds, including simultaneous detection of alkyllead, alkyltin and alkylselenide compounds [69]. Microwave-induced electrical discharge plasma has been used with GC for a wide range of organic and inorganic molecules, for example in gasoline samples [70]. Atomic emission spectroscopy with GC has been used to detect organomercury compounds [71].

Although not a chromatographic method, it should be noted that differential optical absorption spectroscopy (DOAS), which is based on the fact that all chemical compounds absorb light at specific wavelengths, was introduced for real-time monitoring of formaldehyde, ozone and nitrogen dioxide in air more than ten years ago [72]. Lofgren [73] recently used this technique to monitor benzene and toluene in urban air continuously. It has also recently been used to determine biogenic methane flux rates. Further instrumental development may extend the applications of DOAS to lower concentrations.

3. Requirement for continuous and fast-response detectors for hydrocarbons

Although chromatographic analysis can provide detailed information on the complex composition of the atmosphere, it is relatively labour intensive, costly and slow, usually requiring several hours from sample introduction to final tabulation. Thus only a limited number of samples can be collected and analyzed per day. This low sampling frequency makes detailed characterization of spatial and temporal variability difficult. One of the greatest uncertainties in the understanding of the mechanisms that control the chemical composition of the atmosphere concerns the exchange of trace species between the atmosphere and the surface. To investigate surface exchange, measurements of emission and deposition fluxes must be made over selected representative sites. Several techniques to measure these chemical fluxes have been developed, the most direct being that of eddy correlation. This micro-meteorological method is a fundamentally direct technique that has the advantage of not disturbing the nature of the surface. However, it relies on the use of a

continuous fast response detector and so has not been successfully applied to the measurement of hydrocarbon emission fluxes.

In order to continuously monitor individual hydrocarbons in the atmosphere, a separation step as in GC must be excluded. Thus any detector developed for this purpose must be selective and specific to the individual hydrocarbon of interest according to its unique characteristics (e.g., light absorption at specific wavelengths) with minimum interferences under specific conditions.

4. Summary

Although several potential detection methods are available, FID is still the most widely used method for the measurements of VOCs at low concentrations in air. By preconcentrating large sample volumes, concentrations of hydrocarbon in air as low as a few pptv (10^{-12} v/v) can be measured. However, the accuracy and precision of the results at these levels become progressively worse. Moreover, some compounds may be lost or formed by reaction with oxidizing gases (e.g., ozone) during the preconcentration process, making the results unrepresentative. Thus, increased sensitivity is required if the composition of the unpolluted atmosphere is to be better understood. Automation of sampling and analytical methods will allow temporal and spatial variations to be quantified and the development of detectors for specific compounds will allow particular research issues in atmospheric chemistry to be addressed. Finally, the development of continuous fast-response methods will allow measurement of hydrocarbon fluxes by micrometeorological techniques.

Acknowledgement

We would like to thank two anonymous referees for their critical comments and Jim Greenberg for helpful discussions.

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Journal of Chromatography A, 710 (1995) 51–59

JOURNAL OF CHROMATOGRAPHY A

Review

On-site monitoring of volatile organic compounds as hazardous air pollutants by gas chromatography

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Abstract

There are a large number of organic components in air. These components can be classified in six groups. On-site monitoring procedures for two of these groups, oxidant precursors and hazardous air pollutants, are reviewed. For hazardous air pollutants, mainly long-term data are required. Oxidant precursors, however, some of which are very volatile, must be detected and quantified as early and as rapidly as possible. The monitoring techniques differ accordingly. Considerations governing on-site monitoring methods for both purposes are discussed.

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1. Introduction

There are a large number of trace organic compounds in air and the quantity of such components originating from human activity is increasing year by year. These components are emitted from industry, automobile exhaust, agriculture, volatile organic solvents, etc., and then mix with the organic components of natural origin. It is very important to be able to detect and quantify these trace organic components in air in order to identify source contributions, causes of photochemical smog formation and effects on human health. The hazards such trace organic components represent depend on the long-term exposure to them. A number of efforts

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0021-9673/95/$29.00
SSDI 0021-9673(95)00191-3

to detect these trace organic components in air, determine the concentration levels and define the nature and extent of transformation are listed and reviewed [1–5]. The next stage is to develop continuous monitoring methods for longterm observation of the target components.

2. Classification of trace organic components in air

There are long lists of organic components, hazardous air pollutants (HAPs), in environmental air. Many of these components are thought to be carcinogens or mutagens. Many countries have legislation on the maximum admissible concentrations of these components in drinking water, waste water, underground water, environmental water and air, and back this up by monitoring.

It has been proposed that volatile organic components (VOCs) in air should be put into four classes in terms of possible adverse effects: (1) VOC-OXes: VOCs characterized by high photochemical ozone and peroxyacetyl-nitrate (PAN)-creating potentials (mainly alkenes, alkynes and alkanes from C_2 to C_8, arenes from xylenes to tetramethylbenzenes, terpenes), oxidant precursors. (2) VOC-TOXes: VOCs that are either known to be toxic or cause concern with respect to toxicity (HAPs). (3) VOC-STRATs: VOCs characterized by high ozone depletion potentials (freons, halons, chlorinated hydrocarbons). (4) VOC-CLAIMs: VOCs claimed to have positive or negative greenhouse effects [6].

Two more classes are now added to this list. One is secondary pollutants formed by the photochemical oxidization of hydrocarbons. It is very difficult to identify the original source of aldehydes, free fatty acids, ketones and ethers. Aldehyde, PAN and peroxypropionyl nitrate (PPN) groups can better be classified as secondary pollutants (VOC-FORMs: mainly formed by photochemical oxidization) [2]. The other is semi-volatile organic components [semi-VOCs: changing form according to environment, e.g., air-tight packaging, atmosphere, soil (polyaromatic hydrocarbons, pesticides)]. Specifying these two extra groups in the classification will help point efforts to develop monitoring methods in the right direction. It should further be noted that these components are related to their emission sources, and that some of them belong to two or more classes. It is also very important to notice that there is a close relationship between toxic organic compounds in air and in water.

Many monitoring methods (separation and detection procedures) which meet the observation requirements have been developed and examined. A survey of these methods and their applicability is given in Table 1. These methods are also used to complement each other for the purposes of tracking the process of environmental change. But samples need transportation, and time elapses before analysis; consequently, reaction or adsorption often takes place during sample storage [7,8]. The lifetimes of some VOC-TOX components are one day or less [1,2]. The potential change in components such as VOC-OXes within a short time means that a large number of sample analyses is required [9]. In such cases, on-site observation must be the ideal method. Continuous observation of VOC-STRATs and VOC-CLAIMs is also necessary, but in these cases analysis with sample collection by canister or adsorption tube for several times a year, is sufficient [8,10].

This review focuses on the on-site method for monitoring VOCs in air, and examines possible ways of optimizing quantitative analysis for this purpose.

A number of trace organic components of air are present at extremely low concentration levels. This means that a very powerful method is required, especially for VOC-OX and VOC-TOX measurement. Capillary gas chromatography (GC), with sensitive and selective detection, can meet the requirements. In the development of the system, the most important aspects are the selection of the detector and the sample volume appropriate to the analysis. Table 2 shows the appropriate detectors, together with estimates of minimum sample volumes for long-term observation (10 times higher than the detection limit).

Table 1
Classification of VOCs and observation procedure (sample collection–separation–determination)

Classification		On-site monitoring	Sampling/analysis
VOC-OX		TD–GC–FID TD–GC–MS	Canister TD
VOX-TOX	Halogenated hydrocarbon	TD–GC–PID–ECD (+FID) TD–GC–PID–ELCD TD–GC–MS	Canister TD
	Oxidized hydrocarbon	TD–GC–MS	Canister TD
VOC-FORM	PAN,PPN	SL–GC–ECD CT–GC–ECD	CT
	Aldehyde	NA	Reaction–GC–FTD Reaction–GC–MS Reaction–HPLC–UV
Semi-VOC		NA	SPE–GC–MS PUF–GC–MS
VOC-STRAT		NA	Canister–GC–ECD
VOC-CLAIM		SL–GC–FID (methane) TD–GC–FPD (dimethyl sulfide)	Canister

TD = Adsorption–thermal desorption; SL = direct injection by sample loop; CT = cold trapping; Reaction = collection by chemical reaction with reagent; SPE = solid phase extration; PUF = polyurethane foam collection; NA = not available.

3. Problems and key points in the development of on-site monitoring methods

High-resolution gas chromatography is a powerful technique suitable for on-site monitoring for trace and complex volatile organic components in air (VOC-OX and VOC-TOX). However, there are some problems to be solved concerning the optimization of the analysis system. Sample collection and the introduction procedure are key aspects governing the construction of automated systems.

Liquid nitrogen or a similar coolant is commonly used for sample collection and sample injection into a capillary gas chromatograph for gaseous sample analysis. (1) A large proportion of sample collection and concentration is done with liquid nitrogen or liquid argon [11,12]. (2) Liquid nitrogen or liquid carbon dioxide is used for cryogenic focusing during introduction of the sample into the capillary column. There are two techniques: (a) a cryogenic focusing device is attached in front of an analytical column [13–16]; (b) the GC oven is operated at sub-ambient temperature (whole-column cryogenic focusing) [17–25]. In both techniques, plugging problems are caused by water or carbon dioxide in air samples.

When both easy maintenance is required and long-term observation is the objective, liquid nitrogen and liquid argon are not desirable as coolants because of their rapid loss by evaporation. The system developed must be simple in design and readily optimizable. These problems will be solved if the sample is collected and concentrated on an adsorbent, thermally desorbed by rapid heating, then concentrated on a stationary phase. With these techniques the use of coolant would be omitted. Reaction of collected sample with ozone is known to take place on the surface of adsorbent [7,26]. This should be taken into account in system evaluation.

Table 2
Appropriate detectors for on-site monitoring and detection limits

Detection system	Detection limit (estimated sample volume for 0.1 ppb level detection)	Stability /week	Special property	Applicability
Flame ionization detection (FID)	0.1 ng (100 ml)	± 2%	Proportional response to carbon number, very stable. Good for quantitative detection	VOC-OX VOC-TOX VOC-CLAIM (CH_4)
Mass spectrometry (MS)	1 pg/SIM mode (10 ml) 0.1 ng/SCAN mode (100 ml)	± 10%	Poor sensitivity in scan mode. Highly selective. Low-molecular-mass hydrocarbons difficult to detect	VOC-OX VOC-TOX VOC-FORM
Electron-capture detection (ECD)	1 pg (CCl_4) (1 ml)	± 3%	Highly sensitive to over 3 chlorine atoms in molecule. No destruction	VOC-TOX VOC-FORM(PAN) VOC-STRAT
Electrolytic detector (ELCD: halogen mode)	1 ng (1000 ml)	± 5%	Proportional response to the number of chlorines, bromines. Stable	VOC-TOX
Photoionization detector (PID)	0.1 ng (benzene) (100 ml)	± 5%	Selective response to aromatics unsaturates. No response to alkanes. No destruction	VOC-OX VOC-TOX
Flame photometric detector (FPD)	10 pg (sulfur) (50 ml)	± 5%	Non-linear response. Sulfur-, phosphorus-selective	VOC-CLAIM

Nevertheless, an adsorption/thermal desorption system will be preferable to a liquid coolant system for continuous monitoring in a short period because of its simple handling.

From the point of view of system design, the use of liquid carbon dioxide is a possibility. For the design of the rapid monitoring system, the most important point is minimization of the sample volume in such a way that the target components can be reliably detected. This is the fundamental difference between the rapid and long-term monitoring systems in terms of design requirement.

4. On-site monitoring system designed for VOC-OX

The purpose of this system is the observation of change within a short time; thus rapid analysis, as soon as possible after sampling, is required. The ideal would be continuous observation. But the mean concentration based on hourly analysis will be sufficient to provide the information required for emission source monitoring, estimation of photochemical reaction or research into long-range transportation.

4.1. Selection of the detector and GC separation

Flame ionization detection (FID) is the preferable because the target components range from ethane (C_2) up to C_{13} hydrocarbons, and the major components are aliphatic and aromatic. The FID response relative to the number of carbons in the molecule is easy to calibrate by relative response. The system with MS as the detector was applied to the non-methane organic gas analysis method (recording $>C_5$ hydrocarbons for the assessment of automobile exhaust gas). The disadvantage of such a system in air quality monitoring, however, is the difficulty in obtaining quantitative data for $<C_5$ hydrocarbons. It is very hard to design one single on-site

monitoring system to detect and quantify trace components such as alcohols, aldehydes, esters, ketones, etc. The GC–FID system design will differ depending on the target component range, from C_2 to C_9 or C_2 to C_{13} analysis. An aluminium-plot column used for C_2 isomers separation over room temperature has been described [27]. A well-known shortcoming of this column is the change in the retention time of unsaturated components caused by the presence of water. Sample and carrier gas have to be dried, whereby the identification of the component may be missed. Membrane-type dryers such as nafion (Perma pure dryer) will be better than the use of desiccants (e.g., Na_2CO_3, K_2CO_3, $CaCl_2$, $Mg(ClO_4)$, P_2O_5, etc.), which, when used as dryers for air samples, melt on contact with the desorbed water or solve the sample into the desorbed water. It is better to use a molecular sieve or similar desiccant to dry the carrier gas. Also, some components disappeared in the column during separation (e.g., 1,1,1-trichloroethane converted to 1,1-dichloroethene and HCl). Single-column separation is very easy to operate, but separation up to C_{13} hydrocarbons is difficult without sub-ambient temperature operation. Column switching or a multi-dimensional system will be required for C_2 to C_{13} analysis [28].

The practical system design proposed is as follows. (1) C_2 to C_9 separation: sample drying–concentration by adsorbent–thermal desorption–aluminium-plot column separation–temperature programming. (2) C_2 to C_{13} separation [28]: sample drying–concentration by adsorbent–thermal desorption–methyl silicone pre-column–aluminium-plot column separation–temperature programming–column switching. These systems can also operate in long-term monitoring. The sample volume (100–500 ml) is small enough to ensure that the detection limit is below 0.1 ppb.

4.2. Sample concentration

The adsorbent trap design recommended for a wide range of hydrocarbons is useful for multistage trap design, e.g., TENAX–activated aluminium–activated charcoal or graphitized carbon–molecular-sieving carbon. It will be better to dry the sample before adsorption.

5. On-site monitoring system designed for VOC-TOX

The purpose of this system is to observe the average exposure of mankind to harmful air components. The average concentration is important rather than change within a short time. In this context, analysis frequencies of about twice per day will be sufficient.

5.1. Selection of the detector and GC separation

Much effort has been put into air quality and water quality analysis [3,11–25,29–33]. Since the target components are similar in both cases, it is possible to apply the separation and detection system used for water quality analysis direct to air quality analysis [34].

The target components are chlorinated or aromatic hydrocarbons; the recommended detector must provide selective and sensitive detection. MS is suitable for such a purpose. This has the further advantage of compatibility with multiple detection systems: PID–electron-capture detection (ECD), PID–FID (TO-14 method, U.S. EPA air quality analysis) [35], or PID–ELCD (method 502.2, US EPA water quality analysis) [36]. With the exception of a few freons, most of the target components listed in the TO-14 method are included in Method 502.2 (see Table 3). Thus, it is possible to analyse for VOC-TOX components under the same conditions as employed in purge and trap analysis if the sample volume is optimized. The advantage of ELCD compared with ECD is the relative response proportional to the number of chlorine or bromine atoms in a molecule. The sensitivity of ELCD is less than those of FID. A larger sample (>1 l) is required in order to obtain better detection. Fig. 1 shows the chromatogram of an air sample.

Analysis conditions for water quality using MS for detection can also be easily applied to air quality analysis. The breakthrough volume of the

Table 3
Volatile organic components listed according to EPA Method 502.2 for water quality and (underline) EPA TO-14 Method for air quality analysis

	Component		Component
1	Dichlorodifluoromethane	31	1,2-Dibromoethane
2	Chloromethane	32	Chlorobenzene
3	Vinyl chloride	33	1,1,1,2-Tetrachloroethane
4	Bromomethane	34	Ethylbenzene
5	Chloroethane	35	1,3-Xylene
6	Trichlorofluoromethane	36	1,4-Xylene
7	1,1-Dichloroethene	37	1,2-Xylene
8	Methylene chloride	38	Styrene
9	*trans*-1,2-Dichloroethane	39	Bromoform
10	1,1-Dichloroethane	40	iso-Propylbenzene
11	*cis*-1,2-Dichloroethene	41	1,1,2,2,-Tetrachloroethane
12	2,2-Dichloropropane	42	1,2,3,-Trichloropropane
13	Bromochloromethane	43	Bromobenzene
14	Chloroform	44	*n*-Propylbenzene
15	1,1,1-Trichloroethane	45	2-Chlorotoluene
16	1,1-Dichloropropene	46	4-Chlrotoluene
17	Tetrachlorocarbone	47	1,3,5-Trimethylbenzene
18	1,2-Dichloroethane	48	*tert.*-Butylbenzene
19	Benzene	49	1,2,4-Trimethylbenzene
20	Trichloroethene	50	sec-Buthylbenzene
21	1,2-Dichloropropane	51	1,3-Dichlorobenzene
22	Dibromomethane	52	1,4-Dichlorobezene
23	Bromodichloromethane	53	4-Isopropyltoluene
24	*cis*-1,3-Dichloropropene	54	1,2-Dichlorobenzene
25	Toluene	55	*n*-Butylbenzene
26	*trans*-1,3-Dichloropropene	56	1,2-Dibromo-3-chloropropane
27	1,1,2-Trichloroethane	57	1,2,4-Trichlorobenzene
28	1,3-Dichloropropane	58	Naphthalene
29	Tetrachloroethene	59	Hexachlorobutadiene
30	Dibromochloromethane	60	1,2,3-Trichlorobenzene

trap was first tested to establish the purge conditions. It proved to be sufficient for air sample collection. Also, the recovery and the capillary column introduction have been optimized. High resolution was achieved by using a narrow-bore capillary column and high-sensitivity detection was achieved by means of whole-sample introduction into the column. In this case, cryogenic focusing is recommended as a means of obtaining good separation for light hydrocarbons. This procedure will be simplified by miniaturizing the trap (optimized to capillary column) and rapid heating.

Recently, the Japanese water quality regulation method adapted its procedure of purge and trap–capillary GC–MS. This now has direct sample introduction into the capillary column with or without cryogenic focusing.

Depending on the total sample volume and its water content, water in the air often causes plugging. This problem has been overcome by the purge and trap method. The purge gas was saturated by water vapor, and when TENAX was used as a trap adsorbent material, the trapped sample could be introduced into the capillary column. Recently, U.S. EPA Method 524.2 was extended (revision 4) to analyse 83 target components [32]. Fig. 2 shows how some oxygenated hydrocarbons in air can be analysed for VOC-TOX components under the same conditions (the identification of some of the peaks is given in Table 4).

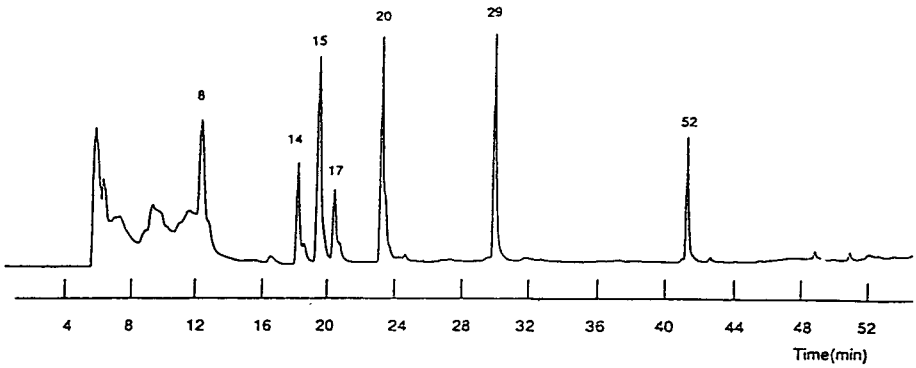

Fig. 1. Chromatogram of halogenated organic hydrocarbons in air obtained via adsorption–thermal desorption–capillary column–GC–ELCD. Analytical conditions: 1-l sample collected on TENAX GC trap at 0°C; desorption temperature 250°C, 2 Quadrex 502 columns 75 m × 0.53 mm I.D.; column temperature profile 40°C, 10 min hold, raised at 4°C/min to 230°C. Numbered peaks show components detected according to the list in Table 3. PID–ELCD dual detection system can be easily applied.

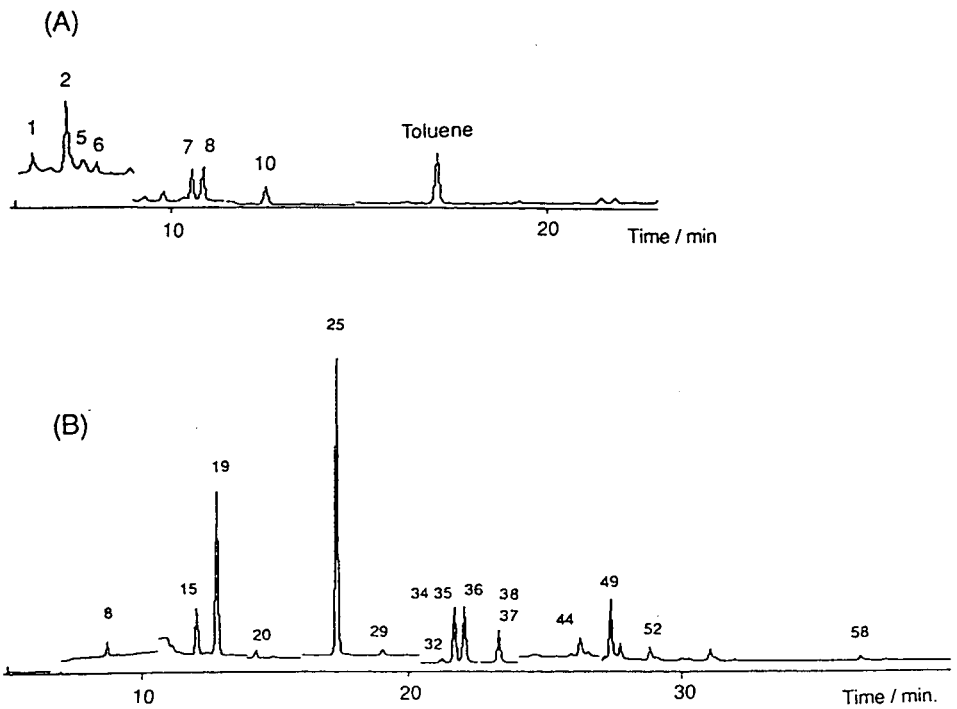

Fig. 2. Chromatogram of VOCs in air obtained via adsorption–thermal desorption–capillary column–GC–MS (SIM mode). The chromatogram is shown as a reconstructed total ion. (A) A 60-ml sample concentrated on TENAX GC at room temperature. Oxygenated components were selected. Target components are listed in Table 4. Numbered peaks show components detected in air according to the list in Table 4. (B) A 100-ml sample concentrated on TENAX GC at room temperature. Target components are listed in Table 3. Numbered peaks show components detected in air, according to the list in Table 3. Analytical conditions: desorption temperature 280°C, Halo-Matics 624 column (Quadrex) 30 × 0.25 mm I.D.; column temperature profile 40°C, 6 min hold, raised at 4°C/min to 200°C; short thick-film methylsilicone column placed in front part of analytical column as a focusing column; this part was cooled by carbon dioxide to about −50°C.

Table 4
Target components list for oxygenated hydrocarbons in air; detailed GC conditions shown in Fig. 2A

No.	Component	No.	Component
1	Methanol	7	2-Butanone
2	Ethanol	8	Ethyl acetate
3	Acetonitrile	9	2-Methoxyethanol
4	Acetone	10	1-Butanol
5	Diethyl ether	11	4-Methyl-2-pentanone
6	2-Propanol	12	Dimethylformamide

To correct the MS sensitivity, the addition of an internal standard is recommended. This technique is commonly used for water quality analysis and will apply to air quality analysis. An internal standard was fed into each sample as shown in Fig. 3. The internal standards used were 1,4-difluorobenzene, d5-chlorobenzene and bromochloromethane [37]. Fluorobenzene is used as an internal standard for water quality analysis [36]. One of the drawbacks of this system is that it is expensive.

5.2. Special considerations for long-term observation

It is very important to determine long-term exposure in order to estimate the hazard caused by trace organic components. Extending the analysis interval to once or twice a day will simplify the analysis and reduce the number of data from which the average concentration is obtained, but then the sample collection procedure and/or storage became very important. If the sample intake remains in the trap for such a long time, the collected volume will be huge, excessively large for MS analysis. In such cases, some of the collected sample can be split off into the second trap, so that the sample volume is optimized [37]. The sample stored in the canister can easily be used to optimize the sample introduction volume. The flow of stored sample through the trap in each analysis will determine the optimum sample volume (canister sampling was used for field sampling under the TO-14 method). If storage is for less than one day, the artifact will be eliminated. Large amounts of sample will be required if MS is operated in the scan mode; sample volume will be much smaller if ion-trap MS is used as the GC detector [38].

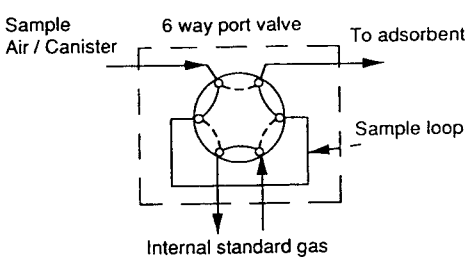

Fig. 3. Flow diagram of internal standard addition for VOCs analysis using GC–MS. During sample collection, internal standard gas was fed into the trap from the sample loop at regular intervals via a six-port injection system.

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Journal of Chromatography A, 710 (1995) 61–70

JOURNAL OF CHROMATOGRAPHY A

Automated gas chromatographic analysis of volatile organic compounds in air

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Abstract

The performance of an automated system developed for environmental trace analysis to collect, preconcentrate and analyse organic atmospheric pollutants present in the ppb and ppt range was evaluated by taking into account the use of several detectors for identification.

Organic compounds present in air, directly taken from the atmosphere or carried to the laboratory in passivated canisters or bags, were sampled with a large volume loop, concentrated in a trap filled with different types of adsorbents, thermally desorbed and stripped by a stream of pure gas and analysed with capillary columns of different length, diameter and polarity.

A programmed temperature vaporization injector (PTV) was also used for refocusing of the sample before analysis. Flame ionization and photoionization detectors were used for the determination of aromatic and aliphatic compounds. The sensitivity and stability of the system were checked. Some examples of application to the analysis of different samples at various concentrations are described.

1. Introduction

Air monitoring for volatile organic compounds (VOC) provides information about the chemical species present in the environment which may play the role of ozone precursors, origin of the oxidizing photochemical smog, and which can be used as indicators of air quality and exposure to toxic substances. Some of the compounds, e.g. the aromatic hydrocarbons, have a direct toxic or carcinogenic action and their measurement in outdoor, indoor and working environments is required [1–4]. The analysis of these substances is generally carried out by gas chromatography, owing to the high sensitivity and/or specificity offered by the various detectors presently available. Separation of the organic pollutants is achieved by proper selection of capillary columns of different diameter and length and filled with stationary phases of various polarities, depending on the chemical nature of the pollutants to be analysed.

Procedures used for sampling (trapping on different adsorbing materials, collection in passivated reservoirs) and analysis have been described [5,6] and official methods are provided [7–12]. The main problem is selection of the correct strategy for sample collection, which depends on many factors, such as pollutant concentration, humidity of the environment, duration and frequency of the sampling periods, location and the number of monitored points.

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0021-9673/95/$09.50
SSDI 0021-9673(95)00282-0

Dedicated systems, often installed in working places or in pollution-monitoring stations to perform on-line continuous analysis, can be optimized to monitor selected pollutants in a well-defined concentration range and have often a rigid hardware and software configuration.

Research laboratories, however, are often requested to separate, identify and measure many different compounds over a wide range of concentrations, from thousands of ppm down to the ppb or ppt level. Possible applications which require increased sensitivity are: analysis of flue gases from the chemical industry, sewage treatment plants; control of working environments for occupational hygiene research; monitoring of the areas surrounding chemical plants or other sources of unpleasant smell or toxic vapours; identification of emission sources to highlight potential risks in the case of pollution incidents; monitoring of urban air pollution due to traffic and domestic heating; research and measurement of organic ozone precursors in areas suffering from photochemical smog.

The above list, far from being exhaustive, indicates that an analytical system suitable for many applications and over a wide range of pollutant concentrations should permit a flexible strategy of sampling and analysis methods; each of those should be applied without modification of the samples taken and analysed in the field and of samples or standard mixtures available in the laboratory, in order to permit direct comparison of the results.

We have therefore evaluated the performance of an automated system originally developed for environmental trace analysis to collect, preconcentrate and analyse many atmospheric pollutants present in the ppb range, taking into account the possibility of application to the analysis of different samples and the use of several detectors for identification purposes.

2. Experimental

Sampling and analysis were carried out by using an environmental trace analyzer Model ETA 85.21 (DANI Strumentazione Analitica Spa, Monza, Italy), equipped with an automated sample collecting and processing unit that allows to collect a given volume of air, to trap the organic compounds, to desorb and dispatch them to the analytical unit, formed by a precolumn, by one or more packed or capillary columns, and by different types of detectors. All these operations are controlled by a flexible programming unit, which operates pneumatic valves, sets temperatures, detector sensitivities etc.

A short description of the standard process and the possible modifications is given below, with some examples of practical application.

2.1. Sample collection and processing

A schematic diagram of the sample collecting and trapping unit is shown in the left section of Fig. 1. All the surfaces that may come into contact with the sample are made of or lined with inert materials such as PTFE.

A pump provides for the aspiration of the air sample from the atmosphere, from a passivated canister or from a plastic bag; by means of automated switching valves (not shown in the figure) an air flow supplied by standard gas cylinders can be sampled at regular intervals for detector and integrator calibration. Zero air or pure inert gases can also be sampled in order to check the residual trap contamination after each analysis cycle at fixed intervals.

The thermostated sample loop, mounted on the sampling 6-ports valve V1, has a volume depending on the required amount of sample. Standard volume is 100 cm^3, but samples up to 300 cm^3 were used to increase sensitivity in some applications. By operating the equilibration valve, the loop pressure is equalized to atmospheric pressure; the valve V1 is then rotated and the sample sent to the trap by means of an auxiliary gas flow. This assures a constant amount of sample, independent of the different pressure of the air supplies (external air, gas cylinders, lecture bottles, canisters or bags).

The organic compounds contained in the loop volume are transferred and adsorbed in the trap mounted on the heated valve V2. Depending on the compounds to be trapped, many different

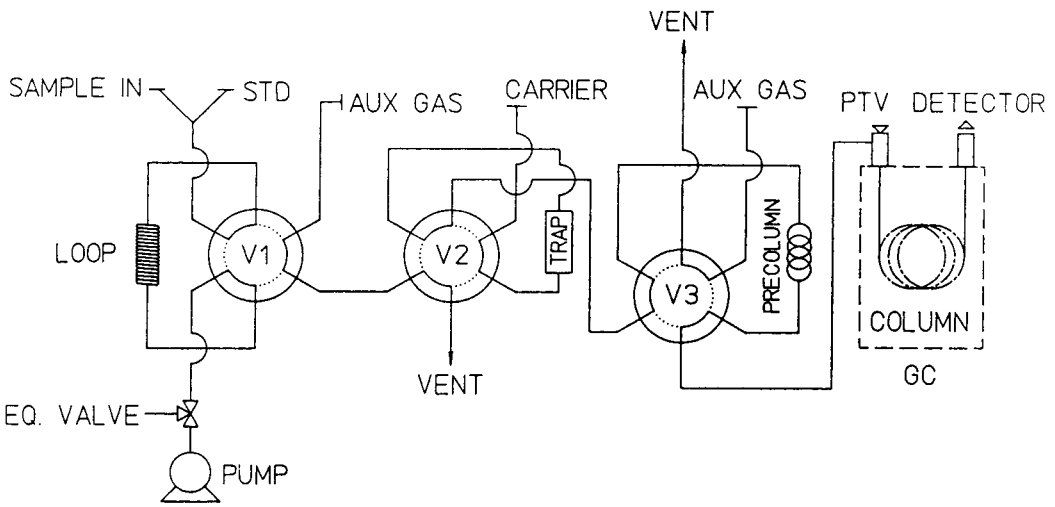

Fig. 1. Simplified diagram of the sampling and analysis system. V1 and V2: valves for loop filling and transfer of the sample to the adsorbing trap or directly to the analytical column. V3: valve for precolumn insertion and backflushing of unwanted compounds, can be replaced with an 8-port valve for multidimensional analysis with two columns.

materials can be used provided they can be effectively cleaned by the conditioning procedure and by the thermal desorption process, have a breakthrough volume large enough to trap the most volatile and less retained compounds, do not produce artifact peaks due to thermal degradation and do not irreversibly adsorb any analyte.

The following products were used: Carbograph (Carbochimica Romana and Alltech Associates); molecular sieves 5A, Chromosorb 106 (Johns-Manville); Graphtrap (Alltech Associates); Tenax (ENKA Research Laboratories) and Carbotrap C (Supelco).

The trap can be cooled by a cryogenic fluid circuit (liquid CO_2 or N_2) and heated by a heating mantle with a maximum speed of about 900°C/min. This procedure gives a high sensitivity also with direct sampling, because of the large volume of the loop. It is not necessary to wait a long time in order to pump enough air through the trap at low speed, to avoid saturation or breakthrough. The transfer of the sample from the loop to the trap is controlled by the flow-rate of the auxiliary gas connected to valve V1 and by the time set for the operation of the valves, and therefore the equilibrium between gas phase and the trap material can be established, optimizing the adsorption of the sample. Integrated or averaged results can also be obtained by transferring to the trap, before thermal desorption, many samples taken at regular intervals in order to sum the amounts of pollutants, provided the breakthrough volumes of the most volatile compounds are not exceeded.

It is known that one of the main limitations in the application of adsorbing samplers is the difference in adsorptive power between different batches of sampling tubes, the initial conditioning, the contamination and artifact formation during storage [13]. In order to give ideal results, each adsorbent tube should be conditioned and tested just before sampling and its blank value checked, but this procedure obviously cannot be applied during routine work. The use of the same trap for all analyses of a given type of sample avoids fluctuation of the results due to the difference in the performance of the various samplers. After the thermal desorption of each sample the trap is clean again and can be used for the next sample. This is checked by blank sampling of pure gas at fixed intervals.

2.2. Sample analysis

When the trap (in which the total amount of VOC contained in the loop volume was collected) is heated and valve V2 is operated, a stream of carrier gas removes the trapped compounds and transfers them to the analytical unit shown in the right part of Fig. 1. Different modes of analysis are possible.

By connecting the ports 1–6 of the heated valve V3, the sample is directly sent to the injector of the gas chromatograph. For some applications (e.g. for the fast analysis of aromatic compounds such as benzene, toluene, xylenes and styrene and when resolution of xylene isomers is not required) the sample is analyzed on a wide-bore column (30 m × 0.53 mm I.D.) operated at a high carrier flow-rate (10–15 cm^3/min). When higher resolution is required, a longer column must be used. When the analysis of some compounds present in the sample is not required, a precolumn can be connected to valve V3 and the heaviest compounds backflushed before entering the analytical column (see below in Section 3).

When a more complex analysis and a greater efficiency are required, longer narrow-bore columns are installed in the oven, and the programmable temperature vaporization injector (PTV) can be refrigerated and next heated in order to trap and concentrate the compounds previously collected in the sampling trap in a narrow band (sample refocusing) [14–16].

Table 1 shows some examples of applications to different types of pollutants and lists the main characteristics of the used adsorbents, columns and detectors.

2.3. Use of precolumns and multidimensional analysis

As seen above, the 6-port valve V3 shown in the right part of the schematic diagram of Fig. 1 is used to insert a precolumn which removes the light or heavy compounds before they enter the analytical column when only few components have to be analyzed in order to shorten the total analysis time. Unwanted compounds can be backflushed by means of an auxiliary gas. This procedure is mainly used to avoid the entering into the capillary column of substances such as water and high-boiling compounds.

Multidimensional analysis, which allows to cut one or more central parts of the chromatogram and send not well resolved compounds to another more efficient column, and dual column separation, with polar and non-polar columns mounted in series [17–21], are easier obtained by

Table 1
Example of system configuration for the analysis of various contaminants in air

Sample	Trap adsorbent	(a) PTV liner (b) precolumn	Column	Detector
Ethylene oxide	Carbosphere 60/80	–	Porapak QS, 2 m × 2 mm	PID
Chlorinated hydrocarbons	80% Graphtrap 60/80 20% Molecular sieves 5A	(a) Graphtrap 60/80	Carbograph VOC 30 m × 0.32 mm	FID ECD
Volatile compounds	activated carbon	–	(a) Carbowax 20M 5 m × 0.53 mm (b) Alumina-KCl 50 m × 0.3 mm	FID
Aromatic hydrocarbons	Graphtrap 60/80	(b) Carbowax 20M 10 m × 0.53 mm	Carbowax 20M 50 m × 0.53 mm	PID
Aliphatic hydrocarbons	Graphtrap 60/80	(a) Graphtrap 60/80	PONA 50 m × 2 mm	FID

installing in the position of V3 an 8-port valve, which allows the direct or reversed connection of two columns in any requested sequence, or the separate elution of the compounds from the polar or non-polar column. Based on isothermal analysis carried out on the two independent columns and by using more or less complex calculation methods [22–26] the most efficient temperature program can be selected which allows the complete and fast separation of the compounds of interest.

Parallel arrangement is achieved by connecting, by means of a zero-volume glass press-fit union, two capillary columns of different length and/or polarity to a short piece of deactivated capillary tubing inserted in the injector. The two columns are connected to two identical detectors (FID is the best choice due to its sensitivity for all organic compounds) which permit simultaneous analysis for identification purposes. Fig. 2 shows the flow-chart for the procedure in which the results of the two parallel runs are compared and names are attributed to the peaks on the basis of the retention times within a fixed tolerance. The identification on each column is cross-confirmed by comparing the retention times and the peak areas: correction factors are applied and the quantitative report for each column is printed. By further elaboration, the ratio between the areas or the corrected amounts of the substances identified is determined. If this ratio is equal or nearly equal to unity, the peak can be considered as free of interferences on both columns and its identity is confirmed. If the ratio is not unity, the chromatogram should be interpreted in terms of column polarity to establish what kind of interference is present and to identify the peaks correctly.

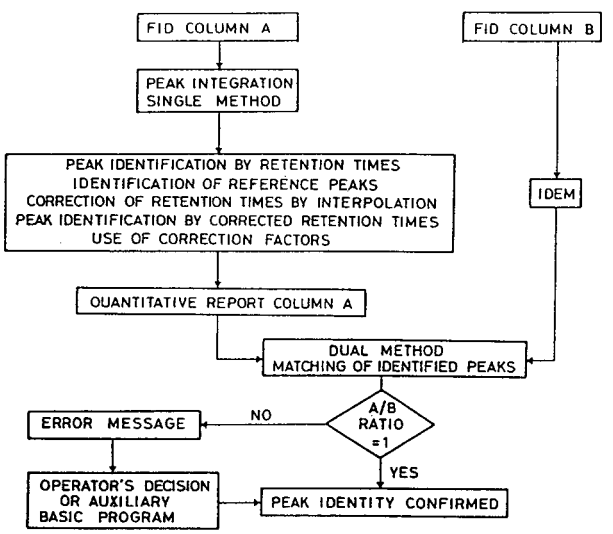

Fig. 2. Logical flow-sheet of the integrator or data system program used to identify peaks by simultaneous analysis on parallel columns of different polarity.

2.4. Choice of detectors

Different detectors can be installed and used separately or simultaneously after connecting them to the end of the column by proper press-fit unions and short tracts of deactivated or better methylsilicone-coated capillary tubings. Simultaneous electron-capture/flame ionization detector (ECD/FID) or FID/PID arrangements are useful for identification. The PID (photo ionization detector) is used for the analysis of aromatic compounds. In fact, notwithstanding the choice of polar columns that retard the elution of aromatic compounds, their interference with high-boiling aliphatic substances is still possible when the non-selective FID is used. However, using the PID no interference was observed (see Fig. 4).

2.5. Calibration methods

A source of standard gas can be connected to the sampling loop mounted on valve V1 of Fig. 1. Gas cylinders containing hydrocarbons and calibrated in the ppb range (SIAD, Bergamo, Italy), sampled at regular intervals, were found to give reliable results for about three months. Long-term stability of very diluted standard samples cannot be guaranteed, owing to the adsorption of the organic compounds on the walls of the cylinder. More concentrated mixtures, dynamically diluted by a stream of pure gas with a known flow-ratio, can be used in order to obtain the requested concentration. For some

compounds, the use of permeation tubes is advisable.

2.6. Multiple sampling

The monitoring of urban air pollution caused by traffic often requires samples to be taken at various heights in order to study the so called canyon effect in narrow streets [27]. Fig. 3 shows how various thermostated (40°C) 300-cm^3 loops connected to sampling tubes of different height are simultaneously filled up by means of separated membrane pumps and then automatically connected in sequence to the sample input port on valve V1 of Fig. 1. While the analysis cycle described previously (filling of the calibrated loop, trapping, desorption, refocusing in the injector and GC separation) is applied to the first sample, the others are stored in the corresponding loop and will be analysed in sequence. The inertness of the lines and valves (all PTFE-lined) is therefore essential in order to avoid sample decomposition and adsorption. In order to check if the different storage times influence the results of the analysis, three urban air samples were taken simultaneously at the same height and analysed in sequence using the PID for aromatics and the FID for all organic substances.

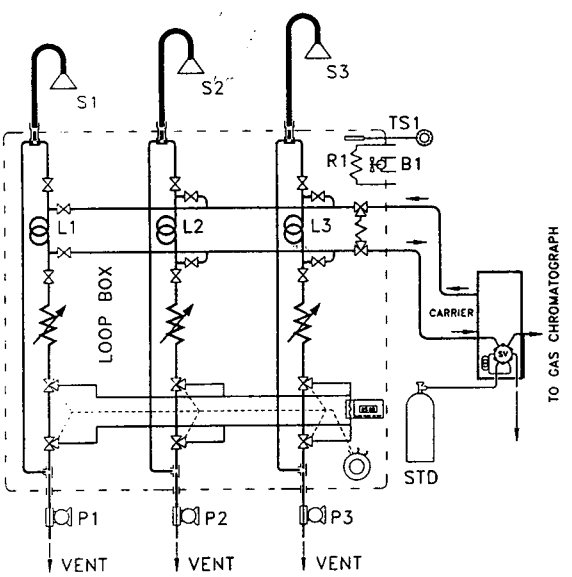

Fig. 3. Automated system for the simultaneous sampling of air at different locations or heights and transfer to the sampling loop and adsorbing trap. S1, S2, S3: sampling probes; L1, L2, L3: loops; P1, P2, P3: pumps; TS1, R1, B1: thermostating circuit.

3. Results

The results of series of measurement carried out with some of the methods summarized in Table 1 are shown.

Fig. 4 shows the analysis of aromatic compounds obtained on a Carbowax 20M bonded-phase capillary column, 50 m × 0.53 mm I.D. The upper trace shows the analysis of a reference standard (concentration 5 and 20 ppb), the second trace reports the chromatogram of a sample of urban air and the lowest trace is the result of the blank control made by repeating the complete analysis cycle with a sample of pure gas. When styrene analysis was not required, a precolumn having the same composition as the analytical column and a length of 10 m was used. After the elution of *o*-xylene the analysis was stopped by operating valve V3 at about 13 min on the 30-m and at 20–21 min on the 50-m column. The heavier compounds are then removed from the precolumn by heating and backflushing.

The reproducibility of the sampling and analysis time is of great importance for the correct automated identification of the compounds in a complex mixture. Table 2 shows the retention times averaged over a month of sampling of aromatic compounds analyzed on a Carbograph VOC column (Carbochimica Romana and Alltech Associates) 50 m × 0.25 mm I.D., filled with SP-1000 polyglycol phase. No appreciable effect of the humidity of the sampled air was observed, notwithstanding the fact that the environmental conditions during the tests changed repeatedly from warm and sunny weather to heavy rain and

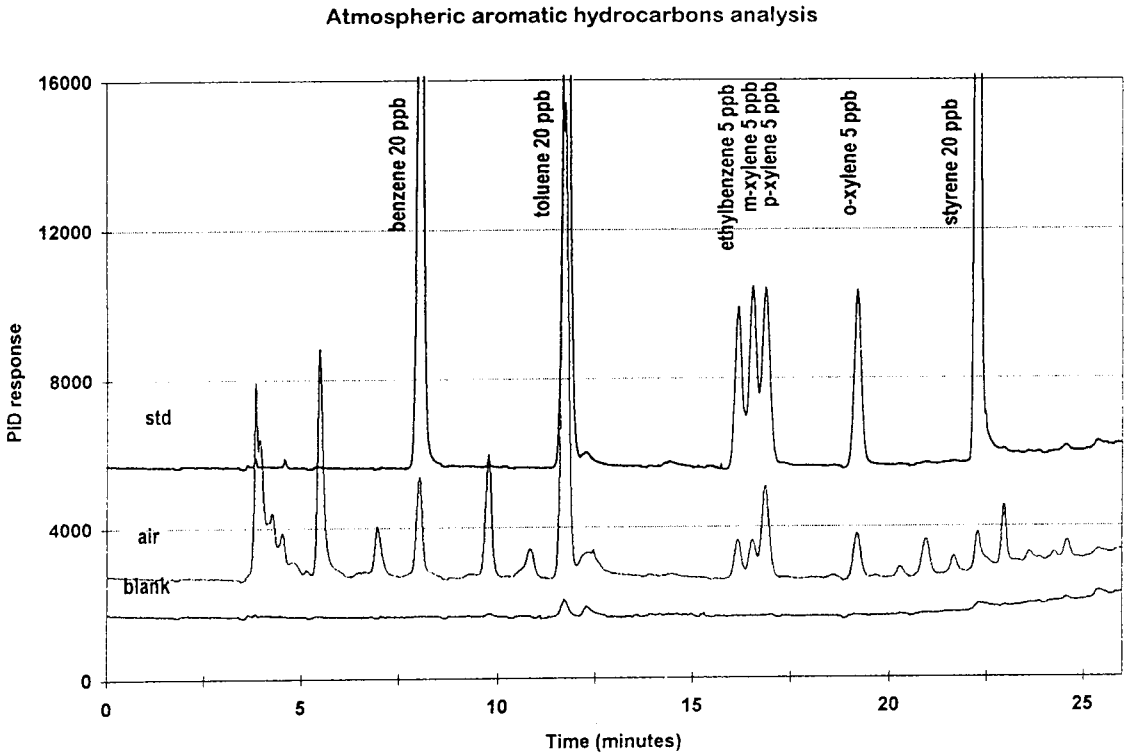

Fig. 4. Analysis of a calibration mixture of aromatic compounds (trace std), blank analysis of pure gas to check the trap cleanliness (trace blank); analysis of a real sample (trace air). Bonded polyglycol capillary column (50 m × 0.53 mm I.D.), PID.

high humidity. The sensitivity achieved with this method for aromatic compounds with a sampling loop of 300 cm^3 capacity ranges between 0.1 and 0.2 ppb.

The stability of the detectors over a wide time range is essential in order to permit comparison of the results obtained on different days. Table 3 shows the reproducibility of the response of the system to benzene, toluene, xylenes and styrene over 45 sampling, trapping, desorption and analysis cycles.

The effect of storage time in the multiple sampling procedure described in Section 2.6 is shown in Fig. 5, where the concentration of benzene measured in many consecutive analysis cycles within a car parking area is reported: the values obtained from the three lines do not show systematic scattering and therefore the different storage times in the loops do not seem to influence the results.

4. Conclusions

The use of multiple sampling and different analysis options permits to select the best strategy depending on the nature and concentration of compounds to be detected and measured. When their concentration is relatively high, direct injection with or without injector refocusing offers the requested sensitivity.

The transfer of the sample and the concentration in the trap of the whole amount of organic substances contained in the volume of the sampling loop and the use of cryofocusing and sensitive and specific detectors permit to

Table 2
Retention times of aromatic compounds analysed over the period of one month

Compound	Averaged retention time (min)	Relative standard deviation (%)
Benzene	9.09	0.19
Toluene	10.71	0.24
Ethylbenzene	13.14	0.26
p-Xylene	13.76	0.27
m-Xylene	13.88	0.27
Isopropylbenzene	15.18	0.22
o-Xylene	15.40	0.24
n-Propyl-benzene	16.67	0.17
1,3 + 1,4-Methylethylbenzene	17.40	0.15
Styrene	17.76	0.13
1,3,5-Trimethylbenzene	18.55	0.14
1-Methyl-2-ethylbenzene	18.78	0.12
p-Cymene	19.48	0.11
1,2,4-Trimethylbenzene	20.02	0.11
1,3-Diethylbenzene	20.64	0.10
1,4-Diethylbenzene	20.88	0.10
1,2-Diethylbenzene	21.56	0.09
1,2,3-Trimethylbenzene	21.85	0.09

Column: Carbograph VOC, 30 m × 0.53 mm I.D.; injection type, solvent split; programmable temperature vaporizing injector: 30°C for sample focusing, 300°C for evaporation; column temperature program, 40°C for 10 min, 2°C/min up to 60°C, 10°C/min up to 190°C.

increase the sensitivity of the method to the sub-ppb range. In comparison to conventional trapping in adsorbent tubes, which takes a long time and therefore does not permit instantaneous sampling, this technique allows more separate samples to be taken at the same time and analysed in the desired sequence and with the proper method.

Table 3
Reproducibility of the system for analysis of aromatic hydrocarbons over 45 analysis cycles

Compound	Averaged concentration (ppb)	Relative standard deviation (%)
Benzene	19.87	0.75
Toluene	19.38	1.01
Ethylbenzene	5.05	1.90
p-Xylene	4.99	1.72
m-Xylene	4.95	1.11
o-Xylene	4.96	0.81
Styrene	21.52	1.68

Bonded Carbowax 20M capillary, precolumn 10 m × 0.53 mm I.D., column 50 m × 0.53 mm I.D., PID (see chromatogram in Fig. 2).

Direct sampling from the atmosphere in fixed monitoring stations or the storage of the samples in passivated canisters or plastic bags for subsequent analysis in remote locations allows the use of the sampling system both for unattended automated monitoring of air pollution and for laboratory research and calibration purposes.

Although tabulated results are available for many VOC contained in air polluted by urban traffic, their identification is generally carried out on the basis of retention times on two columns of different polarity and confirmed by comparison with standard samples [28,29].

The control of pollution due to flue gas emission in industrial areas with many different plants and stacks, or due to improper disposal of industrial wastes, on the contrary, requires the identification of many and often unexpected

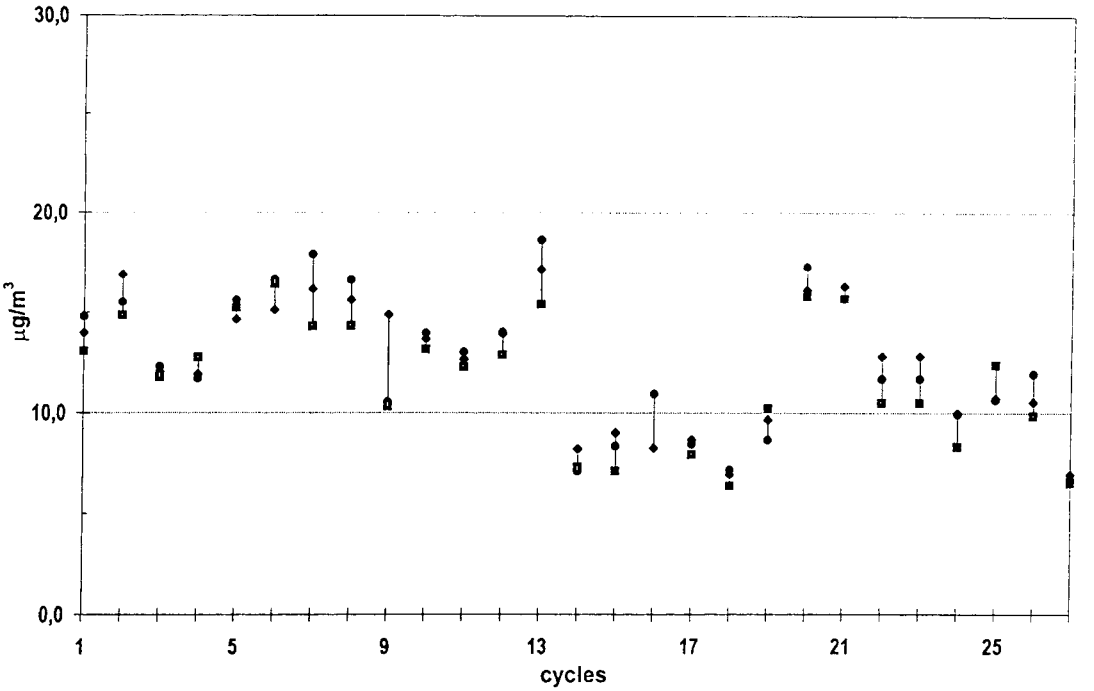

Fig. 5. Results of the analysis of benzene (PID) in many analysis cycles, sampled simultaneously with the system shown in Fig. 3. The different symbols refer to the three sampling lines.

compounds [30,31]. Coupling of conventional gas chromatographic detectors with mass spectrometers is suitable with relatively concentrated samples, as the sensitivity in the total-ion monitoring mode ranges between some nanograms for quadrupole mass analysers and about 2–10 pg for ion-trap detectors [32–36]. The selected-ion monitoring technique offers a ca. ten-fold increase of sensitivity of both detector types but, of course, can only be applied to confirm the presence of expected compounds. The possibility to increase the amount of trapped pollutants by repeated transfer of the loop volume to the refrigerated trap, described above, permits to collect enough material to detect many unknown compounds and identify them by means of automated library search algorithms.

The linearity of the sampling system and the detector can be evaluated over a concentration range of some decades by using an exponential dilution flask [37–39]. However, such a calibration method is time-consuming, does not permit full automation and is justified only for detectors whose sensitivity does not change appreciably with time, as the FID or the PID are. In this instance, if the calibration plot is linear, by checking one or two points of the line by means of known samples, the long-term quantitative accuracy is confirmed; deviations greater than a fixed value, automatically detected by the integration system, indicate that the calibration and linearity checking must be repeated.

The overall stability of the system, however, due to sampling, storage, desorption and analysis of the sample, is high enough to permit the automated operation of the equipment over a long period of time, without the need for calibration.

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Journal of Chromatography A, 710 (1995) 71–77

JOURNAL OF CHROMATOGRAPHY A

Assessment by gas chromatography and gas chromatography–mass spectrometry of volatile hydrocarbons from biomass burning

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Abstract

Well over thirty combustion-formed non-methane hydrocarbons were determined from uncontrolled burning of biogenic materials. Results are given for straw, conifer twigs, newsprint and hardwood. Samples were taken on triple-layer adsorption cartridges. After thermal desorption, the hydrocarbons were separated by gas chromatography on an aluminium oxide column. Samples were also taken with a gas syringe and analyzed after gas injection.

The hydrocarbon compositions were found to be remarkably similar for different kinds of biomass. Among 21 recorded alkenes and alkadienes, ethene was predominant, and the next most prominent species were propene and 1,3-butadiene. The large proportions of ethyne and the carcinogenic benzene increased further with increasing combustion efficiency.

1. Introduction

Natural and controlled forest and grassland fires give rise to vast hydrocarbon emissions of great concern with respect to photooxidant formation [1]. Burning of biomass like wood is used by man all over the world for heating and cooking purposes and causes large emissions [2]. It also causes high human exposure to volatile hydrocarbons, including alkenes and the carcinogenic species benzene and 1,3-butadiene which are genotoxic after metabolic biotransformation [3]. The desirable use of renewable raw materials may increase the amount of paper and other technical biomass products which are eventually burnt. These facts emphasize the need for analytical methods which permit the determination of specific organic compounds emitted from incomplete combustion of biomass.

This report on non-methane hydrocarbons from biomass burning employs analytical methods previously applied to hydrocarbons in urban air [4]. The approach is thought to be of particular value for the comparison of air pollutants from biomass burning, traffic and other sources of hydrocarbon emissions.

2. Experimental

2.1. Biomass burning

Small-scale burning with low oxygen supply was performed in a ceramic pot (1 l). A larger clay pot with a bottom hole was placed upside-down over the ceramic pot before sampling

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0021-9673/95/$09.50
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through the hole. Open burning of twigs from trees was performed on a gridiron and samples were taken nearby in the smoke plume. Samples from a wood-stove were taken in the exit of the chimney of a remote house. The materials and experiments giving the specific results reported are detailed under the tabulated data.

2.2. Sampling

Triple-layer glass cartridges (150 × 4 mm I.D.) were made with separate layers of Carbosieve S-III (rear layer, 0.1–0.3 g, 60–80 mesh, Supelco), Carbotrap (0.1–0.2 g, 20–40 mesh, Supelco), and Tenax TA (front layer, 0.05–0.1 g, 60–80 mesh, Chrompack). The cartridges were conditioned with helium (20–40 ml min^{-1}), initially (285°C, 60 min) and before each sampling (275°C, 10 min).

On sampling, the cartridge was connected by a Swagelok fitting to an air pump providing an accurate constant flow, normally set in the range 10–50 ml min^{-1}. Before and after sampling, the cartridges were kept in tight-stoppered glass tubes placed in brown bottles. Total sampling volumes ranged from less than 10 ml for most of the pot-burning studies to more than 1000 ml for slightly polluted ambient air.

Duplicate samples with widely different air volumes were used to check analytical results and reveal breakthrough. Single-layer Tenax cartridges were used to confirm recovery of compounds potentially sensitive to decomposition on the triple-layer cartridges.

Samples were also taken by a gas-tight syringe (50 ml) without enrichment on adsorption cartridges. This method was applied preferentially for the pot-burning experiments designed to give high hydrocarbon concentrations. It was also used to determine methane.

2.3. Gas chromatography

In the laboratory, the cartridges were placed in a desorption oven and connected to the carrier gas line of a gas chromatograph for desorption (235°C, carrier gas helium with a flow-rate of 20–40 ml min^{-1}, 14 min) into a cold trap (5 m × 0.32 mm I.D. empty FSOT column in liquid N_2). The helium gas was vented to air during desorption. Before the trap was heated (150°C, polyglycol), the vent was closed, and the carrier gas was passed through the analytical column only (30 cm s^{-1}). An optional drying cartridge placed before the cold trap was filled with magnesium perchlorate (0.2–0.4 g). It improved the analytical performance for samples with a high content of water.

Injection of gaseous samples was performed by filling gas from the sampling syringe into an empty column (3.2 ml) which was then connected into the carrier gas line by gas valves. Methane passes the cold trap and is lost with the vented carrier gas. Optional determination of methane was achieved by gas injection without drying, trap cooling, trap heating, and carrier gas venting.

The chromatographic separations were performed on an aluminium oxide column (50 m × 0.32 mm I.D. fused-silica, PLOT, Al_2O_3/5% KCl, Chrompack). The oven temperature program for the reported detailed separations was 30–110°C (10°C/min), 110°C (isothermal, 14 min), 110–200°C (4°C/min), and 200°C (isothermal). The response of the flame ionization detector was determined from hydrocarbon reference mixtures prepared in the laboratory and was set equal for all hydrocarbons. Furans were excluded when the percent composition of non-methane hydrocarbons was calculated.

2.4. Assessments by GC–MS

Mass spectrometric studies were made on a Varian Saturn II ion trap GC–MS instrument. Identifications relied on relative retentions, interpretations of spectra, and computer-based comparisons on the instrument with the NIST library of mass spectra. The reported GC–MS separations were made using a methylsilicone column (50 m × 0.32 mm I.D. FSOT, 1 μm DB-1, J&W). The linear temperature increase was 3°C/min from −30°C. The helium average linear velocity was 20 cm s^{-1}. Injection of combustion gas samples was made by a gas-tight

syringe (1 ml). The data acquisition speed was one mass spectrum (m/z 35–200) per second.

3. Results and discussion

Representative hydrocarbon proportions are given in Table 1 for biomass varieties of particular interest with respect to hydrocarbon emissions from burning. The hydrocarbons are arranged according to structural class, number of carbon atoms, and retention order on the aluminium oxide column. The inefficient flaming and smouldering combustion of straw is similar to that of grassland fires and open burning of agricultural and garden waste. The open burning of twigs from spruce resembles conifer forest fires. Newsprint is likely to be the major type of paper waste used for igniting fires, thereby ending up in uncontrolled burning. Hardwood such as birchwood is commonly used as the major fuel for heating and cooking purposes in stoves and fireplaces.

It is evident from Table 1 that the hydrocarbon proportions are remarkably similar for different kinds of biomass even though the combustion conditions are quite different. Alkenes make up about half of the amount of non-methane hydrocarbons with ethene as the predominant species followed by propene and 1-butene. The major alkadiene is 1,3-butadiene. As with the alkenes, the lowest analogues are the most prominent for alkynes (ethyne and propyne), alkanes (ethane and propane) and arenes (benzene and methylbenzene). Butenyne and styrene are significant products which may also be classified as alkenes.

3.1. Chromatographic separations

The chromatogram in Fig. 1 illustrates the separation of C_2–C_8 hydrocarbons emitted from biomass burning. Contrary to non-polar columns, the aluminium oxide column clearly separates hydrocarbons with the same number of carbon atoms in the order alkanes < alkenes < alkadienes < alkynes. Isomeric alkenes are favourably separated in a retention order which markedly differs from that on the commonly used methylsilicone columns [5]. Complete determinations of all volatile hydrocarbons are facilitated by the fact that compounds other than hydrocarbons are not eluted from the Al_2O_3 column. An exception is the furans with their stable aromatic structure.

The strong retention on the Al_2O_3 column permits the separation of the volatile C_2 hydrocarbons without using subambient column temperatures. On the other hand, the alkylbenzenes elute late even at the maximum recommended temperature (200°C) of the column. The temperature program was chosen to ascertain a clear-cut separation of the carcinogenic 1,3-butadiene from pentane. For routine determinations of the major combustion-formed hydrocarbons, the time required can be much decreased by using a rapid linear temperature program and by leaving out the minor late-eluting alkylbenzenes. The resulting higher elution temperature then makes easily polarized hydrocarbons like alkynes and alkadienes appear earlier relative to alkanes.

3.2. Sampling and recovery

An analytical difficulty is the presence of acidic and other reactive combustion products which may cause chemical decomposition of sensitive hydrocarbons on the adsorption cartridges. As illustrated by Fig. 1, samples taken by a gas syringe can be favourably analyzed by gas sample injection if the concentrations of the combustion-formed hydrocarbons are high. Comparisons with the results for pot-burning samples, taken on the triple-layer adsorption cartridges, did not indicate significant losses for any of the hydrocarbons emitted from inefficient biomass burning.

Aggressive combustion products may give rise to extensive losses of reactive alkenes on the triple-layer adsorption cartridges, as demonstrated for diesel exhaust [6]. Potential losses for samples from biomass burning should therefore be checked, especially for high-volume samples from stoves and other efficient combustion devices. A proper peak for the particularly reactive

Table 1
Proportions (% weight) of C_2–C_8 hydrocarbons from biomass burning[a]

		Straw barley pot-burning	Twigs spruce gridiron	Paper newsprint pot-burning	Wood birch stove
Alkenes					
C2	Ethene	31.0	36.2	41.4	40.2
C3	Propene	9.9	8.6	9.3	4.3
C4	*trans*-2-Butene	0.84	0.33	0.30	0.17
	1-Butene	3.0	2.6	1.57	0.82
	Methylpropene	1.22	0.80	0.59	0.30
	cis-2-Butene	0.61	0.26	0.21	0.12
C5	Cyclopentene	0.3	0.31	0.1	0.1
	3-Methyl-1-butene	0.3	0.27	0.1	0.1
	trans-2-Pentene	0.46	0.30	0.15	0.10
	2-Methyl-2-butene	0.31	0.20	0.07	0.04
	1-Pentene	0.82	0.73	0.31	0.21
	2-Methyl-1-butene	0.43	0.23	0.14	0.07
	cis-2-Pentene	0.31	0.21	0.11	0.06
C6	1-Hexene	1.18	1.41	0.31	0.20
C7	1-Heptene	0.55	0.54	0.16	0.11
C8	1-Octene	0.30	0.27	0.08	0.12
Alkadienes					
C3	Propadiene	0.4	0.5	0.4	0.3
C4	1,3-Butadiene	3.8	4.3	2.6	1.6
C5	Isoprene	0.6	1.5	0.9	0.1
	Cyclopentadiene	1.4	1.5	0,37	0.25
	trans-1,3-Pentadiene	0.75	0.45	0.24	0.08
Alkynes					
C2	Ethyne	7.3	9.2	16.4	22.7
C3	Propyne	2.1	1.4	2.3	1.4
C4	2-Butyne	0.22	0.08	0.11	0.08
	Butenyne	0.59	0.63	0.82	0.73
	1-Butyne	0.27	0.16	0.22	0.15
Alkanes					
C2	Ethane	10.4	5.5	5.6	5.8
C3	Propane	2.3	1.0	1.1	0.8
C4	Butane	0.8	0.3	0.24	0.22
C5	Methylbutane	0.09	0.03	0.03	0.05
	Pentane	0.18	0.2	0.22	0.10
C6	Hexane	0.10	0.2	0.09	0.05
Arenes					
C6	Benzene	7.9	9.6	8.4	13.6
C7	Methylbenzene	4.0	3.6	2.0	2.2
C8	Ethylbenzene	0.4	0.77	0.35	0.4
	Dimethylbenzenes	0.9	1.2	0.27	0.6
	Styrene	0.5	1.3	1.2	0.8

[a] The total concentrations of C_2–C_8 hydrocarbons were 72, 18, 270, and 42 mg m^{-3} for the tabulated samples. The newsprint sample was taken with a gas syringe and the other samples on triple-layer adsorption cartridges. The materials burnt were last year's barley straw, fresh twigs of Norway spruce, an evening newspaper printed on recycled paper, and moderately dried birchwood with bark. The pot samples were taken after enclosing the fire, the grill sample in the open air in the smoke plume, and the stove sample in the chimney exit during flaming fire in the stove.

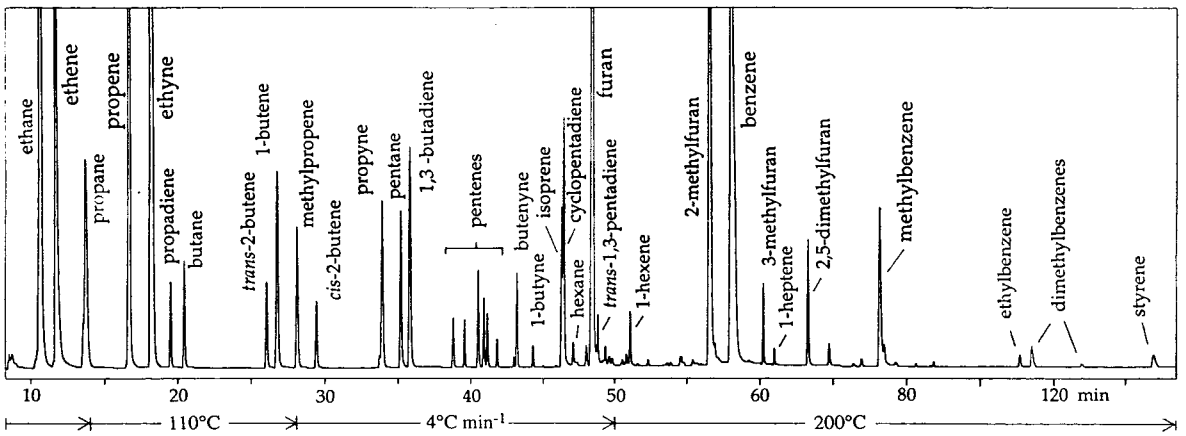

Fig. 1. Gas chromatographic separation of non-methane hydrocarbons from the burning of birchwood (3.2 ml gas sample from pot-burning, aluminium oxide column, flame ionization detection, paper speed decreased after 60 and 80 min).

2-methyl-2-butene was found to indicate complete recovery of the other tabulated alkenes. Isoprene was found to be more easily lost than 1,3-butadiene among the alkadienes. Complementary low-volume samples on single-layer Tenax cartridges were useful for checking complete recovery, although exceptionally reactive hydrocarbons like monoterpenes may still be lost [7].

Ethyne is the non-methane hydrocarbon most easily lost by breakthrough on the triple-layer cartridges. When necessary, low-volume samples were used to ensure correct proportions of ethyne and the other C_2 hydrocarbons.

3.3. Assessments by GC–MS

Identifications and complementary separations on a methylsilicone column were made using the capabilities of an ion trap GC–MS instrument. Relative retentions on methylsilicone and aluminium oxide columns are available for a wide range of C_4–C_7 alkenes [5]. Comparisons were also made with the hydrocarbons identified in vehicle-polluted air and tobacco smoke [4].

The mass fragmentograms in Fig. 2 for the complex mixture of unsaturated C_5 hydrocarbons were chosen to illustrate the use of GC–MS for combustion-formed compounds from biomass. The upper chromatogram illustrates the presence in the combustion gases of the six isomeric acyclic pentenes, by single-ion monitoring of the m/z 70 molecular ion. The lower chromatogram records furan, isoprene, the two 1,3-pentadienes, and cyclopentene, which all give rise to a prominent m/z 68 molecular ion. Cyclopentadiene is recorded from its abundant m/z 66 molecular ion. The separation on the methylsilicone column complements that of the Al_2O_3 column from which 3-methyl-1-butene and cyclopentene as well as furan and *cis*-1,3-pentadiene were eluted as unresolved compound pairs. Furthermore, isoprene and cyclopentadiene were incompletely resolved with rapid temperature programs.

The six isomeric pentenes are also significant components in petrol [5] and vehicle-polluted urban air [4], although in different mutual proportions. The pentadienes are more characteristic products of biomass combustion and are seldom reported in air pollution studies. They are of potential interest with respect to health hazards due to their structural relationship to the carcinogenic 1,3-butadiene. Cyclopentadiene was reproducibly determined in spite of its acidic properties. The proportion of *trans*-1,3-pentadiene was normally almost twice that of *cis*-1,3-pentadiene which is not included in Table 1.

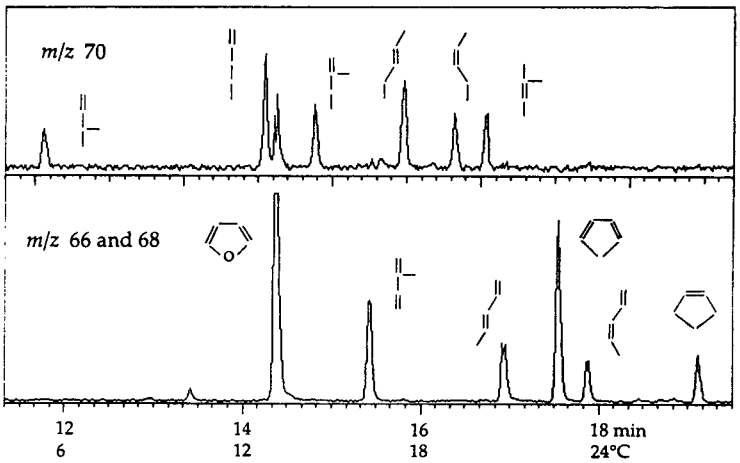

Fig. 2. Single-ion monitoring by GC–MS of C_5 alkenes and alkadienes from the burning of biomass (barley straw, 0.5 ml gas sample, methylsilicone column).

3.4. Combustion-formed compounds

The stove sample in Table 1 deviates from the other three samples by reflecting more efficient and complete combustion. This results in lowered proportions of alkenes other than ethene and increased proportions of ethyne and benzene. Flameless oxygen-deficient burning of glowing biomass such as wood and straw tended to give increased proportions not only of C_3–C_5 alkenes and alkadienes but also of C_2–C_5 alkanes. The chromatogram in Fig. 1 illustrates that inefficient burning of birchwood gives rise to large proportions of furan and alkylfurans, of which 2-methylfuran is the most prominent. The furans were recorded in varying proportions from all samples studied and are likely to be formed from the biomass content of cellulose, hemicelluloses and other carbohydrates.

The hydrocarbons from biomass burning differ markedly from urban hydrocarbons originating mainly from petrol-fuelled vehicles [4]. A prominent portion of the pollutants in urban air consists of exhaust-emitted unburnt C_4–C_8 petrol hydrocarbons with large proportions of alkanes and alkylbenzenes. On the other hand, the major combustion-formed hydrocarbons ethene, propene and ethyne are the same from biomass and petrol. For less prominent combustion-formed products, certain differences pertaining to fuel structures are observed.

The unbranched 1-alkenes are the most prominent alkene isomers from biomass burning. This is probably explained by their formation from unbranched biomass components such as lipids. Analogous formation from unbranched petroleum alkanes [8,9] explains their presence in diesel exhaust [6]. In vehicle-polluted urban air, branched isomers of C_4–C_6 alkenes are the most prominent [4]. They are emitted from petrol-fuelled vehicles as combustion products from branched petrol alkanes [8,9] and as unburnt cat-cracked components of the fuel [5].

The carcinogenic 1,3-butadiene was a prominent component from all biomass samples, although its formation from cyclohexanes has been shown to be favoured [10]. The proportion of isoprene is very high in tobacco smoke [4] and probably linked to a high content of terpenoid components in tobacco. High proportions of biomass lignin with its aromatic nuclei are likely to contribute to an increased formation of benzene, in a similar way as high levels of alkylbenzenes in petroleum fuels [10]. The formation of styrene from biomass appears to be linked to the characteristic phenylpropane units of lignin.

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Journal of Chromatography A, 710 (1995) 79–92

JOURNAL OF CHROMATOGRAPHY A

Review

Recent applications of gas and high-performance liquid chromatographic techniques to the analysis of polycyclic aromatic hydrocarbons in airborne particulates

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Abstract

Advances in the development of analytical separation techniques can be said to have been significantly fueled by the ever-increasing demands of environmental analyses. Complex environmental matrices and sample mixtures have motivated chromatographers to improve their craft to the present level of excellence in terms of functionality and applicability. This paper reviews the most recent application of two of the most important chromatographic methods —gas chromatography and high-performance liquid chromatography— to the analysis of an important class of environmental pollutants, polycyclic aromatic hydrocarbons (PAHs) and their derivatives. The review focuses on the use of the two aforementioned techniques in the characterization of PAHs and related compounds present in airborne particulates, reported in the literature in the past three years.

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1. Introduction

Man has had to contend with environmental pollution since he first appeared on earth. However, it has only been from the beginning of the industrial revolution (generally considered to be in the 1750s) to the present day that environmental problems have assumed a scale of such magnitude that it is incumbent upon the earth's inhabitants to do something about them. Currently, air pollution, water pollution and solid-waste disposal are considered the three most important environmental problems facing the human population [1]. Environmental analyses have therefore assumed a position of critical importance in analytical chemistry.

It is probably true to say that advances in environmental analyses have more or less occurred concomitantly with those in the separation sciences. The reason is not difficult to

0021-9673/95/$29.00
SSDI 0021-9673(95)00429-7

ascertain; environmental samples are extremely complex, and often contain many different classes of compounds in varying amounts. An appropriate chromatographic procedure is therefore necessary to fractionate initially the sample extract into various classes of pollutants. This is followed by a similar technique to resolve, identify and quantify individual components within the respective compound classes. In other words, chromatographic techniques have invariably been part and parcel of this important segment of analytical chemistry. The efficacy and capability of a novel or improved separation technique is usually evaluated in the environmental area, because the latter field arguably places the greatest demands on any particular analytical procedure.

A cursory examination of accepted and certified methods of analysis of many environmental pollutants indicates that chromatographic techniques play a significant role, and may well be the most widely used procedures in this area of application. More specifically, chromatography is a principal technique in the analysis of air pollutants; the continued advent of new or improved instrumentation and novel column technologies have meant that chromatography has remained at the forefront in this area of research, and its preeminent position appears unchallenged in the foreseeable future.

The present review discusses the applications of gas chromatographic and high-performance liquid chromatographic techniques to the analysis of an important class of pollutants present in the air, the polycyclic aromatic hydrocarbons and their derivatives.

2. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) may well be the most widely studied class of environmental pollutants. [PAHs, strictly speaking, comprise carbon and hydrogen atoms only, and are just one class of pollutants classified under the more generic term of polycyclic aromatic compounds (PACs). The term PAC is usually considered to also include substituted PAH containing alkyl, amino, chloro, cyano, hydroxy, carboxy, nitro or thio functionalities as ring substituents, as well as the hetero-PACs in which a nitrogen, oxygen or sulphur atom is part of the ring nucleus. Even polycyclic aromatic quinones may be classified under PACs [2]. Nevertheless, there is as yet no universal appellation, amenable to everyone, to describe all of these aromatic compounds collectively. Even the term PAH itself is often substituted by "PNAHs" (polynuclear aromatic hydrocarbons), and is popularly taken to encompass the heterocyclics. Historically, amongst this category of polycyclic compounds, PAHs were the first to garner attention, and consequently "PAH" has been the most familiar term. It will hence be used here, even though the discussion following may be on those compounds containing other than just carbon and hydrogen atoms.] Fig. 1 shows examples of PAHs and their various derivatives. Boldfaced numbers on the following pages refer to the corresponding structures in this figure.

The interest in PAHs began in earnest in the 18th century, when in 1775, Pott suggested a link between scrotal cancer suffered by chimney sweeps and the soot to which they were exposed [3]. (At that time, of course, these compounds were unknown.) More than 150 years were to pass before Cook et al. [4], in the 1930s, finally confirmed that the cancer-causing substances present in soot were PAHs (specifically, dibenz[*a*,*h*]anthracene and benzo[*a*]pyrene (**12**)). The carcinogenic and mutagenic activities of many types of PAHs [5,6] as well as their widespread presence and persistence have provided the impetus for the subsequent and continuing study of these compounds in environmental samples, 220 years after Pott's initial investigations. The importance attached to PAHs is indicated by the substantial interest given them by analytical chemists today, and it is not uncommon for a novel or improved analytical technique to be evaluated using PAHs as test compounds,

PAHs are formed from the combustion of fossil fuels, and are ubiquitous to the environment, the major contributors to which are anthropogenic sources [7]. Since the sources can be monitored and controlled, knowledge of the

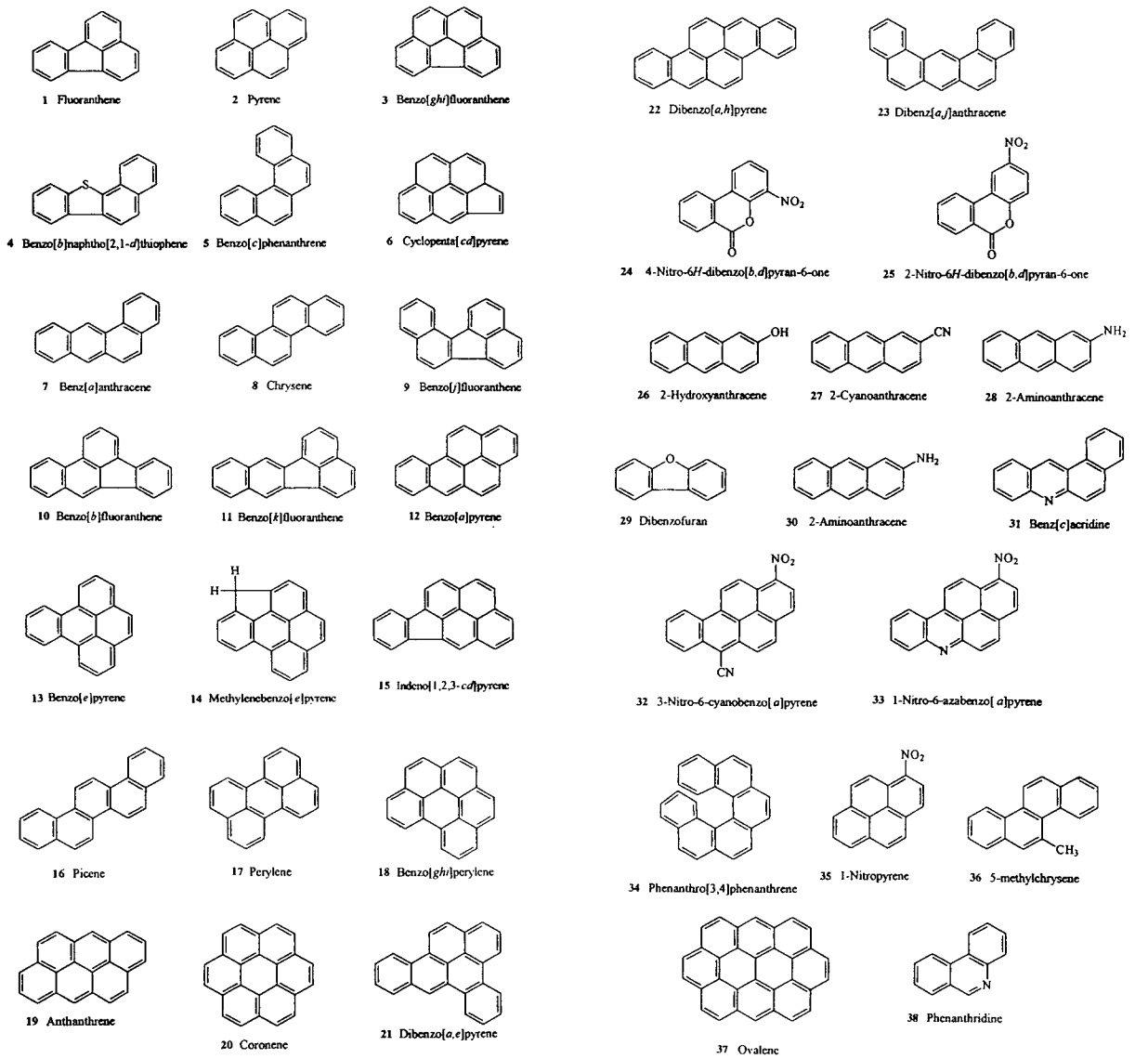

Fig. 1. Examples of some polycyclic aromatic hydrocarbons and derivatives.

analytical chemistry of these compounds is imperative not only in characterizing individual components, but also in attempting to determine the sources or origins of the PAHs emitted so that steps can be taken to eliminate or minimize the discharge of these substances into the environment. The main anthropogenic sources include coke production, motor vehicles (internal combustion engines), residential fireplaces, open fires (e.g. domestic or small-scale burning of refuse, and to a lesser extent, forest fires initiated accidentally or deliberately) and commercial incinerators. From these sources, a significant proportion of the PAH emissions enters the atmosphere directly, adsorbed on airborne particulate matter formed as a result of these combustion processes. Because of their biological properties, the dangers posed by the presence of PAHs in the atmosphere are obvious; their existence in the surrounding air has a direct

impact on the human population. The analysis of PAHs is thus a critical element in air pollution monitoring and control.

3. Gas chromatography

Amongst the various separation techniques, gas chromatography (GC) is still the most widely used in analytical chemistry. This in spite of the fact that, as an analytical tool, it can be considered to be somewhat old-fashioned, having been introduced more than forty years ago by James and Martin [8]. Improvements in GC instrumentation and ancillaries, especially the stationary phases, will, in all likelihood, extend the usefulness and applicability of the technique well into the future. The advantages of GC are many, the most important being the resolving power and the capability to detect low concentrations [9]. Speed of analysis is also a significant factor in its favour.

The fundamental characteristic for a compound to be analyzed by GC is its volatility within the temperature range used. By this measure, PAHs containing up to 24 carbon atoms may be analysed by GC [10], although structural differences may play a significant role in determining the volatilities of PAHs with the same carbon number; for example, the less condensed pyranthrene (which has thirty carbon atoms) can be easily analyzed by GC whereas its counterpart, naphtho[8,1,2-*abc*]coronene, requires special high-temperature GC [10], or supercritical fluid chromatography.

The general amenability of PAHs to GC analysis has caused this technique to be the principal analytical technique for these compounds in environmental samples for more than thirty years. The nature and variability of combustion processes cause the PAH mixtures formed and subsequently emitted into the atmosphere to be extremely complex. Thus, the high resolution furnished by capillary GC, first used for separating PAHs in 1964 [11], is tailor-made for the analysis of these otherwise recalcitrant mixtures. The fact that the analysis of PAHs by GC is well-established and extensively documented has also been instrumental in maintaining its status as the method of choice. A slight modification of an existing GC procedure is usually all that is required to satisfy a particular analyst's requirements.

The enormous improvements in the quality of the chromatography of PAHs can be traced back to the mid-1970s when Lee [12,13] discovered that acid-leaching of Lewis acids (present in the glass used to make capillary columns) resulted in much greater efficiencies and deactivation of the columns. Subsequent improvements in the GC columns used for PAH analysis have primarily been in the development of stationary phases with increased thermal stability. In the early eighties, crosslinked polymeric phases as well as chemically-bonded phases were introduced [14,15]. With these, analyses at temperatures ca. 100°C above those previously used were now possible. Because of the high stability afforded by these phases, in contrast to the older types which were statically coated onto the capillary walls, and which were therefore prone to decomposition and volatilization, more consistent and reproducible chromatographic data could be obtained. This is an important consideration because the proper use of such data for the identification of PAH components in extremely complex samples depends heavily on the reliability and consistency of these data. An important factor that also accelerated the development of these newer phases was the problem of wettability; modern phases have better glass-wetting properties which ensure that as the temperature is varied, the coated film maintains its homogeneity and does not form droplets.

The advent of liquid crystalline phases was another development beneficial to the GC analysis of PAHs [16,17], although in the end these phases were not as successful for routine applications as the more conventional phases. Examples of liquid crystals which were used for separating PAHs include N,N′-bis(*p*-x-benzylidene)-α,α'-bi-*p*-toluidine in which x denotes a butoxy, hexyloxy or phenyl group [16,17]. The interest in liquid crystalline phases was raised because for some isomeric PAH pairs separation is critical

since their carcinogenic or mutagenic properties differ significantly, and it may be difficult to resolve them with conventional phases. For example, the five-ringed PAH, benzo[*a*]pyrene (**12**), is considered to be one of the most potent carcinogens; on the other hand, benzo[*e*]pyrene (**13**) has lower activity [18], and separating them was one of the early challenges faced by chromatographers interested in PAHs, as was resolving important sets of isomers such as the benz[*j*]-, [*b*]- and [*k*]-fluoranthenes (**9**,**10**,**11**), all of which have different carcinogenic activities.

Chromatographers in the mid-eighties [19,20] began developing liquid crystalline stationary phases to exploit the slight structural differences in PAH isomers which translate into variations in their chemical affinities for the stationary phase, which in turn depend on the surface area of interaction [21]. A particular isomer may exhibit a higher retention because its shape and size permit greater interaction with the liquid crystalline surface. Its isomeric counterpart, on the other hand, may lack the structural entity to interact with equivalent facility with the same surface; its retention is therefore different, thus enabling separation. In a study of the retention behaviour of dibenzothiophene derivatives on a smectic liquid crystalline polysiloxane stationary phase [22], it was found that retention, vapour pressure and polarity were influenced by the molecular geometry of the compounds, especially the length-to-width ratio. An earlier study also investigated liquid crystalline phases that were sensitive to the latter parameter of eleven PAHs (each containing five benzene rings) with a molecular mass of 278 [23]. Despite this interesting foray into liquid crystals, however, many PAH analyses that formerly necessitated the use of these or other unconventional phases can now be carried out by capillary GC with commercially available columns packed with more traditional stationary phases; however, there is still an occasional interest in these unorthodox phases [24]. Generally, the popularity of these phases has waned mainly because long equilibrium times are needed between runs, and their properties tend to change with prolonged use, giving rise to irreproducible separations.

In recent years, further improvements in PAH analysis by GC have extended to the development of the more conventional stationary phases specifically for these compounds. For example, Klasson–Wehler et al. [25] and Sinkkoken et al. [26] described the use of improved stationary phases for chromatography of PAHs, while Bemgard et al. [27] compared several high-temperature stationary phases for their separation.

Over the past two to three years, there have been numerous papers on the application of GC to the determination of PAHs extracted from atmospheric samples. Some of these are highlighted in the following paragraphs.

The PAH content in diesel vehicle exhaust particulates received special attention in several of these recent publications, a timely development since diesel-fueled private automobiles appear to be making a comeback, especially in Europe. A short review on the sampling and gas chromatographic analysis of PAHs present in diesel exhaust emissions is available [28]. The US National Institute of Standards and Technology has also been developing or re-certifying diesel particulate extracts as standard reference materials [29].

In their work, Paschke et al. [30] evaluated supercritical fluid extraction with a variety of fluids (carbon dioxide, chlorodifluoromethane and a mixture of the two) to remove the PAHs and nitro-PAHs from diesel particulates, and then used GC for the analysis. Nitro-PAHs were also studied by GC–MS in workplace atmospheres contaminated by diesel exhausts [31]. These workers focused on the 1- (**35**) and 2-nitropyrenes which were reduced and derivatized prior to GC separation and detection. Oxy- as well as unsubstituted PAHs were extracted from air and diesel particulates sampled on glass fibre filters by Kelly et al. [32] with supercritical CO_2 and fractionated by HPLC before analysis by GC. Normal-phase HPLC was used with two different mobile phases to fractionate the PAHs and the oxygenated derivatives before transfer to the GC system via an on-column interface.

In a study of 28 PAHs present in diesel exhaust particulates [33], classical LC with silica gel was used, after initial extraction on a Soxhlet

apparatus to fractionate the extract on the basis of polarity. PAH analysis was performed by GC–MS. The ability of the various fractions to bind to the dioxin (aH) receptor site on cytochrome P450-IA1 was then determined. It is this binding that, in general, initiates the series of events leading to genotoxicity and carcinogenicity. The fraction exhibiting the greatest binding activity was the one containing PAHs and nitro-PAHs, although the authors stated it was not possible to identify the specific components to which the strong dioxin-receptor binding was attributed.

The nitro-PAHs in diesel particulates such as nitropyrenes, nitrofluoranthenes, dinitropyrenes, hydroxynitropyrenes and acetoxynitropyrenes are generally considered to be responsible for the direct-acting mutagenicity of these particles [34]. Thus, these species have been of more interest than the parent PAHs themselves in such samples. Recently, however, Ball and Young [35] claimed to have discovered a new class of mutagens other than the mono- and dinitropyrenes in the dichloromethane extracts of diesel exhaust particulates. They obtained fractions of the mutagenic material with normal-phase HPLC and used GC–MS to determine the concentrations of selected nitro-PAHs; only 1 percent of the total mutagenicity as indicated in the Ames assay with strain TA102 could be attributed to the known nitrated compounds. According to the authors, this is evidence that a new class of mutagens, as yet uncharacterized, is present in diesel exhaust particles.

Sera et al. [36] collected airborne particulate matter and particles discharged from petrol- and diesel-powered vehicles on Teflon-coated filter paper or XAD-4 resin using high-volume samplers in Fukuoka city in Japan, and used GC–MS after HPLC purification to detect and identify nitro-azabenzo[*a*]pyrene derivatives. Some of these mutagens were previously unknown: 1-nitro-6-azabenzo[*a*]pyrene (**33**), 3-nitro-6-azabenzo[*a*]pyrene, 1-nitro-6-azabenzo[*a*]pyrene-N-oxide and 3-nitro-6-azabenzo[*a*]pyrene-N-oxide. These compounds contributed for 34.9, 9.8 and 4.3%, to the total semivolatile extracts from airborne, diesel and petrol vehicular particulates, respectively. The authors believe that diesel emissions may be the primary source of these mutagens.

In another vehicle-related study, Rogge et al. [37] analysed airborne particulates emanating from road dust, tyre debris and brake linings, for their organic composition by using GC–MS. PAHs and oxy-PAHs, including polycyclic aromatic ketones (PAKs) and polycyclic aromatic quinones (PAQs), were identified in all three types of samples. The same authors have also looked at the PAH and oxy-PAH emissions discharged by (i) catalyst-equipped trucks, (ii) non-catalyst-equipped automobiles, and (iii) heavy-duty diesel-fueled trucks, again by GC–MS, after extraction of the sampled particulates by hexane and benzene–2-propanol [38]. For non-catalyst automobiles, the bulk of the identifiable fraction consisted of PAHs and oxy-PAHs, including PAKs and PAQs. These classes of compounds, on the other hand, formed a smaller proportion of the total identifiable organic mass for catalyst-equipped automobiles; most of the PAHs detected were of the higher-molecular-mass species such as benzo[*ghi*]perylene (**18**) and coronene (**20**). The diesel trucks, which were reasonably new, exhibited total PAH emission rates very much lower than those recorded by the automobiles. The PAHs emitted by these diesel trucks were mainly the low-molecular-mass species.

Westerholm and Li [39] investigated the relationship between diesel-fuel parameters and the PAH content in these fuels by using principal component analysis. They used a combination of classical column chromatography (sample clean-up), HPLC (class fractionation), and GC–MS for analyzing the purified PAH fraction. Most abundant of the PAHs in the fuels were alkylated three-ring compounds (phenanthrenes and anthracenes). These comprised uncombusted PAHs as well as those formed from the combustion process. The authors concluded that PAH emissions to the atmosphere by diesel-powered vehicles may be minimized by reducing the PAH contents in commercial diesel fuel to ca. 4 mg/l.

It is known that cigarette smoke is a significant source of PAHs and other compounds in urban atmospheres. Over the last thirty years many

studies have been published on the risks posed by cigarette smoke (see e.g., Ref. [40]). One recent study on this subject has been contributed by Rogge et al. [41] who measured several classes of compounds present in cigarette smoke by GC–MS. The authors focused on three- and four-ring PAHs in an attempt to identify a suitable marker for determining the contribution of this kind of smoke to the overall urban atmospheric particulate load. Because of contributions from other sources of PAHs to the urban atmosphere, these species were deemed unsuitable as tracers. Nevertheless, the use of other tracers by the same authors does indicate the urban pollution load attributable to cigarette smoke, and with it the accompanying risks assumed for the PAHs present in this type of smoke.

Indoor air has an important impact on a person's well-being. Indeed, working adults are exposed more to workplace air pollution than to outdoor pollution. Similarly, non-working adults and very young children may be exposed to air pollution at home. Several recent studies address this significant contribution to the pollution burden borne by the human population. Rogge et al. [42] have looked at the emissions from natural-gas home appliances, including a space heater and a water heater which were both evaluated to be in good condition. Apart from PAHs and oxy-PAHs, azaarenes and thiaarenes were identified by GC–MS in the exhausts of the appliances. The authors calculated that these mutagens formed 22% of the particle mass emitted, prompting them to suggest that exhausts from natural-gas combustion should be given more attention than hitherto by air pollution monitoring authorities.

The characterization of the mutagenic fractions in particulates resulting from indoor coal combustion was the subject of a study by Chuang et al. [43]. The work focused on a rural commune in China in which lung cancer mortality rates for women were the highest in that country even though most of the sufferers were non-smokers. High-volume samplers were used to collect particulates during cooking periods from one household. Soxhlet extraction followed by normal-phase HPLC was used to fractionate the extract. The fraction most active in the bioassay contained mainly PAHs and alkylated-PAHs, which were determined by GC–MS. The authors concluded that alkylated three- and four-ring PAHs produced from smoky coal combustion were probably significant factors linked to the high lung cancer mortalities in the commune. The authors believed that the more polar fractions containing nitrogen heterocyclic compounds could also contribute to the mutagenicity of the smoke extracts.

A preliminary study on the potential risks represented by the burning of plastics has been carried out [44]. With limited land available for landfill, an alternative method to handle the disposal of solid waste including plastics is incineration. However, there is concern over the toxic emissions, including PAHs, resulting from the incineration of solid waste, especially plastics. To address this issue, Wheatly et al. [44] conducted an exploratory laboratory-level investigation on PAH emissions originating from the combustion of common plastics. By using GC, the authors identified a whole series of PAHs produced during the combustion processes. The study sought to identify various incineration parameters which might be adopted to minimize the emission of toxic components, including PAHs, produced by the burning of waste plastics.

There have been several publications describing the use of biological markers to indicate atmospheric PAH pollution. PAHs characterized and measured in kale by GC was used to study the effect of climatic factors on PAH emissions [45]; the identities of these PAHs provided information on the combustion sources contributing to the PAH load. In a similar study, tree bark was used as a "passive sampler" for PAHs in the urban and rural environment [46]. The authors measured the concentrations of PAHs by GC in these materials and found a correlation with the extent of pollution, type of traffic conditions and the height from the ground of the bark sampled.

Nitrated fluorenes have also been the subject of interest amongst environmental chemists. Hel-

mig and Arey [23] used a GC column packed with a smectic liquid crystal phase to separate various isomeric nitrofluorenes present in the air. They also compared the retention characteristics of these species on this phase with other conventional GC packings.

Mention was made above of some studies which considered the carcinogenic and mutagenic potential of airborne particulates in urban atmospheres attributable to the PAHs present in diesel emissions. In a similar way, cancer risks due to exposure to PAHs faced by commuters in busy streets were evaluated by Chan et al. [47]. They used GC–MS to determine the PAHs collected on Tenax adsorbents. They claimed that motor cyclists faced two times the cancer risk encountered by bus commuters. The latter, in turn, were three times more at risk than non-commuters.

A recent study on PAHs focused on determining the particle size fraction associated with these compounds [48], the rationale being that controls on emission sources can be better effected by establishing the link between particulate sizes with emission processes producing the particulates. The ramifications of this are that the health effects posed by various size fractions of particulate matter can then be better understood and investigated. In the work in question, GC–MS was the principal technique used to identify the PAHs detected in the airborne particulates.

Other recent studies involving the use of GC or GC–MS as the primary technique for airborne PAHs include those by the following workers: Beard et al. [49] looked at the formation of polychlorinated dibenzofurans and other PAHs in petroleum refining processes; Luijk et al. [50] also studied the formation of dibenzofurans (**29**), but from the catalysed combustion of fly ash residual carbon; Rogge et al. [51] investigated the contribution of biogenic sources (leaf surface abrasion products) of trace amounts of PAHs to urban atmospheres; Hippelein et al. [52] used separate particle and gaseous samplers for collecting particulate and gas-phase PAHs respectively in ambient air; Fernandez et al. [53] identified and quantified 15 PAHs in urban and semi-urban atmospheres; Östman and co-workers used automated clean-up systems consisting of a coupled LC–negative-ion GC–MS setup [54], and an on-line LC–GC [55] to detect, respectively, chlorinated PAHs and ordinary PAHs in urban air; Roussel et al. [56] used both HPLC and GC–MS to establish the point source of atmospheric PAH emissions; Escrivó et al. [57] compared the analysis of PAHs in airborne particulates by GC with flame ionization detection and MS, with that by reversed-phase HPLC with UV and fluorescence detection; and Odum et al. [58] carried out a study on the photodegradation of benz[*a*]anthracene (**7**), one of the known carcinogenic PAHs commonly present in atmospheric samples, in the presence of methoxyphenols, which form a large proportion of the organic material associated with wood smoke.

In addition to these studies, there is available a recent review on the use of chromatographic techniques for the analysis of benz[*c*]acridines (**31**) [59] in atmospheric samples.

4. High-performance liquid chromatography

The development and progress of high-performance liquid chromatography (HPLC) can be considered to have suffered from the explosive success of GC which began in the fifties, and continued, especially with the advent of capillary GC, from the late seventies onwards. Scott [60] has remarked that due to the remarkable successes of GC during this period, developments in HPLC were held up and it was not until the major advances in the former were completed that HPLC development became a priority with scientists. In a sense, however, HPLC has caught up to be an established separation technique, even though "its progress has been slow and arduous relative to that of GC" [60]. It is probably safe to say without fear of contradiction that it is today the most popular chromatographic technique, with 100 000 systems in current use [61]. HPLC has also been claimed to be the most important analytical technique [61]. As judged by the number of papers on HPLC that are currently being published in the major journals specializing in chromatography in particular and

the analytical sciences in general, it is difficult to dispute this statement. Thus, from a promising conception, HPLC went through a difficult childhood, but having reached maturity has attained a respectable status today. It has yet to exhibit any signs of senescence and the large amount of work currently devoted to it suggests that significant advances can still be expected in the future.

The majority of PAH compounds, including the sixteen listed by the US EPA, can be conveniently analysed by GC. Indeed, the biologically active PAHs are usually also the more volatile ones, so GC is, intuitively, the appropriate method for their analysis. Conversely, the larger or less volatile compounds must be separated by another techniques; HPLC is the most popular of these alternative techniques. Apart from being well-suited to handle less- or non-volatile species, HPLC has several other advantages over GC, including the fact that it is a milder technique that, in most cases, is conducted at ambient temperatures, and is thus more acceptable for thermally-unstable PAHs. The literature, however, abounds with HPLC analyses of even the smaller and more volatile PAHs, including those designated by the US EPA. Thus, the use of this technique is not confined to the larger PAHs only–this is obviously another advantage that HPLC has over GC in that it can be used for a much wider range of PAHs (based on number of rings) of which volatility is not a problem. For instance, Jinno et al. [62] have reported the reversed-phase HPLC of a ten-ring system, ovalene (**37**). Indeed, the US EPA specifies HPLC as the technique to use for PAHs present in aqueous effluents [63].

In HPLC, UV- and fluorescence detection are the most popular for PAHs. Fluorescence detection has two obvious advantages over UV detection: greater selectivity and higher sensitivity. These are crucial considerations since genuine environmental samples usually contain very low levels of PAHs, and because of the presence of many interfering compounds that may cause problems with the analysis.

Since both normal- and reversed-phase HPLC may be used with equal facility for these compounds, about the only requirement necessary for a PAH to be analyzed by HPLC is its solubility in the common solvents used for either of these HPLC modes. Reversed-phase HPLC has tended to be more popular for PAH separation than normal-phase HPLC [64]. Based on the foregoing, it is no wonder that in many situations, HPLC is preferred over GC for PAH analyses. In fact, already in the early eighties, it was shown that PAHs could be separated very rapidly by HPLC [65,66].

The versatility of HPLC in terms of the development of an optimum set of analytical conditions cannot be matched by GC. In the latter, apart from a judicious choice of stationary phases, only single- or multi-step temperature-programming and the rate of temperature increase provide a degree of control over the establishment of optimum separation conditions. With HPLC, the use of suitable solvents for the mobile phase and subsequent manipulation of their composition, and appropriate selection of a bewildering array of normal- and reversed-phase stationary phases all offer more flexible method developmental strategies. In addition, although separations are usually performed isothermally, temperature-programming may be used, if desired, as has been done for PAH analysis [67,68]. However, this does not always mean that it is easier to develop a method for HPLC since the greater number of parameters that may be exploited to effect a more satisfactory separation can also be a disadvantage. Specifically, the optimization of a particular combination of several possible parameters for satisfactory analysis (which encompasses not only favourable separation efficiency, but also analysis time, resolution, etc.) can be carried out by trial-and-error, but this is time-consuming, and may not always lead to the best results. More efficient would be a systematic, possibly computer-assisted, optimization procedure. Examples of such systematic procedures which have been used for optimizing the separation of PAHs have been published [69–71]. Nitroaromatics have also been the subject of such a study [72]. Although these studies did not particularly concern the analysis of PAHs or their derivatives as air pollutants, the optimized HPLC conditions determined by these

systematic procedures may be applied to the routine analyses of these compounds extracted from atmospheric samples.

As pointed out earlier, reversed-phase HPLC is the most popular mode for the analysis of PAHs. The universal appellation "C_{18}" or "ODS" is applied to most, if not all, commercially available columns packed with the octadecylsilane stationary phase. Despite this, it is well known that in reality, there are significant differences in the selectivities of phases produced by different manufacturers for PAH separations. Previous investigations have established that several factors can influence the separation of PAHs on these C_{18} materials; Wise et al. [64] have stated that the most important of these factors is the way the C_{18} stationary phase was prepared. Specifically, monomeric phases (synthesized by reacting monofunctional silanes with silica) exhibit different selectivities for PAHs than their polymeric counterparts (prepared by the reaction of trifunctional silanes with silica in the presence of water) [64]. Thus, under gradient elution conditions with acetonitrile and water, all the sixteen EPA-listed PAHs could be resolved on the latter phase, but with the monomeric phase, which was manufactured by a different company, some critical ring-isomeric pairs [for example, chrysene (**8**) and benz[*a*]anthracene (**7**); and benzo[*ghi*]perylene (**18**) and indeno-[1,2,3-*cd*]pyrene (**15**)] could not be separated from each other [64]. These authors reported a general scheme which could be used to determine the selectivity of monomeric and polymeric C_{18} phases for separating PAHs. The scheme [73] is based on investigating the relative order of elution of three specially selected PAHs on these two types of phases. The selectivity, which is based on the planarity or otherwise of the three PAHs (benzo[*a*]pyrene (**12**), phenanthro-[3,4-*c*]phenanthrene (**34**) and 1,2:3,4:5,6:7,8-tetrabenzonaphthalene) can be defined quantitatively, which subsequently allows the classification of various commercially available C_{18} stationary phases into monomeric, polymeric or intermediate types. By this yardstick, only the first-named phase can be used to separate all sixteen EPA-listed PAHs; some of these are currently being advertised by their manufacturers as being specially produced for the complete separation of these priority PAHs. It should be noted, however, that in the majority, if not in all cases, gradient elution must still be used to resolve the sixteen components. (Although the capital cost of acquiring a gradient elution HPLC system is becoming lower, most laboratories with isocratic systems would nevertheless use GC for the actual PAH analysis, and employ HPLC as a clean-up or fractionation procedure. In many of the applications mentioned above in which GC or GC–MS was used as the primary technique for PAH characterization, HPLC was used to isolate compound classes.)

The selectivity of stationary phases for PAHs can also be exploited in a manner similar to that in GC described above. To distinguish ring isomers, the shape-recognition capabilities of some stationary phases can be employed. Specifically, the length–width ratios of PAHs, which effectively determine the shape of the respective molecules, are the basis of such chromatographic discrimination. The more "rod-like" the PAHs are (i.e. the greater the length–width ratio), the greater is the retention [74]. In an extension of this type of selectivity studies, the use of a liquid crystalline bonded phase for reversed-phase HPLC has been reported [75] for several PAHs. The [4-(allyloxy)benzoyl]biphenyl phase was claimed [75] to have greater planarity recognition power than the polymeric C_{18} phases described earlier. This greater ability was attributed to the greater structural orderliness of the liquid crystal in comparison to the polymeric C_{18} phases.

Fu et al. [76] have also investigated the HPLC retention characteristics of PAHs. They studied a large group of structurally-related nitro-PAHs and their corresponding parent PAHs using reversed-phase HPLC. It was observed that the larger the molecule, the greater its retention time. Saturation of the rings led to shorter retention times. Nitro-groups which are perpendicular to the ring eluted earlier, whereas those that are parallel to the ring had longer retention times. The addition of a nitro group resulted in a decrease in the retention time relative to the

parent PAHs. These observations led the authors to conclude that the polarity of these molecules was the determining factor in their retention behaviour.

Recent papers focusing on the analysis of PAHs present in atmospheric samples include those by Nilsson and Östman [77], McDow et al. [78], Gundel et al. [79] and Halsall et al. [80]. In their paper [77], Nilsson and Östman described the sensitive and selective analysis of chlorinated PAHs by first isolating the PAH and chlorinated-PAH fraction by two-dimensional HPLC, then using GC–MS with negative-ion chemical ionization and selective-ion monitoring to detect and quantify the chlorinated PAHs. Urban particulates were collected on glass fibre filters and polyurethane foam plugs, and the compounds of interest isolated by Soxhlet extraction.

As a follow-up to an earlier work (Ref. [58]) on the photodegradation of PAHs, McDow et al. [78] investigated six of these compounds in atmospheric aerosols and reported that the organic composition (methoxyphenols which are found in wood smoke, and hexadecane, present in diesel and automobile exhaust) of atmospheric particulates can influence PAH decay. The authors used reversed-phase gradient elution HPLC with fluorescence detection to determine the PAHs.

Gundel et al. [79] collected inhalable particulates from the air and analysed the acetone extracts on a reversed-phase HPLC system with UV and fluorescence detection. Mutagenic studies were carried out, and although they did not identify any compounds, based on the results, the authors suspected that nitro-containing compounds, such as oxygenated nitro-PAHs and azaarenes, were present in the extracts.

Halsall et al. [80] reported PAH data from the first two years (1991–1992) of a long-term study of a nationwide urban air monitoring scheme covering four cities in the UK. HPLC with fluorescence detection and GC with mass-selective detection were the techniques used in the study in which it was found that common sources were responsible for the PAHs at each sampling site. The PAH data for London indicated that air quality (at least as far as benzo[*a*]pyrene is concerned) has improved by two orders of magnitude over the previous 45 years.

Oxy- and nitro-substituted PAHs were also the subject of a study by Galceran and Moyano [81] who detected these substances in atmospheric aerosols by HPLC with electrochemical detection at sub-nanogram levels.

Hayakawa and co-workers have described the analysis of 1-nitropyrene (**35**) and dinitropyrenes extracted from airborne particulates, and petrol and diesel engine exhausts [82–84]. They used HPLC with pre-column or post-column conversion of the nitropyrenes to chemiluminescent derivatives before detection. They claimed that the analytes could be determined to femtomole levels by chemiluminescence detection which was 30–60 times more sensitive than fluorescence detection. Li and Westerholm [85] have also developed an HPLC–chemiluminescence detection technique for mono- and 1,3-, 1,6- and 1,8-dinitropyrenes in which reduction to the chemiluminescent derivatives was performed on-line. They applied their method to the determination of dinitropyrenes in diesel exhaust particulates. A study on 1- and other nitropyrenes present in diesel exhaust particulates was reported by Veigl et al. [86] who performed multi-column HPLC with post-column on-line reduction of the species of interest to aminopyrenes which were detected by fluorescence. The HPLC system consisted of three columns. The first column was packed with pyrenebutyric acid amide stationary phase and was used to isolate the nitropyrene fraction. This fraction was eluted into the second reversed-phase (C_{18}) column for separation. A third column was used for the reduction of the nitropyrenes to fluorescent derivatives to improve the detectability.

Heterocyclic aromatic amines are a class of carcinogenic compounds that are currently the subject of widespread interest [87,88]. While they are usually found in foods (cooked fish and meats) and beverages (wines and beers), some work has been conducted on their presence in cigarette smoke [89], airborne particulates, diesel exhaust particles and incineration ash from garbage-burning plants [90]. HPLC is the method most commonly applied for the determination

of these compounds [87–90], often with UV and/or fluorescence detection, and sometimes MS detection [91,92], since it is not necessary to derivatize the compounds for the chromatography. However, the use of GC–MS for the analysis of these amines (converted to their 1,3-bis-trifluoromethylbenzyl derivatives before chromatography) in cooking fumes generated in the workplace has recently been reported [93]. The method of collecting the fumes used in this work resembled that for airborne particulate matter, i.e. filtration of the fume aerosols through glass fibre filters and XAD-2 sorbent tubes.

The availability of pure reference standards is essential in environmental analysis, for qualitative and quantitative purposes. In this respect, Auger et al. [94] have improved the methods to synthesize polychlorinated naphthalenes and carried out the complete characterization (including X-ray crystallographic analysis) of these widespread pollutants. Hitherto, the physico-chemical data on these compounds were not sufficient to enable analytical studies. The authors used both GC–MS and HPLC for their purity analyses.

Other recently reported investigations on the use of HPLC as the primary analytical technique for PAHs and related compounds in airborne pollution studies include work by the following authors: Weisweiler et al. [95] collected particle-based and gaseous PAHs with glass fibre filters and tandem polyurethane foam plugs, respectively, and used reversed-phase HPLC with fluorescence detection to determine 15 PAHs in German cities in the late winter to spring period; Ignesti et al. [96] used olive fruits as a measure of air pollution by measuring several low-molecular-mass carcinogenic PAHs using reversed-phase HPLC with fluorescence detection; Librando and Fazzino [97] quantified PAHs and nitro-PAHs in airborne particulate matter in Augusta city in Italy using primarily HPLC; Dumont et al. [98] used HPLC with fluorescence detection to quantify PAHs present in cigarette smoke, which, as previously mentioned, can contribute to the overall air pollution load; Venkataraman et al. [99] also used HPLC with fluorescence detection to determine PAHs in particulate samples to characterize and compare vehicular and ambient aerosols as well as to study the effects of atmospheric processes on PAH size distributions; DeMarini et al. [100] evaluated the mutagenic potential of emissions resulting from the open burning of scrap rubber tyres by using the *Salmonella* mutagenicity test on fractions of the emission extracts isolated by HPLC; and Garcia Pinto et al. [101] used a micellar solution of Triton X114 for the extraction and preconcentration of PAHs from airborne particulates and wood ash, and subsequent centrifugation, before injection of the surfactant-rich phase into an HPLC–fluorescence system for analysis.

A paper published recently [102], while not specifically focusing on airborne PAHs, reviewed recent advances, including GC and HPLC in the analysis of PAHs and related compounds. Similarly, the following studies are relevant for the novelties in the analysis of PAHs: Doerge et al. [103], and Singh et al. [104] reported the use of HPLC–particle beam MS for the analysis of PAHs and their oxygenated metabolites; Galceran and Moyano [105] used HPLC–pneumatically-assisted electrospray ionization MS to characterize hydroxy-PAHs; and finally, Garcia et al. [106] used micellar HPLC to investigate the retention behaviour of benzene derivatives and PAHs.

Acknowledgement

The author thanks Ms Cui-ying Lin for assistance in the preparation of this manuscript.

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Journal of Chromatography A, 710 (1995) 93–108

JOURNAL OF CHROMATOGRAPHY A

Review

Air sampling and analysis of polycyclic aromatic hydrocarbons

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) occur in particles or in vapour phase. The size of the particles is affected by the season: in the winter there is a shift from large to small particles. PAHs, which are associated with particulate matter, are usually collected on filters and are then vaporized from the filter, or exist in the vapour phase and are trapped by a back-up solid sorbent. Many PAHs can react with other environmental pollutants. Benzo[*a*]pyrene deposited on a filter was reported to undergo chemical reactions with ozone and nitric acid. The loss of benzo[*a*]pyrene can be as high as 85%. The most common sampling method applied is integration of the sample by pumping the air stream through a sample device (active sampling). Passive sampling relies on the diffusion-controlled gradients towards a surface. Passive sampling is more often used for vapour-phase PAHs in occupational environments. Sample clean-up is increasingly performed by solid-phase extraction and is also applied to air samples. The samples are traditionally desorbed using Soxhlet apparatus, ultrasonication and various organic solvents, but supercritical fluid extraction is getting more popular. The analysis of PAH samples is usually carried out by high-performance liquid chromatography equipped with a fluorescence detector or gas chromatography–mass spectrometry with electron and negative chemical ionization methods. For quantitative analysis the correlation of these two methods have shown to be good. In qualitative analysis mass spectrometry lacks the ability to resolve the isomeric structures and high-performance liquid chromatography with time programming fluorescence seems to be the detection method of choice.

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0021-9673/95/$29.00
SSDI 0021-9673(95)00207-3

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which are formed in combustion processes of carbonaceous materials at high temperature. These combustion sources include emissions from automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking, and several natural sources including forest fires and volcanic eruptions [1]. Human exposure to polycyclic aromatic hydrocarbons may occur via food, water, air, and direct contact with materials containing PAHs. PAHs have been measured in many matrices (air, water, sediment and tissue samples) because some of them are known to be mutagens and/or carcinogens [2].

Typically environmental samples contain an extremely complex mixture of various PAHs, including isomeric structures, and both alkylated and non-alkylated forms of PAHs. The structures of the 16 PAHs identified as priority pollutants by The U.S. EPA are shown in Fig. 1. In the atmosphere PAHs are known to be distributed between the gas and particle phases according to their volatility. In the particle phase PAHs are

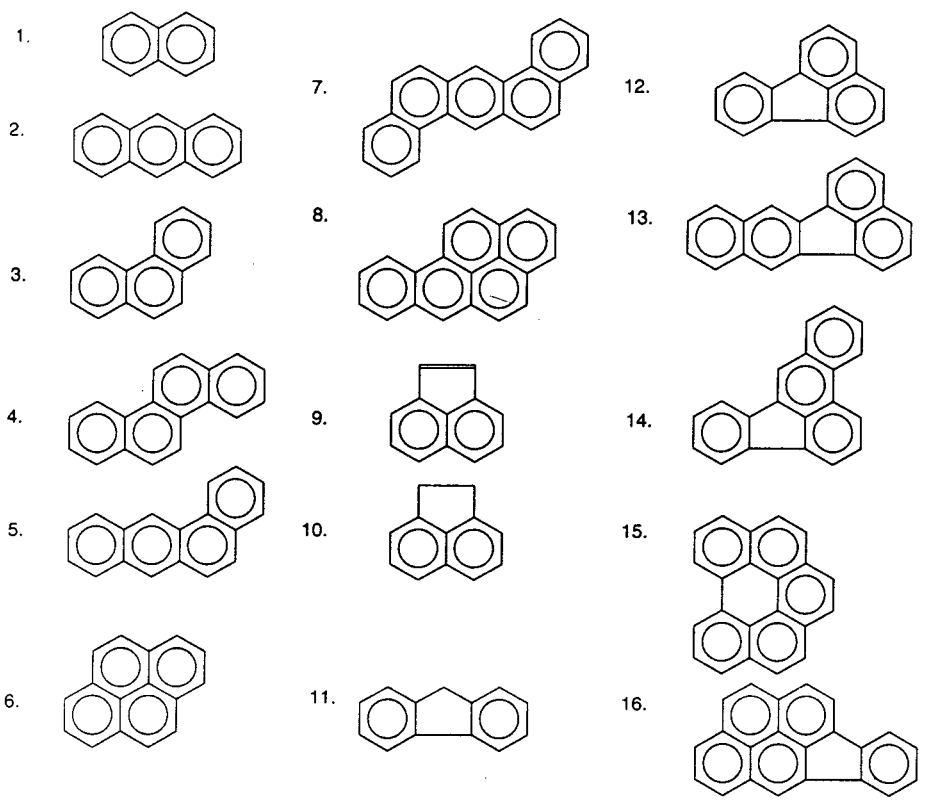

Fig. 1. Structures of the 16 PAHs as priority pollutants by the U.S. Environmental Protection Agency. The suspected carcinogens are marked with asterisk, 1 = naphthalene, 2 = anthracene, 3 = phenanthrene, 4 = chrysene, 5 = benz[*a*]anthracene*, 6 = pyrene, 7 = dibenz[*a*,*h*]anthracene*, 8 = benzo[*a*]pyrene* 9 = acenaphthylene, 10 = acenaphthene, 11 = fluorene, 12 = fluoranthene, 13 = benzo[*k*]fluoranthene*, 14 = benzo[*b*]fluoranthene*, 15 = benzo[*ghi*]perylene*, 16 = indeno[1,2,3-*cd*]pyrene*.

adsorbed mainly onto the respirable fraction (<5 μm) of suspended material. A seasonal variation in the size of the particles has also been observed [3]. Several techniques have been developed and used for sampling of PAH compounds from outdoor and indoor air. Environmental monitoring is conventionally performed by trapping the particulate bound fraction of PAHs onto filters using high-volume sampling techniques. In order to improve the determination of personal exposure integrative low-volume portable equipment is generally used for direct sampling of the breathing zone. In both approaches solid adsorbents which are known to effectively trap volatile organics have been used to collect low-molecular-mass PAHs. The most commonly used analytical methods are based either on liquid chromatographic separation and fluorescence detection or gas chromatographic separation together with mass spectrometry. These two analytical techniques have been reported to provide comparable results [4]. In addition to these conventional approaches some new techniques such as capillary electrophoresis have successfully been used to analyze PAH compounds. The intent of this review is to cover some basic factors, which affect air sampling of PAHs from occupational (low volume) and environmental (high volume) sources. Experiences about the different filters and adsorbents concerning sampling and recovery efficiencies of PAHs are given. Finally, a short discussion of the current analytical methods is presented.

2. Chemical reactivity of PAH compounds

Benzo[*a*]pyrene deposited on a filter was reported to undergo reactions with ozone and nitrogen dioxide. Benzo[*a*]pyrene, benzo[*b*]-fluoranthene or benzo[*h*]fluoranthene were exposed at sub-ppm levels of ozone both in the dark and sunlight for up to 12 h [5]. The decomposition rate was found to be linear and dependent on the ozone concentration. Half-lives for the decomposition in the dark on exposure to ozone were 52.7 to 29 h for benzo[*a*]pyrene, and 34.9 to 3.3 h for benzo[*b*]-fluoranthene. Benzo[*a*]pyrene deposited on glass fibre filters, and exposed to ppm levels of ozone for 24 h, was shown to form benzo[*a*]pyrene quinones and 4,5-benzo[*a*]pyrene oxide [6,7]. When benzo[*a*]pyrene was exposed to 200 ppm of ozone for 1 and 4 h, losses of 50% and 80% were detected, respectively [7].

The reactions of ozone with PAHs, collected during previous ambient high-volume sampling, have been studied by some authors [8–11]. The losses of benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene from filters after exposure to an air stream with 0–200 ppb ozone for up to 24 h were studied and only benzo[*a*]pyrene had any significant loss attributable to ozone [10]. However, losses attributable to volatilization ranged from 25% for benzo[*ghi*]perylene to 85% for benzo[*k*]fluoranthene. The total loss for benzo[*a*]pyrene was about 45%.

Losses from 68 to 84% for fluoranthene, pyrene, benzo[*a*]pyrene, 3-methylcholanthrene and 1,2,4,5-dibenzanthracene were observed in the presence of 140 ppb ozone for 24 h. These, however, include volatilization losses. The losses in the presence of the denuder were from 41 to 59% for the same PAH compounds [12]. The use of a denuder to remove ozone from the ambient air stream during high-volume sampling showed promising results in reducing reactions of collected PAHs with ozone.

Diesel exhaust particles, <0.5 μm aerodynamic diameter, collected on glass fibre filters and subsequently exposed to 1.5 ppm ozone for up to 4 h showed losses of PAHs (such as phenanthrene/anthracene, methylated fluorenes and pyrenes) due to volatilization. However, these as well as less volatile compounds such as benzo[*a*]pyrene, benzo[*e*]pyrene, and perylene showed considerable reactivity to ozone. The conversions ranged from 47 to 100% in 4 h under the experimental conditions applied [13].

Fitz et al. reported that the exposure of filters loaded with ambient airborne particles to ozone concentrations of up to 290 ppb resulted in no changes in mutagenic activity, relative to ozone concentrations [11].

Exposure of pyrene on filter paper to NO_2 (10 ppm) resulted in formation of nitropyrene [14]. Up to 2.8% of the pyrene was converted to nitropyrene. The presence of nitric acid impurity in NO_2 streams has been suggested as the prime cause of the formation of nitro-PAH derivatives [6,15]. No nitro-PAHs were found when a nylon filter was used to remove HNO_3 from a 100 ppb NO_2 stream passing through PTFE and glass fibre filters with PAH-loaded coal fly ash, diesel exhaust or ambient particles [15]. An experiment using benzo[*a*]pyrene spiked onto similar filters and exposed to ppb level of NO_2, also indicated no loss of benzo[*a*]pyrene [6].

Benzo[*a*]pyrene was added to PTFE filters with and without diesel exhaust particles. These were exposed to an equilibrium concentration of nitric acid vapour over nitric acid, resulting in complete degradation of benzo[*a*]pyrene. Mono-nitro- and dinitro-benzo[*a*]pyrene products were identified [15]. The addition of ppb levels of HNO_3 to the air stream during sampling resulted in losses of benzo[*a*]pyrene (95%), benz[*a*]anthracene and perylene (55%) and benzo[*ghi*]perylene (20%). The mutagenicity of filter extracts also increased [16]. The addition of 200 ppb NO_2 during high-volume sampling in the winter resulted in degradation of pyrene, benzo[*a*]pyrene and benz[*a*]anthracene, however, several benzofluoranthenes, and chrysene were not degraded [16,17]. The mutagenicity of extracts was enhanced compared to sampling without addition of NO_2.

The age and origin of the aerosol sampled seemed to affect the extent of degradation. Considerable uncertainty still exists about the effect of co-pollutants present (O_3, NO, NO_2, HNO_3) in PAH samples on filters.

3. Air sampling of PAHs

The monitoring methods for airborne PAHs may be classified into those concerned with either direct occupational exposures or with ambient exposures. PAH concentrations in the former class are usually higher. The PAHs occur in particles of respirable size and reported median diameters are typically 0.5 μm or less. Diameters of 0.7 μm for benzo[*a*]pyrene and 0.32 μm for pyrene were reported [18]. The season has an impact on the size of the aerosols; in the winter, there was a shift from large to small particles and the size distribution of the more volatile low-molecular-mass PAHs is more uniform in the small particle size range. More than 95% of the PAHs in winter aerosols are in the size fraction 3 μm. The fraction below 1 μm contained 70–80% of PAHs in the winter but only 10% or less in other seasons [3]. Aerosols from a coke oven emission source had maximum amounts of PAHs in the 1.86 to 0.85 μm size fraction range and 94% of the PAHs measured were in the 2.9 μm or smaller fraction [19].

PAHs have been associated with particulate matter, but three- to five-ring PAHs have been shown to occur in the vapour-phase as well [20–26]. It has also been shown in several publications that volatilization of particulate PAHs collected on filters represents a considerable loss, especially of PAHs containing less than five rings. Vapour-phase PAHs and those volatilized during sampling have been captured by using backup sorbents. The distribution of PAHs between particle-sorbed and vapour-phase fractions has also been estimated with such sampling systems. Several studies have been undertaken to determine the vapour–particle distribution in high-volume as well as in low-volume sampling [12,21,27–32].

The distribution ratios of particulate to gas phase concentration of several PAHs as well as other classes of organics were reported by Cautreels and Van Cauwenberghe [21]. For phenanthrene, anthracene, methylpyrene and methylanthracene, the distribution factors ranged from 0.027 to 0.088. Fluoranthene, pyrene and benzofluorenes had intermediate values 0.26, 0.49 and 1.25, respectively, while benz[*a*]anthracene, chrysene, benzo[*k*]fluoranthene, benzo[*b*]-fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene and perylene were primarily in the particle phase with distribution factors ranging from 3.15 to 11.5. It should be noted that losses of particle-bound material due to blow off from the filter and gains on the cartridge due to material

volatilized during sampling may have introduced errors in the distribution ratios.

The amounts of PAHs retained on filters and sorbents collected by low-volume techniques in aluminum reduction plants, coke plants, iron and steel works, foundries and ferroalloy plants were summarized by Bjørseth [30]. Quantitative data for aluminum and coke plants revealed similar distributions between the particle and vapour phase. Fluorene, methylfluorenes, phenanthrene, methylanthracenes, fluoranthene, dihydrobenzo[*a*]- and benzo[*b*]fluorene and pyrene were found in both phases with percentages in the vapour-phase ranging from 100 to 35%. For heavier PAHs, the filter catch contained nearly all the PAHs measured.

In a study at a coke plant, two aluminum plants and a creosote plant silver membrane/glass fibre filters with XAD-2 backup sorbents were used [31]. More than 99% of benzo[*a*]pyrene, benzo[*k*]fluoranthene, benzo[*b*]-fluoranthene and chrysene were retained on the filter. For naphthalene, phenanthrene, anthracene and fluoranthene, the amounts retained on the filter ranged from 0 to 35%.

It is clear that current sampling methods (i.e. cascade impactors, high- and low-volume samplers using filters and/or back-up sorbent traps) are inadequate for the determination of accurate concentrations of PAHs in air or bound on airborne particles. The sampling process using available techniques can produce redistribution of the PAHs both between the vapour and particle phase and among different particle sizes. Methods to overcome these deficiencies are not yet available.

3.1. Active sampling

Active sampling methods that rely on integration of the sample, require pumping the air stream through a medium (e.g., filter, sorbent, impinger, cryogenic trap) which will retain the target compounds. In environmental monitoring, sampling rates in the range of 300 to 1500 l/min^{-1} are used and much lower flow-rates are used in occupational exposure monitoring.

For particle size measurement in which particles are fractionated into specific size ranges, based on aerodynamic particle diameters, cascade impactors designed to complement high-volume samplers or as separate units are commercially available. The separate units typically employ flow-rates in the range of 30 to 90 l min^{-1}. Other particle size measuring devices, such as dichotomous samplers or optical particle counters have not been used extensively in sampling for PAHs [33].

Impregnated filters, impingers, solid sorbents and cryogenic traps are used to collect vapour-phase PAHs. Studies using multiple filters, some of which were impregnated, simply used filters placed on top of each other or in specially fabricated multiple filter holders [8,20,34]. Cartridges for housing solid sorbents are often used. Modifications to standard high-volume samplers have been provided for partial flow diversion through the sorbent cartridge [12,18,21,27–29,35–37].

Low-volume samplers used in occupational environments often have battery operated personal sampling pumps. In addition, readily available vacuum pumps are also used. The usual flow-rates in these samplers are 1–3 l min^{-1} through filter holders or cassettes housing 37 or 47 mm filters.

For low-volume sampling, in which sorbents in combination with single or multiple filters are used, commercial devices specifically designed for PAH sampling are not widely available but are generally assembled from commercially available components [38–40].

3.2. Passive sampling

Passive sampling techniques rely on the controlled transport of the analyte material along a concentration gradient towards a surface which acts as a sink for the target compound. If the surface adsorbs the compound completely, the concentration at the surface is zero and this serves to establish the concentration gradient. It should be noted that because there is an order of magnitude difference between the diffusion coefficients of gases and fine particles (if turbulent diffusion is ignored), the diffusion of particles in

the tube is therefore negligible. These and closely related devices may involve diffusion through a membrane or filter before reaching the sink [35,41].

Passive sampling techniques have been applied infrequently to ambient (outdoor) monitoring of PAHs, mainly because of the long sampling times required due to the low PAH levels and limited analytical sensitivity.

The PAH dosimeter utilizes a filter paper disc or a solid substrate treated with sorbent material such as a heavy-atom doped chemical reagent [42]. The heavy-atom doped sorbent allows detection and analysis by room temperature phosphorescence. This technique is convenient and sensitive but does not allow resolution of many components in mixtures [43]. Detection limits of several homocyclic and heterocyclic PAHs have been reported in the picogram range [44]. Laboratory and field tests of the dosimeter demonstrated the capability of measuring vapour-phase levels of azarenes such as quinoline, phenanthridine and acridine and PAHs such as fluoranthene, naphthalene, methylnaphthalene, phenanthrene and pyrene [41,43,45–49].

Passive sampling methods have also been successfully employed in monitoring occupational levels. This technique has been applied only relatively recently to specific vapour-phase PAH compounds but has been commonly used for monitoring other low-molecular-mass organics in occupational environments. The low cost and reasonably good sensitivity of this technique for specific compounds, are very useful for sampling surveys requiring the collection of large numbers of samples.

The passive monitor has several highly desirable features. It is sensitive, light-weight, inexpensive, amenable to large sampling volumes, analytical costs are low, and turn-around times are short. Currently, it is the only device that allows the true vapour-phase measurement of PAHs.

3.3. Sampling of particulate PAHs

Several types of filter materials have been used to collect PAHs. Two types of filters — glass fibre and silver membrane — have been utilized most often in the sampling of airborne PAHs with high- and low-volume samplers.

The high-volume sampler has been used in most cases where ambient monitoring has been required and 25 × 20 cm glass fibre filters have been used most frequently in the USA and a 12.5 cm diameter filter in Germany. For occupational sampling, filter cassettes employing 37 mm diameter silver-membrane filters have been most widely used. The choice of the glass fibre filter is based on the ability to obtain consistently low organic blank levels on filters. Pretreatment of glass fibre filters most often involves firing at 400–500°C, but pre-extraction of filters with a variety of solvents is used as well. PTFE-coated glass fibre filters, are enjoying increased use as a collection medium for sampling of organics. A comparison of the regular glass fibre filter and the PTFE-coated filter showed no differences in the high-volume sampling of PAHs of diesel exhausts [50].

The PAH collection on glass fibre, quartz and PTFE were compared in sampling ambient air at varying flow-rates to give similar face velocities [51]. The quartz and glass fibre filters collected lesser amounts of PAHs (85 and 83%, respectively) than the PTFE filters, and it was suggested that reported ambient PAH levels are underestimated as a result of the use of glass fibre filters [52]. This assumes that the PTFE filters are not absorbing PAH vapour. It was not possible to determine whether or not the smaller amount of PAHs from quartz or glass fibre filters could be attributed to chemical reaction with other air pollutants [15].

Five filter types, namely glass fibre, silica quartz, microglass fibre with PTFE binder on fibres, PTFE membrane bonded to polyethylene net, and PTFE membrane supported by PTFE fibres, were compared for blank levels, amount of PAHs retained and losses from filters [53]. PTFE gave the lowest levels of background impurities in methylene chloride extracts. The polar fraction of the extract from PTFE/polyethylene was clean but there were non-polar impurities, probably from the polymeric backing material, that are potential interferents in fluo-

rescence determinations. The PTFE membrane type filter retained most of the PAHs based on recovery of ^{14}C-labeled benzo[*a*]pyrene spiked on filters prior to sampling. The order of recovery was PTFE membrane > TA60A20 > glass fibre or silica fibre. The superior performance of PTFE filters was attributed to less degradation of collected PAHs on PTFE filters compared to the other filters. This degradation was monitored for benzo[*a*]pyrene during storage in the dark. It was postulated that an active surface such as quartz or silica is necessary for reaction of collected material during and/or after sampling. The extent of degradation was dependent on the filter loading, i.e., lightly loaded filters were more susceptible to degradation due to the greater percentage of particles contacting the filter surface [53]. The loss of benzo[*a*]pyrene in stored samples of diesel exhaust particulates collected on glass fibre filters amounted to 67% after 150 days [54].

In a recent evaluation of membrane filters for PAH sampling, cellulose acetate filters collected more of the PAHs with three or four rings than glass fibre filters [8]. The amounts of phenanthrene, fluoranthene and pyrene on the glass fibre filter ranged from 7 to 42% of that collected on a single membrane filter. For benzo[*b*]-fluoranthene, benzo[*j*]fluoranthene, benzo[*e*]-pyrene, benzo[*a*]pyrene and benzo[*ghi*]-perylene, similar amounts were collected on the glass fibre and membrane filters [8]. However, even the use of membrane filters led to losses of small amounts of anthracene and pyrene; up to 20% of anthracene and pyrene were lost from upstream membrane filters indicating that the capacity of membrane filter for low-molecular-mass PAHs is low.

The use of silver membrane filters in sampling for PAHs in occupational environments was initially suggested in view of the difficulty of obtaining a suitable low blank from glass fibre filters on extraction with benzene and the better weight stability of silver membrane filters. Because the silver membrane filter tends to be easily plugged by particulate matter, the use of the glass fibre filter preceding the silver membrane filter has been a standard NIOSH procedure for sampling in occupational environments [55]. The high resistance of the silver membrane filter to air flow limits the sampling rate [56]. The NIOSH method and other applications in which silver membrane filters are used typically have sampling rates of 1–5 l min^{-1}.

3.4. Sampling of volatile PAHs

Improvements in sampling methods designed to minimize the losses of PAHs volatilized during sampling, have relied on impregnated filters, reduction in sampling duration, addition of solid sorbent back-up cartridges and cryogenic traps.

Several solid sorbents or liquids coated on supports acting as stationary phases have been used to trap vapour-phase air pollutants. The choice of sorbent is determined by several factors such as collection efficiency, capacity of sorbent (breakthrough volume), chemical stability of sorbent during sampling, storage and extraction, low blank levels, low affinity for water vapour and high and facile recovery of sorbed vapours. For the sampling of PAHs the sorbents used include Tenax, XAD-2, polyurethane foam (PUF), Florisil, Chromosorb 102 and SepPak-C_{18} on Porasil [36,38]. The use of charcoal tubes for the collection of organic vapours was widespread and these tubes have been used to collect three-ring PAHs, but the release of PAHs from charcoal is usually difficult [57]. Tenax GC was utilized as a sorbent in source sampling of combustion sources [58,59].

Glass fibre filters impregnated with glycerotricaprylate captured larger amounts of volatile PAHs than untreated filters, but impregnated filters also lost volatile PAHs when sampling periods were extended to 4–12 weeks. For example, 78% less fluoranthene was found in a sample using a 12-week period compared to sampling carried out with three filters for the concurrent three 4-week periods. Less volatile PAHs were not found on back-up impregnated filters, but losses of these compounds were attributed to reaction with other air pollutants [20]. Filters impregnated with tricaprylate or liquid paraffin retained similar amounts of PAHs [60]. Although the impregnated filters trapped vaporized PAHs,

losses were observed during prolonged sampling periods. As a curiosity, the treatment of filters with a 3:1 mixture of methanol and glycerine was used successfully for sampling in coke oven plants [55].

Shorter sampling times has been recommended to minimize losses of PAHs during sampling [61]. The PAHs and total extractable organic matter retained on filters have been shown to decrease if the sampling duration is extended [20,60,61]. Shorter duration time was recommended to minimize these losses and it was found that the PAH concentrations determined from 6-h sampling were up to 6.5 times larger than those obtained using 24-h sampling periods [50].

In high-volume samplers, sorbents such as Porapak Q and S, Chromosorb, Tenax and polyurethane foam have been used in the sampling of vapour-phase organics [42,62–65]. The use of Tenax GC as a sorbent for PAHs, however, was found to be prone to contamination and exhibited poor flow characteristics [66].

Polyurethane foam (PUF) has gained in popularity, particularly for the use in high-volume samplers because of the low pressure drop caused by PUF, low blanks, low cost and ease of handling. Flow-rates of 225–416 l min^{-1} were reported in PAH sampling using glass fibre filter PUF sorbent samplers [32,95]. Several studies have reported on the use high-volume samplers with a PUF plug as a back-up sorbent for sampling of ambient PAHs [36].

Jackson and Cupps used a personal monitor consisting of a 37-mm glass fibre–silver membrane filter combination before a solid sorbent cartridge of Chromosorb 102. Flow-rates of 2 or 10 l min^{-1} were used in different samplers [38]. Andersson et al. while sampling in occupational environments with coal tar sources, used a standard filter cassette without a silver membrane filter and with Amberlite XAD-2 [31].

The collection efficiencies of sorbents have not been systematically investigated in order to define and quantify relationships between parameters such as flow-rates, linear face velocities, retention volume, effects of temperature and nature of target compound.

4. Sample desorption and clean-up

The PAHs from solid environmental samples such as air particulates, soils and sediments are traditionally extracted by Soxhlet extraction or ultrasonication using a variety of organic solvents including acetone, benzene, toluene, methylene chloride, etc. These traditional methods are efficient for many samples; however, they often require large volumes of solvents, are time consuming, and yield incomplete recovery of higher-molecular-mass PAHs from materials on which they are strongly adsorbed (i.e., carbon black or coal fly ash). For these reasons, supercritical fluid extraction (SFE) has received considerable attention as an alternative to these classical methods. Since environmental samples generally contain interferents and trace amounts of PAHs of interest, concentration and clean-up procedures are usually required prior to the final chromatographic analysis. In many cases, the sample pretreatment procedure is the critical step in achieving reliable quantitative results.

PAH concentration and clean-up is increasingly being performed by solid-phase extraction (SPE). For preconcentration of PAHs from drinking water samples, best results were obtained for combined octadecylsilane (C_{18})–ammonia (NH_2) solid-phase cartridges, whereas the enrichment of PAHs from soil samples was best achieved with silica (Si)–cyano (CN) or C_{18}–CN combinations [67]. The choice of SPE sorbent type is often dictated by the chromatographic method used for PAH separation and identification. For example, a recent study showed that for the determination of PAHs in lake sediments, C_{18} and silica columns could be used satisfactorily to clean up extracts for subsequent HPLC analysis with fluorescence detection; however, they could not be used for gas chromatography (GC)–mass spectrometry (MS) for PAHs greater than chrysene due to interferences from aliphatic waxes. Fully activated silicic acid and neutral alumina columns were recommended [68]. A standard leaching test employing SPE with C_{18} packings has proven to be a fast reliable method for determining the PAH leachability from waste materials [69]. Florisil (SiO_2 and MgO) car-

tridges have yielded rapid and efficient recovery of PAHs for petroleum and sediment extracts [70]. Extraction and concentration of PAHs in oils was achieved by charge-transfer liquid chromatography on improved tetrachlorophthalimidopropyl-bonded silica [71]. A quantitative procedure for the determination of PAHs in biomass tar has been described using SPE with aminopropylsilane packings [72]. Chromosorb T and XAD-2 have been compared for in situ extraction of PAHs from fresh water and seawater. Neither sorbent was useful for PAHs with molecular masses less than that of phenanthrene due to low recoveries or PAH contaminants, and were comparable for the study of three-ring and higher PAHs [73].

Most of the air samples collected do not need purification prior to analysis. However, some laboratories uses normal-phase LC clean up and isolation of the total PAH fraction prior the analysis, especially when performed with GC–FID [74].

SFE has proven to be a powerful alternative to conventional liquid extraction methods used in environmental analysis [75,76]. PAHs have been extracted directly from endogenous solid and liquid matrices, as well as trapped onto solid adsorbents with subsequent recovery by SFE [77,78]. One major advantage of SFE is the relative ease with which it can be coupled to chromatographic techniques, particularly GC and supercritical fluid chromatography (SFC). Hyphenated SFE–GC and SFE–SFC techniques have recently been applied for the determination of PAHs from environmental samples [79–81].

Carbon dioxide is the primary fluid used in most SFE applications, because it has low critical points, it is non-toxic, non-flammable, odourless, readily available in high purity, inexpensive, and eliminates solvent waste disposal problems. Unfortunately, the non-polar nature of carbon dioxide has hindered its application for the recovery of higher-molecular-mass PAHs or those strongly adsorbed to (or trapped in) the environmental matrix. Alternative fluids such as N_2O and $CHClF_2$ (Freon-22) yield higher recovery of PAHs from petroleum waste sludge and railroad bed soil, compared to CO_2 [82]. Alternatively, the use of organic solvent modifiers (i.e., methanol) or in situ chemical derivatization has been shown to improve the recovery of PAHs while still employing the preferred supercritical fluid, carbon dioxide [83]. Other studies have focused on optimizing the major controllable SFE variables and minimizing problems including restrictor plugging, particularly when extracting high-molecular-mass PAHs or employing samples with a high sulfur content [84,85].

A model for dynamic SFE has been proposed and applied to the SFE of the PAH, phenanthrene, from railroad-bed soil with good agreement [86]. Models such as this are useful as they provide an extrapolation method for obtaining quantitative analytical extractions in the shortest analysis time. A dynamic tracer response technique has been applied for simultaneous measurement of equilibrium and rate parameters for the dynamic extraction of analytes from solid matrices. The technique allows the determination of adsorption equilibrium constants, effective diffusivities and axial dispersion coefficients for the system naphthalene–alumina–supercritical CO_2 [87–90]. More thorough discussions of the effect of SFE variables and comparisons for different SPE matrix–analyte types have recently been published [91–93].

5. Chromatographic analysis of PAHs

5.1. HPLC analysis

For about two decades high-performance liquid chromatography (HPLC) has been successfully used for the separation of individual PAHs from complex mixtures. Since Schmit et al. first reported [94] the separation of PAHs with a chemically bonded octadecylsilane (C_{18}) stationary phase in 1971, Reversed-phase HPLC (RP-LC) on chemically bonded C_{18} phases have been widely used in PAH analyses of environmental samples. The popularity of this technique is based on several factors: its good selectivity in separating individual PAH compounds and their isomers, sensitive and selective detection by fluorescence spectroscopy, and its use as a frac-

tionation technique before analysis by other chromatographic and spectroscopic techniques [74].

Although it may be concluded that HPLC on C_{18} stationary phases is excellent in separating PAHs in complex mixtures, considerable differences in selectivity (i.e., relative separation) have been shown between different commercial columns. Intensive investigations have been conducted at NIST to get more detailed knowledge about numerous factors affecting selectivity in PAH separation by RP-LC. Studies by Sander and Wise have been summarized in the recent reviews [95,96].

C_{18} bonded phases are classified as 'monomeric' or 'polymeric' depending on the nature of silane reagents and the conditions of the bonded phase synthesis. As a summary of several studies it has been concluded that this monomeric–polymeric character of C_{18} has a great influence on the separation of PAHs (Fig. 2) [74]. The elution order of the three-component mixture of phenanthro[3,4-*c*]phenanthrene (PhPh), 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN), and benzo[*a*]pyrene (BaP) has been shown to gauge the nature of a phase [97]. On a monomeric phase the order is BaP, PhPh, TBN, and on a polymeric phase PhPh, TBN, BaP. On the basis of this test column selectivity toward more complex PAH mixtures can be predicted. Sander and Wise [97] also stated that the effect of endcapping on PAH selectivity is negligible. Commercial C_{18} columns have also been classified according to the selectivity factor $\alpha_{TNB/BaP}$ (Table 1) [74]. $\alpha_{TNB/BaP}$ values of 1 indicate polymeric phases, which have been shown to separate PAHs more selectively. Some other characteristics to be mentioned are: surface coverage [98], alkyl chain length [99], and temperature [100] which have been shown to have an influence on PAH retention behaviour. On polymeric C_{18} phases planar PAHs have longer

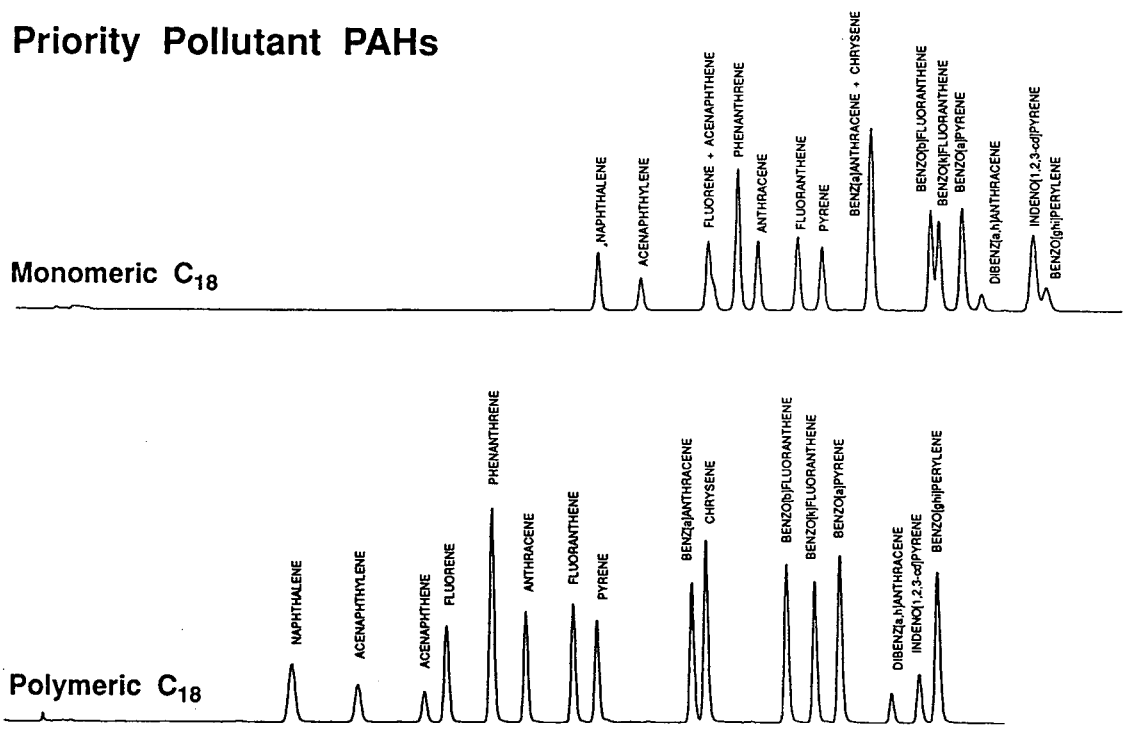

Fig. 2. Comparison of the separation of the 16 PAHs on a monomeric and a polymeric C_{18} stationary phase (reproduced with permission from Ref. [74]).

Table 1
Selectivity classification ($\alpha_{TBN/BaP}$) for various commercial C_{18} columns (reproduced with the permission from Ref. [74])

Column	$\alpha_{TBN/BaP}$
Polymeric phases	
Bakerbond C_{18} Wide-Pore	0.56
Hypersil Green PAH	0.8
Phenomenex Envirosep PP	0.58
Chromspher PAH	0.59
BioRad RP 318	0.59
Supelcosil LC-PAH	0.63
Vydac 201TP	0.74
Spherisorb PAH	0.82
Erbasil C_{18} H	0.91
Intermediate phases	
ES Industries BF-C_{18}	1.04
LiChrospher 100 RP-18	1.11
Bakerbond C_{18}	1.27
Erbasil C_{18} M	1.28
LiChrospher 60 RP-select B	1.36
Partisil 5 ODS-2	1.40
Partisil 5 ODS	1.48
Spherisorb ODS-1	1.50
Zorbax RX C_{18}	1.50
Brownlee ODS 5A	1.51
Sepralyte C_{18}	1.61
Spherisorb ODS-2	1.68
Monomeric phases	
Erbasil C_{18} L	1.76
Pecospher 5 Cr C_{18}	1.76
Partisphere C_{18}	1.79
Zorbax ODS	1.80
Serva C_{18}	1.84
Partisil 5 ODS-3	1.93
Hypersil ODS (HP)	1.94
Microsorb C_{18}	1.95
J and W Accuphase ODS 2	1.96
Novapak C_{18}	1.97
Ultrasphere ODS	1.98
Capcell C_{18} SG120 Å	1.99
Supelcosil LC-18	2.00
IBM ODS	2.00
Brownlee Spheri 5 RP-18	2.02
ODS Hypersil	2.04
Cosmosil C_{18}-P	2.04
Ultracarb 5 C_{18} (20%)	2.05
J and W Accuphase ODS	2.07
YMC 120 Å "A"	2.08
Ultracarb 5 C_{18} (30%)	2.10
Adsorbosphere C_{18} HS	2.10
Supelcosil LC-18-DB	2.18

retention times relative to non-planar ones [101,102].

Traditional PAH separations by RP-HPLC are made by gradient elution. The most widely used detectors with HPLC are the UV absorption and fluorescence detectors. In environmental analyses the far better sensitivity of the latter is usually needed. The selectivity of fluorescence detection is also essential for the sensitivity of LC in PAH analyses. Optimum excitation and emission wavelengths in detection do not necessarily correspond to the maxima in spectra of each compound, but best separation wavelengths depend on the interfering compounds in the sample matrix. Quantitation in HPLC is made by external or internal standards. As internal standards perdeuterated PAHs have at least two advantages: elution immediately prior to the non-deuterated PAHs, and fluorescence characteristics near the corresponding non-deuterated compound [103].

One advantage of selective fluorescence detection is the need for less sample clean-up than in GC analysis. Recently Sisovic and Fugas [104] evaluated the suitability of low-volume samples (2–4 m^3/24 h) for PAH analysis from suspended particles without any clean-up or separation steps. The conclusion was that the sensitivity of the HPLC–fluorescence method permits the application of low-volume suspended particulate matter (SPM) samples for PAH determination, and separation of interfering substances before analysis is not necessary unless PAHs with short retention time are of interest [104].

Multidimensional liquid chromatographic techniques have also been routinely used in PAH analyses. Normal-phase HPLC has been used as a prefractionation technique to analyze environmental samples (e.g., atmospheric particles) which contain a complex matrix of adsorbed organic compounds. This chromatographic technique overcomes many of the disadvantages of liquid–liquid extraction [105].

In a very recent paper a new application of a RP-HPLC column switching technique is presented in which a 20-component PAH mixture is rapidly and efficiently separated under isocratic conditions by use of two Superspher-100 ('mono-

meric') cartridges thermostatted at different temperatures [106]. The authors expect that this time and material saving method will become an attractive alternative to conventional gradient elution in HPLC.

Different column package materials can also be utilized in column switching techniques for sample clean-up, depending on the nature of the matrix. For example silica–dinitro-aryl silica columns for the determination of benzo[*a*]pyrene in oil fractions have been used [107].

A sample fractioning technique, low-volume liquid chromatography, also called 'dry' column chromatography, suitable for air particulate matter has been presented in which the sample is eluted sequentially from an Al_2O_3 cartridge. Final analysis was made by gas chromatography [108].

5.2. Gas chromatography and gas chromatography–mass spectrometry

Gas chromatography is the method with a high resolution power in PAH mixture analysis. A recent comparison of some high temperature GC columns also illustrated their applicability to the analysis of moderately high-molecular-mass PAHs (seven ring) with a reasonable retention time [109]. Recent studies have focused on relationships between GC retention data and molecular properties of PAHs and some regularities between the molecular shape of PAHs and retention behaviour have been observed [110–112]. The temperature-programmed retention indices of volatile fractions of PAHs were studied using moderate and non-polar phases [113,114].

For the detectors used in GC analysis of PAH compounds the most utilized detectors are flame ionization (FID) and mass spectrometric (MS) detectors, but also FTIR has been applied [105,115,116]. The electron impact (EI) ionization technique is widely used and characteristic fragmentations allow identification of the PAHs. Another technique is based on chemical ionization and registration of negative ions (NCI). Thermal electrons are captured competitively by sample molecules with high electron affinity. Compared to the EI technique little fragmentation is seen in the NCI mass spectra due to the low energy of the electrons [117]. Hilpert studied the usefulness of NCI to the quantitative determination of PAHs [118]. Benzo[*a*]pyrene was shown to be a good analyte for the NCI method due to its high sensitivity and the fact that benzo[*e*]pyrene is insensitive under NCI. Benzo[*e*]pyrene can cause impreciseness in the analysis if EI is used, and an SD of 25% was observed when the standard samples were analyzed. If the NCI method is used a good SD of 3.3% was observed. GC matrix isolation infrared spectrometry has been used to identify isomeric PAHs and 33 PAHs have been quantitatively measured and identified [119].

Electron-capture detection after derivatization with bromine and selective detection using photoionization detection have been also presented [120,121]. The optimal analytical conditions and solvent of choice in splitless injection has been investigated [122]. The use of toluene and xylene gave enhanced signals up to 100 times greater than other solvents tested, especially with high-molecular-mass PAHs.

5.3 Miscellaneous techniques

Thin-layer chromatography (TLC) was used especially in earlier works to analyze complex PAH extracts before the development of gas and liquid chromatographic methods which are nowadays usually preferred. However, TLC has proved to be a convenient technique if complete separation is not required. Individual PAHs on TLC plates are generally quantitated with fluorimetry, either directly on the plate or in solution after elution from the plate. Today TLC is still used as a sample preparation method in special applications with GC, which has been recently reviewed by Furton et al. [123]. A technique combining TLC with laser mass spectrometry (LMS) was demonstrated to effectively distinguish and determine even partly overlapping PAH compounds directly from the plate [124]. A high-performance thin-layer chromatography (HPTLC) method was described as a low-cost screening method for PAHs in crude en-

vironmental samples. In this application separation is made on octadecylsilanized silica gel plates and individual compounds are determined by fluorescence scanning densitometer [125].

SFC has recently been applied to the determination of PAHs from environmental samples [80,81]. Carbon dioxide is the primary fluid used in most SFC applications, and the detection is carried out by FID and MS [126]. The retention behaviour of PAHs in SFC for different stationary phases has been shown to be controlled by molecular size, but was also influenced by additional parameters such as dipole–dipole interactions and solubilities [127,128]. Furton et al. have found that of numerous physical and molecular descriptors studied, the molecular connectivity correlates best with SFC retention data for normal- and reversed-phase systems [124].

Capillary electrophoresis (CE) is a powerful technique and well suited for analysing complex microsamples because of its high separation efficiency. The CE analysis of PAHs is not straightforward since the electrophoretic separation of these neutral and highly hydrophobic compounds is difficult. However, methods were developed for electrophoretic separation of PAHs using solvophobic interaction of the analyte [129,130] and the use of organic additives in micellar electrokinetic chromatography [131]. In a recent paper Nie et al. reported on the use of CE with UV-laser-excited native fluorescence for ultra sensitive determination of polycyclic aromatic hydrocarbons [130]. The separation is based on solvophobic association of the analytes with tetraalkylammonium ions in acetonitrile–water solution. The reported mass detection limits were in the range 10^{-20} mol, with linear fluorescence response spanning over 4 orders of magnitude.

6. Conclusions

The most critical point in the evaluation of PAH compounds in air samples is the choice of sampling strategy. A different approach is needed if particulate or volatile PAHs are measured. In high-volume sampling the glass fibre filters are most often used and PUF is used as a back-up 'sorbent'. The sampling volumes which are recommended are 10 000 to 25 000 liters with a flow of 10 l/min. In the occupational environment the choice of the filter is PTFE with XAD-2 as a back-up section. The sampling volume is normally 400 to 1000 l at a flow-rate of 1.5 l/min. The instrumentation in the analysis is not that critical, and most of the analysis can be carried out with HPLC and GC.

Acknowledgement

The Academy of Finland is acknowledged for the financial support.

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Journal of Chromatography A, 710 (1995) 109–116

JOURNAL OF CHROMATOGRAPHY A

Review

Determination of benzanthrone in environmental samples

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Abstract

This paper summarizes advances in the determination of benzanthrone and other polycyclic aromatic ketones in environmental samples in the last 20 years. Data on toxicity and mutagenicity are also reviewed. Methods of determination include liquid chromatography, high-performance liquid chromatography, gas chromatography and gas chromatography–mass spectrometry.

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1. Introduction

7*H*-Benz[*de*]anthracen-7-one (benzanthrone) (Fig. 1) is a precursor of dyestuffs in industry [1] and its toxic effects have been recognized for a long time [2]. Its determination in airborne particulate matter became feasible only recently after the development of efficient chromatographic methods of analysis.

Fluoranthene (Fig. 1), a major component of polycyclic aromatic hydrocarbons (PAHs) emitted from combustion engines, can be obtained from benzanthrone by elimination of CO, since the elimination of CO is a well known reaction in the pyrolysis of some ketones [3]. Hence, it is

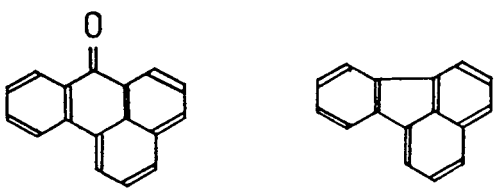

Fig. 1. Structural formulae of (left) benzanthrone (m.p. 170°C) and (right) fluoranthene (m.p. 110°C).

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0021-9673/95/$29.00
SSDI 0021-9673(95)00203-0

not surprising that benzanthrone and other polycyclic aromatic ketones always accompany PAHs in particulate emissions of combustion sources.

Sublimation of polycyclic aromatic compounds at 300°C reveals that both PAHs and polycyclic aromatic ketones are not decomposed, whereas diketones are less stable [4]. These data prove considerable stability of polycyclic aromatic ketones at increased temperature.

Benzanthrone is almost completely adsorbed on particulate matter in the atmosphere. Only 3% of total benzanthrone was found in the gas phase when high-volume sampling was done in Portland, OR, USA, in 1984 [5]. In the same sampling experiment, 28% of total chrysene and 94% of total fluoranthene were found in the gas phase. These data indicate a lower volatility of benzanthrone compared with these PAHs.

It is well known that the concentration of benzo[*a*]pyrene shows a large short-term variation in the atmosphere. The average concentration of benzo[*a*]pyrene in Essen (Germany) during 50 weeks varied between 6 and 40 ng/m^3, whereas short-term concentrations ranged from 0.2 to 299 ng/m^3 [6]. A similar concentration range of three orders of magnitude can be expected for benzanthrone, although it decays slightly faster than benzo[*a*]pyrene in the atmosphere. It is normally lost during clean-up of samples for PAHs [6].

Benzanthrone, the industrial precursor of dyestuffs, which is also among the major polycyclic aromatic ketones found in emissions from all combustion sources, is the subject of this review. Owing to the close structural relationship between benzanthrone and other polycyclic aromatic ketones and PAHs, the purpose of this review is to provide a literature survey on the determination, properties and environmental occurrence of benzanthrone and its relationship to other polycyclic aromatic compounds during analytical procedures.

2. Liquid chromatography

Liquid chromatography routinely is used for sample clean-up prior to the determination of benzanthrone. Although compound separation can also be done by HPLC, supplemental methods such as GC, GC–MS or LC–MS are applied more frequently owing to the large number of different PAHs other than benzanthrone in environmental samples.

The isolation of PAHs is effected by a precolumn clean-up on silica columns, followed by chromatography on Sephadex LH-20 with 2-propanol as the eluent [6]. This clean-up separates benzanthrone from PAHs owing to its higher polarity, and it is then discarded with contaminants of similar polarity and thus escapes detection. Multi-step clean-up procedures have also been developed (7), and benzanthrone will be found in a column eluate not containing PAHs.

Liquid chromatography on Sephadex LH-20 with 2-propanol as eluent will elute benzanthrone just before chrysene and benz[*a*]anthracene, and this method alone is therefore not suitable for the separation of benzanthrone from PAHs.

A separation of organic compound classes in synthetic fuels has been performed. Stepwise elution of compounds from neutral alumina with hexane, benzene, chloroform–0.75% ethanol and tetrahydrofuran THF–10% ethanol was performed. Benzanthrone was found in the chloroform fraction. This fraction was subjected to column chromatography on silica gel, and benzanthrone and amino-PAHs were found in the benzene eluate [8].

Polycyclic aromatic compounds were isolated from fish tissue by adsorption chromatography on alumina and gel chromatography on biobeads, and the detection limit was below 0.2 μg/kg [9]. Clean-up on an alumina column yielded well defined compound classes [10]. Compound class separation was also achieved by normal-phase HPLC [11]. Oxygenated and nitro-substituted PAHs were determined by HPLC with electrochemical detection [12].

A clean-up based on XAD-2 was developed in order to isolate polar and non-polar polycyclic compounds [13,14]. This method is based on the polycyclic aromatic structure of solutes rather than polarity. It provides a column eluate containing all non-polar and slightly polar polycyclic

aromatic compounds in one fraction. Thus, nitroarenes, heterocycles, PAHs and benzanthrone are isolated together, while most interfering compounds are absent. The mixture of polycyclic compounds obtained by this clean-up often contains too many polycyclic compounds, and a direct determination of benzanthrone without a second clean-up can only be done by high-resolution GC.

A combination of gel chromatography on Bio-Beads SX-12 and normal-phase LC was used for clean-up of aromatic ketones and related compounds followed by capillary GC [15].

An HPLC method for mixtures of up to 600 organic compounds, followed by GC–MS, has been published [16]. Narrow-bore columns of 1 mm I.D. were used in HPLC for the separation of compounds, and subsequent off-line MS was performed [17]. HPLC in conjunction with diode-array UV detection and MS was found suitable for the analysis of complex mixtures of polycyclic aromatic compounds [18].

On-line LC–GC has also been applied to polycyclic compounds in airborne particulate matter and diesel exhaust particulate extracts [19,20]. LC–GC is used directly with crude extracts without prior sample clean-up. Compounds present in the sample are split up between different gas chromatograms. This is not satisfactory, because it should be the aim of GC analysis to produce one gas chromatogram representing total amounts of compounds to be determined.

3. Gas chromatography and gas chromatography–mass spectrometry

Diesel particulate matter has been analysed. Polycyclic compounds were separated by normal-phase HPLC with gradient elution. PAHs and polar polycyclic compounds are found in different fractions, and the concentration of benzanthrone is about one quarter of that of fluoranthene. Compound identification was achieved by GC–MS using non-polar stationary phases. Mass spectra for polar aromatic compounds were given [21]. Benzanthrone was also identified in treated wood after supercritical fluid extraction and GC–flame ionization detection [22]. Liquid crystalline stationary phases were applied to the determination of polycyclic materials in airborne particulate matter. Benzanthrone and other polycyclic compounds were separated from PAHs by HPLC on silica gel prior to GC [23]. Mass spectra of benzanthrone and related compounds have been reported and fragmentation pathways investigated [24,25]. MS fragmentation and GC retention of benzanthrone among 80 other compounds frequently encountered in environmental samples has been described [26].

Polycyclic aromatic ketones and PAHs have been isolated from urban airborne particulate matter and both compound classes separated by LC on silica gel. A second clean-up by column chromatography on Sephadex LH-20 with 2-propanol as eluent was applied in order to separate oxygenated polycyclic compounds from aliphatic polar compounds. The sample originated from urban airborne particulate matter collected in Duisburg (Germany). Benzanthrone was the most abundant polycyclic aromatic ketone, and its concentration ranged from 0.46 to 3.66 ng/m^3. Many other polycyclic compounds were identified in addition to benzanthrone by GC–MS [27]. A characteristic profile of benzanthrone and other polycyclic compounds in aircraft turbine particulate emissions has been obtained by a selective clean-up and GC [28].

A comprehensive presentation of polycyclic aromatic ketones in environmental samples has been given, and methods for the characterization of polycyclic aromatic ketones have been reviewed [29,30]. Benzanthrone and other oxygenated polycyclic aromatic compounds were sampled from Diesel exhaust, separated from PAHs by clean-up on silica gel and identified by GC–MS [31]. Condensate from brown coal combustion flue gas in residential heating also contained benzanthrone, among other oxygen-containing polycyclic compounds [32]. The seasonal variation of organic aerosols in California has been investigated by GC–MS [33]. Extracts from gasoline exhaust particulates were separated into five fractions according to polarity, and individual compounds were identified by GC–MS

[34]. During the determination of benzanthrone and other polycyclic aromatic ketones by capillary GC, random overlap with PAHs may occur, and stationary phases of different polarities should be employed in compound identification by GC [35].

Polar polycyclic aromatic compounds have been characterized by GC–MS with negative-ion chemical ionization [36]. The sample used was NBS standard reference material SRM 1650, which originated from Diesel exhaust particulate matter and was fractionated by normal-phase HPLC prior to GC–MS.

4. Mutagenicity

Numerous investigations into the mutagenicity of benzanthrone have been performed in the past 15 years. Benzanthrone was found to be mutagenic in a test with *Salmonella typhimurium* strains after activation, and it is suspected that its oxidation in air may also lead to mutagenic products [37]. The Ames test for mutagenicity was performed with 30 polycyclic compounds from urban air particulate matter [38]. Soot and 70 associated polycyclic compounds were tested for mutagenicity [39]. The mutagenicity of indoor air pollutants was measured [40,41]. Weak mutagenicity was found for keto derivatives of PAHs [42]. Dilute wood smoke was reacted with sub-ppm levels of O_3 and NO_2 in a Teflon chamber. Aromatic ketones contributed 4% of total mutagenicity before reaction and 16–30% after reaction [43]. Residential wood combustion contributed to Contra Costa County community airborne mutagens in a winter inversion [44]. The polar neutral fraction of urban airborne particulate matter was found to be more mutagenic in the Ames assay than aliphatic or aromatic hydrocarbons [45].

Polar neutral compounds isolated from airborne particulate matter originating from residential heating and exhaust gases were more mutagenic than PAHs [46]. A mutagenicity-directed approach was undertaken to the determination of genotoxic components in coastal sediments. Fractionation was carried out by normal- and reversed-phase LC and gel permeation chromatography (GPC), and the Ames test for mutagenicity was performed [47]. A bioassay-directed fractionation and interseasonal study was also undertaken [48].

5. Toxicity

Since benzanthrone is also an industrial chemical, data on its toxicity have been reported. More than six hepatic microsomal metabolites were isolated [49]. Algal cancer was observed in the marine alga *Porphyra tenera* in the presence of benzanthrone in Fukuoka, Japan [50]. The effect of benzanthrone on the bladder of guinea pigs has been investigated, and localized damage was observed at a dose of 25 mg/kg [51]. The long-term effect of benzanthrone in rats at a biweekly administration rate of 25 μg/kg has been described [52]. Benzanthrone was administered to mice, rats and rabbits, and a low acute and a strong subchronic toxicity to liver and blood were observed [53]. The health status of workers in the production of benzanthrone was surveyed, and disorders of the liver were attributed to combined effects of several chemicals [54]. The interaction of benzanthrone with serum proteins was found to be strongest at pH 7–8 [55]. The toxicity of PAHs and related compounds to *Daphnia magna* was investigated, and PAHs were classified as toxic, moderately toxic and non-toxic [56]. Photoinduced toxicity to larvae was reported [57]. Bioelimination and organ retention of benzanthrone in scorbutic and non-scorbutic guinea pigs was investigated, and ascorbic acid facilitated the bioelimination of benzanthrone [58,59]. Ascorbic acid also reversed the effects of benzanthrone in mice [60]. Bioelimination of benzanthrone was slower in guinea pigs than in rats [61].

6. Environmental occurrence

As benzanthrone is not only an industrial chemical but also accompanies PAHs in combustion related particulate emissions, it is found

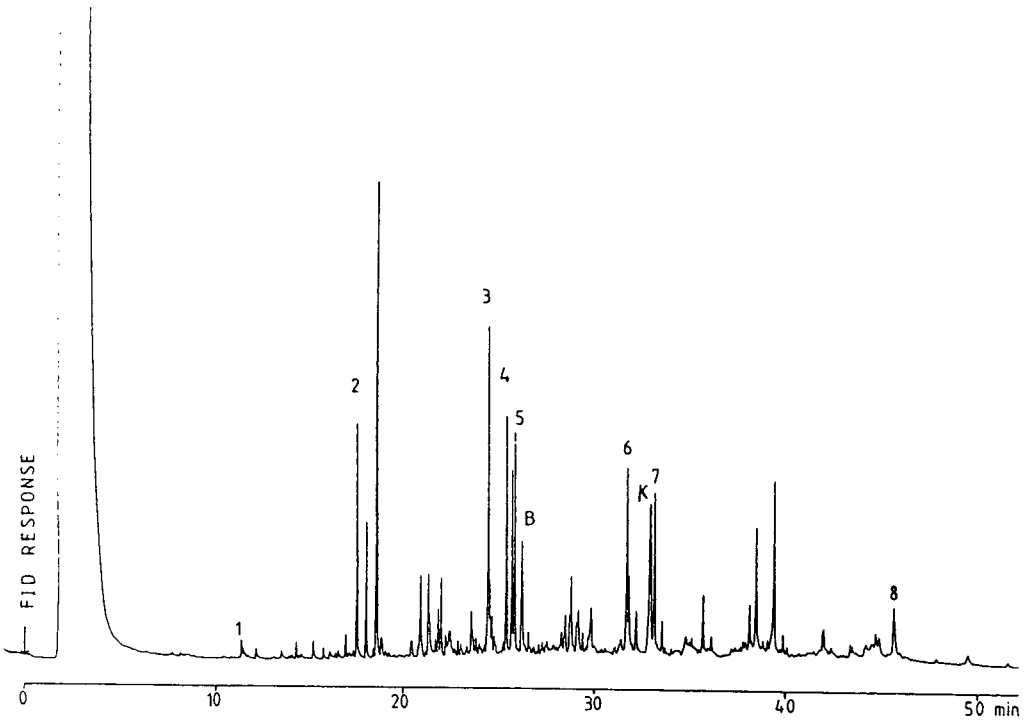

Fig. 2. Gas chromatogram of polycyclic aromatic compounds isolated from aircraft turbine particulate emissions (Pratt and Whitney JT3D3, gas turbine). Stationary phase, OV-1; column, 60 m × 0.03 mm I.D., temperature, programmed from 110 to 280°C at 4°C/min. Y Ordinate scale: peak 2 (fluoranthene) represents 4.5 ng. Peaks: 1 = phenanthrene; 2 = fluoranthene; 3 = benzo[*ghi*]fluoranthene; 4 = cyclopenta[*cd*]pyrene; 5 = chrysene; 6 = benzo[*b*]fluoranthene; 7 = benzo[*a*]pyrene; 8 = coronene; B = benzanthrone; K = 6-*H*-benzo[*cd*]pyrene-6-one.

virtually everywhere in the environment. Most interesting is the fact that it was also found in a meteorite [62]. A characteristic fingerprint of benzanthrone among other polycyclic aromatic emissions is displayed in Fig. 2. This sample was obtained from gas turbine particulate emissions and also reveals the quantitative ratio of benzanthrone to PAHs. The concentrations of benzanthrone in air particulate matter and surface soil are listed in Table 1.

Table 1
Contents of benzanthrone in airborne particulate matter and surface soil

Sample	Location	Concentration	
		ng/m^3 air	μg/kg
Urban air particulate matter [5]	Oregon, USA	1.7	
Urban air particulate matter [27]	Duisburg, Germany	0.46–3.66	
Surface soil [77]	Nagoya, Japan		10
Exhaust particulate matter [21]	In-use VW Diesel engines, USA		243–1281

Owing to its widespread distribution in the environment, there is a comprehensive literature available on the environmental occurrence of benzanthrone. Oxygenated arenes were identified in urban air in Toronto, Canada [63]. Diesel exhaust contains polycyclic aromatic ketones in the most mutagenic fractions separated from diesel soot extracts, and benzanthrone was identified among other oxygen-containing derivatives of PAHs such as anthracenedione, 4*H*-cyclopenta[*def*]phenanthren-4-one and fluorenones [64]. Polar subfractions of Diesel exhaust account for 65% of direct-acting mutagenicity in the Ames assay [65]. Polycyclic ketones were also identified in urban airborne particulate matter from St, Louis, MO, USA [66]. Emission rates of benzanthrone were found to be twice as high from gasoline engines than Diesel engines in Japan [67]. Emissions of polycyclic compounds from rubber combustion were characterized [68]. Ambient airborne particulate matter was investigated in the Philadelphia industrial area, and mutagenicity testing was done [69]. Polycyclic aromatic ketones were also present in the pot room of an aluminium production plant [70]. Higher mutagenic activity is found for PAHs in Diesel exhaust after oxidation [71]. An interesting area is the gas/particle distribution of atmospheric organic compounds including polycyclic compounds [5,72]. The analysis of organic matter in coke oven emissions also revealed polycyclic compounds [73]. Sources of fine organic aerosol were systematically investigated [74–76]. Benzanthrone was also determined in urban surface soil from Japan, and it was found that it had originated from air particulate matter precipitated from the atmosphere [77].

7. Conclusion

The determination of benzanthrone is mostly done by multi-stage clean-up procedures and characterization by instrumental methods involving MS in addition to HPLC or GC. Owing to the complex analytical procedure, fewer data have been published on the environmental occurrence of benzanthrone and other related polycyclic aromatic ketones than on parent PAHs. It is recommended that any determination of polycyclic compounds should include polycyclic aromatic ketones of molecular masses 230 and 254, since they are always abundant in emissions from combustion sources, and obviously contribute to the total mutagenicity after being derivatized by secondary reactions.

Minor components among polynuclear aromatic compounds and the atmospheric reaction products of primary emissions including benzanthrone form an exceedingly large group of slightly or strongly polar polynuclear aromatic compounds. Multi-step clean-up procedures must be applied, and determination of selected compounds poses a challenge to current efficient analytical methods. An increase in mutagenic activity after atmospheric reactions has been reported [71]. The ratio of benzanthrone and benzo[*a*]pyrene to benzo[*e*]pyrene decreases during atmospheric degradation, and this ratio thus gives an important indication whether such atmospheric reactions have occurred or not.

Profile analysis of polycyclic aromatic ketones must be performed if the ratio of benzanthrone to minor polycyclic aromatic compounds is to be determined. A multi-step clean-up procedure is performed, and PAHs are absent from the profile of polycyclic aromatic ketones obtained by capillary GC [27].

The ratio of benzanthrone to benzo[*e*]pyrene and other PAHs is most rapidly revealed by clean-up on XAD-2 and profile analysis by capillary GC. Quantitative ratios of benzanthrone to all other major polycyclic compounds, including PAHs, are directly available from the chromatogram, whereas some overlap may occur among minor components [13].

HPLC is an efficient method for sample clean-up but cannot provide comprehensive information on related compounds that occur together with benzanthrone at similar concentration. Combined techniques such as GC–MS, LC–GC or LC–MS were all applied successfully and allow direct compound identification without sample clean-up.

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Journal of Chromatography A, 710 (1995) 117–128

JOURNAL OF CHROMATOGRAPHY A

Review

Chromatographic determination of benz[*c*]acridines and related compounds in airborne carcinogens

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Abstract

Carcinogenic benzacridines from air, ground, and water pollution are determined by a variety of chromatographic methods. In all, five different chromatographic modes were in some cases used consecutively.

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1. Introduction

Air pollution has been increasingly associated with the rise of many types of cancer in man. A study of air pollution and the sources of man-made pollutants seem to indicate that there is a disproportionate rise in the incidence of cancers in urban population groups [1,2]. Various polycyclic aromatic hydrocarbons, their alkyl derivatives, and their azaheterocyclic analogues, including benzacridines, are well-known carcinogens.

Determination of benz[*c*]acridine (Fig. 1, **1**) and related compounds (azaarenes) is very important because of their known carcinogenicity. They have been found in many different environ-

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0021-9673/95/$29.00
SSDI 0021-9673(95)00133-6

ments such as urban air, petroleum distillates, coal tar, automobile exhaust, tobacco smoke, and marine and lake sediments. All these sources in the environment are likely contributors to the air pollution.

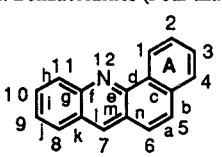
Benz[*c*]acridine (**1**) and benz[*a*]acridine (**2**) have not shown carcinogenic activity on mouse skin, whereas their 7-methyl derivatives show strong carcinogenic activity and many of their other derivatives are carcinogenic as well. The relatively large sizes of alkylated fused-ringed compounds found in some types of air pollution could cause a significant carcinogenic activity in the etiology of lung cancer [3–5]. Organic air pollutants can be subdivided into two regions: urban atmospheres and air pollution source effluents [6]. The quantum-chemical relationship between the structures of benzacridines and their carcinogenicity has recently been discussed [7–12], and the relative toxicological hazards of benzacridines vs. polycyclic aromatic hydrocarbons have been addressed.

Table 1
Molecular formula and molecular mass (*m*/*z*) of benzacridines

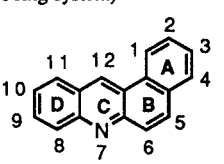
Compound	Mol. formula	Mol. mass (*m*/*z*)
Benzadridines		
Benzadridine	$C_{17}H_{11}N$	229
Monomethylbenzacridine	$C_{18}H_{13}N$	243
Dimethylbenzacridine	$C_{19}H_{15}N$	257
Trimethyllbenzacridine	$C_{20}H_{17}N$	271
Dibenzacridines		
Dibenzacridine	$C_{21}H_{13}N$	279
Monomethyldibenzacridine	$C_{22}H_{15}N$	293

Because of the apparent connection between benzacridines and cancer, chromatographic separation of the isomers of benzacridines was investigated [13–18]. Some of the investigated methodologies are reported below (Fig. 1) (Table 1).

1. Benzacridines (Four azaarene's ring system)

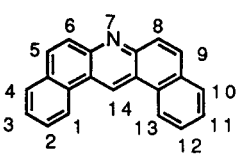


benz[*c*]acridine (**1**)
(1,2-benzacridine)

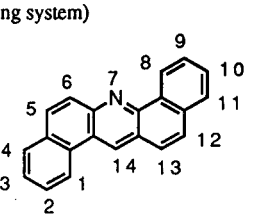


benz[*a*]acridine (**2**)
(3,4-benzacridine)

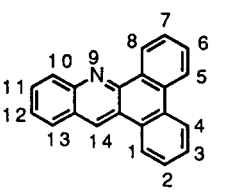
2. Dibenzacridines (Five azaarene's ring system)



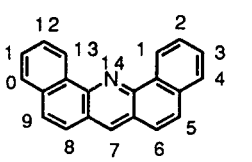
dibenz[*a*,*j*]acridine (**3**)
(1,2,7,8-dibenzacridine;
3,4,6,7-dinaphthacridine;
β-naphthacridine)



dibenz[*a*,*h*]acridine (**4**)
(1,2,5,6-dibenzacridine;
α-N-β-dinaphth-
acridine)



dibenz[*a*,*c*]acridine (**5**)
(1,2,3,4-dibenzacridine;
phenophenanthracridine)



dibenz[*c*,*h*]acridine (**6**)
(3,4,5,6-dibenzacridine;
α-naphthacridine;
α-N-α-dinaphthacridine)

Fig. 1. Benzacridines (four azaarene's ring system) and dibenzacridines (five azaarene's ring system).

2. Paper chromatography

Back to some decades, a dust extract was analyzed by paper chromatography using aqueous solvents [19,20].

3. Column chromatography

Benz[*c*]acridine (**1**), a common contaminant in automotive exhaust, has been found at concentrations of 200 μg/1000 m^3 gas by column chromatography on alumina. This was done by extracting the benz[*c*]acridine with 100 ml of pentane containing increasing amounts of diethyl ether, in increments of 8%, up to and including 64% [21].

The basic fractions in air pollution source effluents were column chromatographed on alumina with 100 ml of solvent mixtures at elution concentrations from 8% to 56% diethyl ether in pentane, 5% to 30% acetone in pentane, 100% acetone, and 100% methanol. Consequently, benz[*c*]acridine (**1**), benz[*a*]acridine (**2**), dibenz[*a,j*]acridine (**3**) and dibenz[*a,h*]acridine (**4**) were determined at concentrations of 60, 18, 1.8 and 0.7 mg/1000 m^3 gas, respectively, via ultraviolet–visible spectrometry [22].

Collected particulates from urban atmospheres polluted by coal-tar-pitch fumes, from the effluent gases emanating from incinerators, and stacks of residential coal-burning furnaces were Soxhlet-extracted with benzene. The basic fraction was chromatographed on an aluminium oxide G column with 100 ml volumes of pentane solutions containing 8, 16, 24, 32, 40, 48 and 56% diethyl ether or 5, 10, 15, 20, 25, 30, 35 and 40% acetone followed by 100 ml volumes of 100% diethyl ether and then 100% methanol. Finally, each fraction of the eluents was separated on thin-layer (250 μm) plates coated with MN-cellulose powder 300 G using dimethylformamide–water (35:65) or with aluminum oxide G using pentane–diethyl ether (9:1). Air pollution source effluents such as a coal-tar-pitch fumes and coal-tar-pitch air samples analyzed by these procedures found benz[*c*]acridine (**1**) and its alkylated derivatives, benz[*a*]acridine (**2**) and its alkylated derivatives, dibenz[*a,j*]acridine (**3**), and dibenz[*a,h*]acridine (**4**) [23].

In 1963, samples of urban airborne particulates from the USA were separated by alumina column chromatography using pentane–diethyl ether (1:1). The samples were followed on cellulose thin-layer chromatography with fluorophotometry using dimethylformamide–water (65:35). Benz[*c*]acridine (**1**), benz[*a*]acridine (**2**), dibenz[*a,j*]acridine (**3**) and dibenz[*a,h*]acridine (**4**) in these urban atmospheres were detected at concentrations of 0.6, 0.2, 0.08 and 0.04 μg/1000 m^3 air, respectively [24].

For the detection of air pollutants from high-boiling petroleum distillates, separation was performed on the non-reactive base fraction using Amberlyst 15 cation-exchange resin. Then the base fractions were dissolved in cyclohexane and were separated by column chromatography with Cellex-P cation-exchange cellulose followed by chromatography on an acidic alumina column. After this eluate was treated, each eluted fraction was separated on a basic alumina column using cyclohexane–methylene chloride (9:1), methylene chloride, or absolute ethanol. Benz[*c*]acridine (**1**), benz[*a*]acridine (**2**) and dibenzacridines in a subfraction were identified by mass spectrometry, fluorescence, and infrared spectrometry [25].

Asphaltenes and coal hydrogenation oils, obtained from Millmerran coal of Australia and New Wakefield of South Africa were separated by established procedures. The basic fraction was separated by Amberlyst 15 cation-exchange resin and fractionated by column chromatography on acidic and then basic alumina. Benz[*a*]acridine (**2**), from hydrogenation oil of New Wakefield coal and benz[*c*]acridine (**1**), dibenz[*a,h*]acridine (**4**), and dibenz[*a,j*]acridine (**3**), in the basic asphaltene fraction from a flash pyrolysis tar of Millmerran coal, were identified by comparison of the fluorescence emission and excitation spectra in both neutral and acid medium with library UV spectra [26]. Benz[*b*]acridine from Australian coal was identified by comparison of the fluorescence excitation spectra

in both neutral and acid medium with Library UV spectra [26]. All of these compounds {benz[*c*]acridine (**1**), benz[*a*]acridine (**2**), dibenz[*a,j*]acridine (**3**) and dibenz[*a,h*]acridine (**4**) except benz[*b*]acridine} are known weak carcinogens [27].

4. Thin-layer chromatography

By using thin-layer chromatography with spectrophotofluorimetry, benz[*c*]acridine (**1**) and its carcinogenic alkylated derivatives, benz[*a*]acridine (**2**) and its carcinogenic alkylated derivatives, carcinogenic dibenz[*a,j*]acridine (**3**), and carcinogenic dibenz[*a,h*]acridine (**4**) have been found in air pollution source effluents [28].

Dibenz[*a,h*]acridine (**4**) was separated from an air sample polluted with coal-tar pitch by cellulose thin-layer chromatography with dimethylformamide–water (35:65) on an alumina column [29].

For the coal-tar pitch basic fraction, benz[*c*]acridine (**1**), benz[*a*]acridine (**2**) and dibenz[*a,h*]acridine (**4**) were found by two-dimensional thin-layer chromatography using two solvent systems such as cyclohexane–ethyl acetate (19:1) and dimethylformamide–water (35:65) on alumina–cellulose (2:1). Benz[*c*]acridine (**1**) was also detected by using two-dimensional thin-layer chromatography using solvent mixtures such as pentane and dimethylformamide–water (35:65) on alumina–cellulose (2:1), benz[*c*]acridine (**1**) was also detected from the basic benzene-soluble fraction of urban airborne particulates [30].

Benz[*c*]acridine (**1**) was also detected in a sample of air pollution source effluent through a Soxhlet extraction procedure with benzene–dimethylamine (4:1). The extracted residue was separated on a one-dimensional thin-layer alumina plate using pentane–diethyl ether (19:1) or on a two-dimensional thin-layer alumina plate using pentane–diethyl ether (19:1) and dimethylformamide–water (35:65), followed either by direct spectrophotofluorimetric analysis, elution and fluorimetric analysis, or by elution and filter spectrophotofluorimetric analysis [31].

Benz[*c*]acridine (**1**) also has been reported in urban atmospheres by Sawicki et al. [32].

These samples of urban and air pollution source effluents were Soxhlet-extracted with benzene–diethylamine (4:1). The treated residue was dissolved in methylene chloride and then developed on an alumina thin-layer plate using pentane–diethyl ether (19:1). Each spot adjacent to the standard samples was scraped off the plate. After treatment, the residue was dissolved in pentane–trifluoroacetic acid (50:1) and detected at $\lambda_{ex.}$ 282 nm/$\lambda_{em.}$ 475 nm by spectrophotofluorimetry. Benz[*c*]acridine (**1**) was found in the benzene-soluble fraction of urban airborne particulates and the detection limit of benz[*c*]acridine (**1**) in this study was shown to be 40 ng/ml [33].

Composite residues of benzene extracts of airborne particulates collected for 6 months in 1966 were dissolved in dichloromethane. The dichloromethane solution was developed by thin-layer chromatography on aluminum oxide G and silica gel G (1:1) using pentane–diethyl ether (19:1). Each spot was observed under a 360 nm light source, and the fluorescence areas of the standards and corresponding areas of the benzene-soluble sample were marked. Benz[*c*]acridine (**1**) in the sample area and the benz[*c*]acridine (**1**) standard were measured at $\lambda_{ex.}$ 290 nm/$\lambda_{em.}$ 470 nm by spectrophotofluorimetry. For example, benz[*c*]acridine (**1**) from the benzene-soluble fraction of suspended particulates collected in Los Angeles, Kansas City and New York from January to June 1966 were measured at concentrations of 0.2, 0.2 and 0.3 μg/1000 m^3 air, respectively. The city with the highest concentrations of benz[*c*]acridine (**1**) among 51 cities under investigation in the USA was Indianapolis, which had concentration levels of 1.5 μg/1000 m^3 air. Phoenix showed no detectable levels of this type of carcinogen. The concentrations of benz[*c*]acridine (**1**) in the 51 cities ranged from none detected to 1.5 μg/1000 m^3 air [34].

A tar fraction was collected from the air of a roadway tunnel and was Soxhlet-extracted with benzene–ethanol (3:1) and dissolved in benzene. The benzene solution was separated by two-

dimensional dual-band thin-layer chromatography coated with alumina G–Kieselguhr G (2:1) and 26% acetylated cellulose. Dibenz[*a,h*]acridine (**4**), 7,9-dimethylbenz[*c*]acridine and 7,10-dimethylbenz[*c*]acridine from gasoline powered vehicles were found at concentrations of 6.5, $1.8 \cdot 10^{-1}$, 1.2 μg/h, and $5.4 \cdot 10^{-1}$, 2.1, 6.0 μg/h, respectively. The average emission rate (μg/h) per vehicle of three benz[*c*]acridines from diesel vehicles was found to be higher than from gasoline engine vehicles. This was especially true of the average emission rates of 7,9-dimethylbenz[*c*]acridine and 7,10-dimethylbenz[*c*]acridine [35].

Pollution of groundwater and river water was investigated in Beijing, China. After partition separation of 12, 46, 70, and 10–70 m deep groundwater and river water, each basic fraction was separated by silica gel G thin-layer chromatography using *n*-pentane–ethyl acetate (19:1) and identified by mass spectrometry. Benz[*c*]acridine (**1**) was quantitatively determined by fluorometry at 384 nm. The highest concentration of benz[*c*]acridine (**1**) at 0.36 μg/l was found in 70 m deep groundwater. Other depths of groundwater and river water showed concentrations ranging from 0.01 to 0.193 μg/l. Benz[*a*]acridine (**2**) in the waters was determined qualitatively [36].

5. High-performance liquid chromatography

Azaarenes present in urban atmospheres have been analyzed by high-performance liquid chromatography (HPLC) coupled with on-line fluorescence detection after a pre-separation of the azaarene fraction by one-dimensional dual-band thin-layer chromatography. The HPLC column was a Zorbax ODS coupled with an Unisil ODS guard column with acetonitrile–water (7:3) as the mobile phase. The HPLC fraction was identified by comparison with retention times and fluorescence emission spectra of authentic azaarenes. Benzacridines from atmospheric particulate matter were analyzed in Tokyo in April 1983. Benz[*a*]acridine (**2**), dibenz[*a,j*]acridine (**3**), dibenz[*a,h*]acridine (**4**), and dibenz[*a,c*]acridine (**5**) were found at concentrations of 3.3, $4.3 \cdot 10^{-1}$, $3.6 \cdot 10^{-1}$, and $2.9 \cdot 10^{-1}$ μg/g of particulates, respectively [37].

A fast direct high-performance liquid chromatography (HPLC) method without pre-separation for determining azaarenes in atmospheric aerosols of Paris, France was achieved with high sensitivity. First, the samples were Soxhlet-extracted by dichloromethane–cyclohexane. The extract was separated by HPLC and fluorimetrically detected at variable wavelengths ($\lambda_{em.}$ 313–375 nm, $\lambda_{ex.}$ 366–425 nm). Picogram detection levels were obtained in the most favorable case. The HPLC column was a 5-m Vydac glass, 5 μm 201TP silica gel column using gradient solvents of 65–70% methanol with water and 70–100% methanol. Seven benzacridines have been determined at concentrations ranging from 0.49 ng/m^3 to 6.10 ng/m^3 in atmospheric aerosols from diesel motors and from 0.01 ng/m^3 to 0.19 ng/m^3 in atmospheric aerosol from gasoline motors, respectively. In this case, the detection limits of benz[*c*]acridine (**1**) and benz[*a*]acridine (**2**) were both 4 pg/unit [38] (Table 2).

Azaarenes have been Soxhlet-extracted from cigarette smoke condensates on filter tips using chlorobenzene. The extract was pre-separated by liquid–liquid partition with a cation-exchange SP-Sephadex C25 glass column. Finally, the fractions were separated by HPLC with Cosmosil 5C18-AR or a reversed-phase ODS column with acetonitrile–water (3:1) as the mobile phase. Benz[*c*]acridine (**1**) and 9-methylbenz[*c*]acridine in cigarette filter tips were measured at concentrations of 0.37 ng/tip and 0.11 ng/tip, respectively. The detection limit was determined to be 5 pg/tip [39].

Creosote oils were treated with liquid–liquid partition. The basic portion was transferred to a Sephadex LH 20 column and followed by a SP-Sephadex C25 cation-exchange column. The pre-separated basic fraction was separated by HPLC with a pre-packed Ultron S C_{18} column with acetonitrile–water (7:3) as the mobile phase. The sub-fractions were again separated by HPLC with a TSK gel 120T reversed-phase column and followed by thin-layer chromatography (HPTLC) on a pre-coated RP-18 column with an

Table 2
Benzacridines in an atmospheric aerosols

Compound	Source	
	Diesel (ng/m^3)	Petrol (ng/m^3)
Benzacridines		
Benz[*c*]acridine (**1**)	5.80	0.07
Benz[*a*]acridine (**2**)	6.10 ± 0.5	0.19
2-Methylbenz[*a*]acridine	1.12	0.01
7-Methylbenz[*a*]acridine	0.49	0.01
Dibenzacridines		
Dibenz[*a,j*]acridine (**3**)	0.84 ± 0.8	
Dibenz[*a,h*]acridine (**4**)	0.82	
Dibenz[*c,h*]acridine (**6**)	0.72	

acetonitrile–chloroform (4:1) mobile phase. The basic fraction was scraped from TLC plate and measured by fluorescence spectrometry. The basic sample was analyzed by gas chromatography on a fused-silica capillary column with bound OV-1 equipped with a thermionic specific detector (TSD). The identification of azaarenes in the creosote oils was achieved by gas chromatography–mass spectrometry (GC–MS) connected with a mass selective detector. Benz[*c*]acridine (**1**), 9-methylbenz[*c*]acridine, 10-methylbenz[*c*]acridine in creosote oils have been detected at concentrations of 192.7, 7.7 and 18.4 μg/g, respectively [40].

6. Gas–liquid chromatography

Sawicki found benz[*c*]acridine (**1**) and dibenz[*a,h*]acridine (**4**) as a composite average in American urban air in 1963 at 1 μg/1000 m^3 and $2 \cdot 10^{-1}$ μg/1000 m^3, respectively [41]. Four-fused ring benzacridines, benz[*c*]acridine (**1**) and its related carcinogenic methylated benz[*c*]acridines, and benz[*a*]acridine (**2**) and its related carcinogenic methylated benz[*a*]acridines were all found in urban American atmospheres [3,41]. Additionally, five-fused ring benzacridines, carcinogenic dibenz[*a,h*]acridine (**4**), and dibenz[*a,j*]acridine (**3**) with its related alkylated carcinogenic dibenz[*a,j*]acridines have been found in the same cities [3,41].

Dust samples were collected from the air by means of an high-volume Staplex pump. The pump was situated about 15 meters above the ground. Samples of 0.3–0.5 g of dust collected from 1000 to 2000 m^3 air were Soxhlet-extracted with cyclohexane. After extraction and chemical treatments, the basic samples were analyzed by GC with a glass capillary column coated with SE-52 at 180°C, with flame ionization or electron-capture detection. Consequently, benz[*c*]acridine (**1**), 10-methylbenz[*c*]acridine, 10-methylbenz[*a*]acridine, 1,10-dimethylbenz[*a*]acridine and 8,10-dimethylbenz[*c*]acridine were found in these atmospheric dust extracts [20].

Tobacco was pyrolyzed at 850°C in an atmosphere of nitrogen. The various fractions were then analyzed by GC on a stainless-steel column containing 15% Carbowax on Chromosorb W, equipped with a flame ionization detector. Thin-layer chromatography on each basic fraction extract was carried out on silica gel G using ethyl acetate–methyl alcohol–formic acid (80:10:10) and benzene–methyl alcohol (95:5). Benzacridines have been found in tobacco of the pyrolyzates and tobacco smoke condensate. Dibenzacridines could not be found in this study [42]. However, Van Duuren et al. reported that dibenzacridines were found in tobacco smoke, in

nicotine and pyridine pyrolysates [43]. Dibenzacridines found also in nicotine itself.

Airborne particulate matter was analyzed in buildings in a residential area of Antwerp, Belgium. Samples were collected on Whatman GFA glass fiber filters. After pretreatment, a benzene-soluble basic fraction was separated by GC on a 5-m packed column containing 4% Dexsil 300 on Gas Chrom Q 100–120 mesh support. The determinations were carried out with a Finnigan Model 3100 gas chromatograph–mass spectrometer. These samples showed azabenz[*a*]anthracenes containing four isomers of molecular mass 229 {benz[*c*]acridine (**1**) and benz[*a*]acridine (**2**)}, four isomers of molecular mass 243 (including methylbenzacridines), and two isomers of molecular mass 279 {including dibenz[*a,h*]acridine (**2**) and dibenz[*a,j*]acridine (**3**)}. These were detected at concentrations of 16, 3, and 4 ppm, respectively [44].

A raw shale oil was extracted and separated into five complex fractions. These were analyzed by GC–MS. The raw shale oil and a basic fraction were found to be mutagenic against the *Salmonella typhimurium* test strains such as TA98 and TA100. Mutagenicity was dependent on metabolic activation by microsomal (S9) enzyme reactions which form active mutagens from premutagenic precursors such as metabolic activation reactions. In this regard, both inhibition and inactivation of S9 enzymes are possibilities that must be considered. The effect of a neutral arene's fraction on the mutagenicity of 7,9-dimethylbenz[*c*]acridine was determined by the Ames assay. Premutagen, 7,9-dimethylbenz-[*c*]acridine, requiring metabolic activation was added to the basic and neutral arene fractions, and the numbers of revertants obtained in the presence of the fractions were compared with mutation induced by 7,9-dimethylbenz[*c*]acridine alone. The mutagenicity of 25 μg/plate of 7,9-dimethylbenz[*c*]acridine as a function of increasing arene concentration was inhibited in much the same way as observed for benzo[*a*]pyrene and dibenzanthracene. On the other hand, the response curve observed for the concentrations from 10 to 50 μg/plate of 7,9-dimethylbenz[*c*]acridine was similar in the levels of maximum response in the presence or absence of the basic fraction. However, the rates of mutagenesis were somewhat reduced by the basic fractions. This fact suggests that a fraction from the raw shale oil could also contain dimethylbenz[*c*]acridines in small amounts [45].

Additionally, the relationship between a basic fraction and carcinogenicity by the Ames test has been shown by Pelroy et al. [46]. The raw shale oil was fractionated into five sub-fractions. Both basic and arene subfractions were most mutagenic in *S. typhimurium* strains TA98 and TA100. 7,9-Dimethylbenz[*c*]acridine showed more of the mutagenicity in the presence of shale oil than did benzo[*a*]pyrene. The basic shale oil fraction was also toxic to *S. typhimurium* sTA100 over the same concentration range required for mutagenesis and this toxicity was enhanced by metabolic activation [46].

A sub-fraction of ether-soluble bases from petroleum crude oils and coal- and shale-derived petroleum substitutes was separated first on a basic alumina column using benzene. The extracted sample was eluted first with benzene and then ethanol. After the ethanol was removed, the residue was dissolved in 2-propanol then transferred to a Sephadex LH-20 column first using 2-propanol and then acetone as the mobile phase. Each elution sample was separated by GC on 3% Dexsil 400 and detected with MS. Benzacridine was found in an acetone sub-fraction of the petroleum substitutes [47].

The extract from coal liquefaction products have been analyzed for benzacridine molecules. Coupled GC [with flame ionization detection (FID) and nitrogen-selective alkali-flame detection (AFD)–mass spectrometry (GC–MS)] before and after derivatization with dimethylformamide dimethylacetal (Methyl-8) was utilized. Splitless injections of 0.2 μl were made onto a 40-m SGE glass support-coated open tubular (SCOT) capillary column which was coated with SP-2250 (methyl silicone–phenyl silicone, 1:1) stationary phase. Hydrogen carrier gas was used for FID analyses and helium for AFD analyses. The basic fraction sample was analyzed by GC–FID using dibenzyl as an internal standard. From these studies, benz[*a*]acridine (**2**) with a molecu-

lar mass 229 was found at a concentration of 10 ppm in a basic fraction of the coal product [48].

Groundwater samples obtained from a well are a mixture of oily-tar and aqueous phases. A fluid sample was obtained from well W13 located 205 m south of the site of the former coal-tar distillation plant in St. Louis Park, MN, USA. A composite sample was allowed to stand undisturbed in a separatory funnel so that the two phases were gravity separated. The lower black, oily-tar phase with the higher density was separated from the brown, aqueous phase by centrifugation at 4000 rpm in a high-speed centrifuge and filtered under vacuum through a glass fiber filter (Gelman, Type A–E). Organic bases were isolated from each phase by pH adjustment and solvent extraction. Organic bases in the oily-tar phase were further purified by micro-column adsorption chromatography with neutral alumina. The separation and identification of the organic bases in each phase were achieved by automated capillary GC–MS and probe distillation–high resolution mass spectrometry (PD–HRMS) techniques. The gas chromatograph was equipped with a wall-coated open tubular, fused-silica capillary column coated with SE-54. By a reconstructed ion chromatogram (RIC) of the base fraction of the oily-tar phase from the groundwater, two isomers of benzacridine and two isomers of dibenzacridine were detected. Further analysis of the organic bases in the oily-tar phase of groundwater by automated GC–MS identified benzacridine with molecular mass 229, its monomethylated derivative with molecular mass 243, its dimethylated derivative with molecular mass 257, and three isomers of dibenzacridine with molecular mass 279 and one monomethylated derivative with molecular mass 293 [49].

The polycyclic aromatic compound fraction from diesel fuels was isolated on a silica gel column. Filter paper exposed to diesel exhaust isolated the polycyclic aromatic compound fraction which was then Soxhlet-extracted using benzene–methanol. After appropriate dilution, the samples of the polycyclic aromatic compound fraction were spiked internally with standards for quantification purposes. The samples were analysed on a gas chromatograph, which employed a novel three-way effluent splitter thus enabling simultaneous parallel detection of the standards by means of FID, and nitrogen selective (NPD), and sulphur selective (SSD) detectors. The instrument was equipped with a cold on-column injector and a silica capillary column, coated with cross-linked SE-54. Benz[*c*]acridine (**1**) and benz[*a*]acridine (**2**) were determined at concentrations lower than 1 ppm in both diesel fuels and gas oils [50].

Samples from an anthracene oil, a coke oven pitch and a low-temperature coal tar were obtained as unfractionated materials. The bases were separated on SGE glass support-coated open tubular (SCOT) capillary columns coated with an SP-2250 (50% methylphenyl silicone–50% phenyl silicone) stationary phase, dual gas chromatography–alkali flame detection (AFD) and gas chromatography–flame ionization detection (FID). Consequently, benz[*a*]acridine (**2**) in anthracene oil, coke-oven pitch and Gray-King tar in coal tar products was detected by GC–AFD at concentrations of 400, 730 and 84 ppm, respectively. Additionally, identification was determined by drawing single-ion chromatograms for normal m/z values corresponding to possible azaarenes [51].

Basic effluents of anthracene oil of coal tar products were separated by aqueous acid extraction of dichloromethane, cation-exchange chromatography on Amberlyst 15, liquid chromatography on a polar, bonded-phase silica OPN/Porasil C Durapak and organometallic coordination chromatography on anhydrous $FeCl_3$/Chromosorb W. The basic fraction was analyzed by GC–FID. Splitless injections of 0.2 μl were made onto a 40-m SGE glass support-coated open tubular (SCOT) capillary column coated with an SP-2250 (50% methylsilicone–50% phenylsilicone) stationary phase, using hydrogen as the carrier gas. For the identification of azaarenes in the basic fractions, GC–MS was used. The chromatograph was interfaced with a Kratos MS-30 double-beam mass spectrometer/DS-55 data system. Splitless injections of 1–5 μl were made on a 33-m SGE SP-2250 glass SCOT capillary column under chromatographic condi-

tions similar to those used for the GC–FID analyses. Benz[*a*]acridine (**2**) with *m/z* 229 at concentrations of 363, 349, 418 (a neutral nitrogen fraction separated by hexane–15% benzene), and 473 ppm in basic fractions from an anthracene oil was detected by aqueous acid extraction, cation-exchange chromatography, liquid chromatography on OPN/Porasil C Durapak and co-ordination chromatography on $FeCl_3$/Chromosorb W, respectively [52].

Anthracene oils were separated by liquid chromatography on a Waters 80–100 mesh OPN/Porasil Durapak, with a glass Whatman 'MultiSystem' chromatographic column. The fraction samples were analyzed by GC using a Perkin-Elmer F-17 chromatograph fitted with a flame-ionization detector and a nitrogen-selective alkali flame detector. Splitless injections of 0.2 μl were made onto a 40-m SGE glass SCOT capillary column coated with SP-2250 (50% methyl silicone–50% phenyl silicone) stationary phase. The neutral fraction was analysed by GC–FID and benz[*a*]acridine (**2**) in the neutral nitrogen fraction (hexane–15% benzene eluate) was at a concentration of 418 ppm [53].

A sample of a solvent refined coal material (SRC II) was obtained from the processing of Pawhatan Mine No. 5 coal on Process Development Unit P-99 operated by Gulf Science and Technology Co. at Harmarville, PA, USA. The material was fractionally distilled to produce the following five boiling point cuts: 300–700, 700–750, 750–800, 800–850 and 850°F + bottoms. The five distillate cuts were fractionated by an adsorption alumina column chromatography to obtain arene and azaarene fractions. Then, the azaarene fraction was identified by a fused-silica DB-5 capillary column with GC–FID detection, in conjunction with a HP5982A capillary gas chromatograph mass spectrometer. Benz[*c*]acridine (**1**) of the three SRC II boiling point cuts 700–750, 750–800 and 800–850°F has been found at concentrations of 578, 1237 and 2357 ppm, respectively [54].

Several integrated two-stage coal liquefaction (ITSL) samples were collected from ITSL process plant at C.E. Lummus in New Brunswick, NJ, USA. The samples were fractionated by alumina column chromatography. Further chromatographic separation isolated azaarene fractions. High-resolution gas chromatography using a 25-m fused-silica capillary column coated with DB-5 and FID, coupled with a mass spectrometer, was used to determine the concentrations of the azaarene fractions of the ITSL. Concentrations in parts per thousand (ppt) of three benzacridine fractions, benz[*c*]acridine (**1**), 7,10-dimethylbenz[*c*]acridine and dibenz[*a,j*]acridine (**3**) (or dibenzo[*a,j*]carbazole or an isomer), of 32 azaarenes measured in azaarene fractions of ITSL materials were found at concentrations ranging from 1.3 to 2.6, 0.10 to 5.8 and 0.04 to 0.63 ppt, respectively [55].

Organic pollutants from airborne particulates in the Taiyuan area of China were analyzed on a 25-m flexible quartz capillary Dexsil-300 column-gas chromatograph. Benz[*c*]acridine (**1**) was determined at concentration of 33.51 ng/m^3 and showed carcinogenicity in the Ames test [56].

A river sediment sample was Soxhlet-extracted by using dichloromethane and then the extract was pre-separated onto a Sephadex LH-20 column using 2-propanol. The azaarene fraction was analysed on a fused-silica capillary OV-101 glass column with GC–FID and a coupled mass spectrometer. Benz[*c*]acridine (**1**), benz[*a*]acridine (**2**), dibenz[*a,h*]acridine (**4**) and dibenz[*a,c*]acridine (**5**) were qualitatively detected in these sediment samples [57].

Sediments collected in Eagle Harbor, Puget Sound, WA, USA and commercial creosotes were analyzed for azaarenes by capillary GC with NPD, FID, and MS. The organic sediment extracts and the creosotes were fractionated by silica gel/alumina column with methanol–methylene chloride (1:4) as the mobile phase. The basic fractions were separated on a gas chromatograph with a fused-silica gel capillary column bonded with SE-54, equipped with a thermionic-specific (nitrogen-phosphorus) detector. The bonded-phase SE-54 fused-silica gel capillary column was interfaced to a Finnigan 3200 MS. Concentrations were confirmed by comparison with spectra obtained from the standard samples analyzed under the identical conditions. Benzacridine and all isomers of molecu-

lar mass 229, and methylbenzacridine and all isomers of molecular mass 243 in the sediment were measured at concentrations ranging from 7.7 to 8.5 μg/g, and from 1.0 to 1.4 μg/g, respectively. Benzacridine and all isomers of molecular mass 229, and methylbenzacridine and all isomers of molecular mass 243 in creosote were measured at concentrations ranging from 600 to 4900 μg/g and from 71 to 110 μg/g, respectively [58].

Azaarenes from samples of airborne particulate matter in Copenhagen collected during 5 years were extracted by toluene with an ultrasonic treatment. Isolated basic azaarenes were extracted twice with 8.25 *M* phosphoric acid. Both phosphoric acid phases were combined and adjusted to about pH 14 with 11 *M* potassium hydroxide. The azaarenes were extracted with dichloromethane and determined by GC with a fused-silica column Ultra-1 equipped with a nitrogen-sensitive detector (NPD). Air samples were collected in February from 1976 to 1982 in suburban, residential areas and busy streets of Copenhagen. Benz[*a*]acridine (**2**), dibenz[*a,j*]acridine (**3**) and dibenz[*a,h*]acridine (**4**) were detected at 0.09, 0.2, 0.2 ng/m^3 in the residential area and 0.17, 0.07, 0.08 ng/m^3 in the busy street area, respectively [59].

Particles and semi-volatiles in main- and sidestream smoke of cigarettes were collected. The separation of basic fractions was achieved by a S-Sepharose ion exchange chromatography, Sephadex LH20, and then again an S-Sepharose. The fraction was then separated by gas chromatography on a fused-silica capillary column coated with SE-54 and interfaced with a nitrogen-flame ionization detector (N-FID). When the chromatograms were compared with the standard samples, benz[*c*]acridine (**1**) in a sidestream smoke was found [60].

Air pollution particulates collected in Calcutta, India, were consecutively extracted with benzene and methanol. The samples were separated by gas chromatography on a fused-silica 25-m capillary column coated with Sil 5 and coupled with a mass spectrometer. Benz[*c*]acridine (**1**), and an isomer mixture of dibenz[*a,j*]acridine (**3**) and dibenz[*a,h*]acridine (**4**) were at concentrations ranging from 1.06 ng/m^3 to 4.76 ng/m^3 and from 7.27 ng/m^3 to 13.16 ng/m^3, respectively. The concentrations of three azaarenes found in Calcutta during January–February 1984 were higher than the results from Wilrijk, Belgium [61].

7. Conclusions

Different techniques are available and have been used for the chromatographic determination of benzacridines. The methods discussed in this review include paper chromatography, column chromatography, thin-layer chromatography, high-performance liquid chromatography and gas–liquid chromatography.

Paper chromatography, although used some decades ago, is no longer one of the major techniques used for quantitative determination of benzacridines. In the case of column chromatography, alumina (adsorption chromatography) and ion exchange resins were employed.

Thin-layer chromatography (on alumina, alumina–cellulose, alumina–silica gel, etc.) is a very convenient and rapid technique used in the determination of benzacridines in polluted air and in ground and river water.

High-performance liquid chromatography has been successfully used in Tokyo and Paris for analysis of urban atmospheres as well as in other situations.

Finally, gas–liquid chromatography, as a convenient, and highly successful method, has been widely used as the principal method of analysis in numerous publications devoted to air pollution (urban atmospheres), tobacco, cigarette smoke, shale oils, petroleum, diesel fuel, coal liquefaction products, coal tar, groundwater, etc.

All these methods are being constantly improved upon, with various modifications leading to a higher accuracy and reliability of results.

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Journal of Chromatography A, 710 (1995) 129–137

JOURNAL OF CHROMATOGRAPHY A

Monitoring polycyclic aromatic hydrocarbons in waste gases

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Abstract

A fast off-line monitoring system based on supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) is introduced that allows the quantification of polycyclic aromatic hydrocarbons (PAHs) in the crude gas of fuel-oil-stoked industrial boiler plants. In this paper we present a comparison of our recently developed monitoring system with a standard method of a reference laboratory. Samples were taken according to VDI-3873 (dilution method) on polyurethane foam (PUF) plugs. The PUF plugs were extracted with toluene-modified carbon dioxide within 60 min. The extracts were analysed using packed column SFC with fluorescence detection.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) form a large class of organic compounds, which is of great environmental concern. Polynuclear aromatics are toxic and many of them are known to be carcinogenic and/or mutagenic [1]. They are produced through incomplete combustion of organic matter and therefore may be present in any kind of waste gas. This leads to the necessity of monitoring PAH-emissions of various combustion plants in order to avoid pollution of the environment.

PAHs occur both in the vapour phase and adsorbed on particulate matter. The analytical process, especially the sampling method, has to take this into account. Existing methods use for example paraffined fibre glass filters for collection of all compounds [2]. An alternative is deposition of particulate phase PAHs on fibre glass filters with subsequent collection of vapour phase PAHs using solid adsorbents, for example polyurethane foam.

The extraction of the analytes usually is accomplished with organic solvents, in most cases using a Soxhlet extractor. One of the drawbacks of liquid extractions is the large amount of harmful organic solvents which have to be used. Another problem is the relatively high extraction time, which may exceed 24 h. Following the liquid extraction, several time-consuming clean-up steps have to be performed. The separation and quantification is usually accomplished with high-performance liquid chromatography (HPLC). This method requires organic solvents as well and the total run time, including an equilibration step, is about 60 min. An alternative for HPLC is gas chromatography with flame ionisation detection (FID). The drawback of this method, especially for real-world samples, is mainly the missing selectivity of FID.

In recent years a lot of effort was put into the development of solvent reduced analytical techniques [3,4]. Ideal substitutes for harmful organic solvents are non-toxic and inflammable

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0021-9673/95/$09.50
SSDI 0021-9673(95)00379-7

supercritical fluids like carbon dioxide. Conventional liquid extraction methods can be replaced by supercritical fluid extraction (SFE). SFE allows one to separate the components from the matrix and to concentrate and clean them simultaneously [5,6]. Hawthorne et al. [7] and Wright et al. [8] already used supercritical fluids for the extraction of polyurethane foams. Supercritical fluid chromatography (SFC) is an attractive alternative for many HPLC applications [9]. For the analysis of PAHs it was already used by Sandra et al. [10] and Wenclawiak and Hees [11]. Furthermore the combination of both SFE and SFC may allow on-site extraction and analysis.

For these reasons the aim of the present work is the development of a fast and solvent-free PAH monitoring system based on SFE and SFC methods. In a further stage of development this monitoring system should allow on-site measurements and thus quasi-continuous emission monitoring of combustion plants.

In this paper we present a comparison of our recently developed monitoring system with a standard method of a reference laboratory.

2. Experimental

2.1. SFE–SFC monitoring system

Sampling system

The sampling procedure of the new monitoring system is similar to that described in guideline VDI 3873 [2]. This method relates both to gaseous and to particle-attached PAHs, which are quantitatively collected on a silicone-bonded fibre glass filter impregnated with paraffin oil. For the collection of lower-volatility PAHs a solid adsorbent can be linked downstream. The sample gas is diluted with air and cooled to temperatures below 50°C. For the experiments described herein the sampling device was modified. A disk of fibre glass filters (5 cm diameter, Schleicher und Schuell, Germany) and three polyurethane foam (PUF) plugs (5 cm diameter, K. Ziemer, Germany) were used instead of paraffin-impregnated fibre glass filters. The polyurethane foam plugs were precleaned using SFE. The total sample volume was about 1.4 m^3 (see Table 1).

Supercritical fluid extraction

The extractions were carried out using a Dionex SFE system (SFE-703) equipped with a Dionex SFE-703M modifier module. Extraction cells (10 ml) (Keystone Scientific) and Dionex linear restrictors (wafer restrictors, flow-rates ca. 1200 ml/min of gaseous CO_2) were used. The optimised extraction conditions were as follows: extraction fluid CO_2–10% toluene, pressure 40 MPa, oven temperature 130°C, restrictor temperature 150°C. For analyte collection a modified dual chamber trapping vial (solid–liquid collection) with an integrated clean-up system (ICUS) was used [5,6]. This clean-up system consists of

Table 1
Operating conditions for crude gas sampling (date 29.06.1994)

	Sample No.		
	1	2	3
Sampling time from:	14:00	15:15	16:30
to:	15:00	16:15	17:30
Crude gas temperature (K)	462	464	465
Sample volume ($V_{p0,T0}$) (m^3)	4.56	4.10	4.50
Temperature at the PU-foam (°C)	42	42	42
Sample volume ($V_{p0,T0}$)[a] (m^3)	1.42	1.45	1.37
Temperature at the PUF[a] (°C)	40	40	39

[a] Sampling for the SFE–SFC monitoring system.

silica gel and *n*-hexane. For all supercritical fluid extractions no further clean-up was performed. The solvent was evaporated under a gentle stream of nitrogen. For the preliminary investigations acetonitrile was added to the sample prior to HPLC analysis. In the comparison studies methanol–water (90:10) instead of acetonitrile was used.

HPLC analysis

For HPLC analysis a HP Series 1050 liquid chromatograph (Hewlett Packard) with autosampler, quaternary pump, degasser, HP 1046A programmable fluorescence detector and HP ChemStation for data analysis was used. The PAHs were separated on a Bakerbond PAH 16-Plus column (250 × 3 mm I.D.) with a 20-mm precolumn at a column temperature of 30°C. Acetonitrile and water were used as the mobile phase with a flow-rate of 0.5 ml/min. For identification the retention times were compared and for quantification an external calibration with the SRM 1647c standard in acetonitrile (Promochem, Germany) was performed.

SFC system

The SFC experiments were performed using a Dionex series 600-D system. A multiple-wavelength detector Model UVIS-206 and a fluorescence detector Model FLUOR LC304, both from Linear Instruments, were connected in series. The injection system consisted of two Valco injection valves, one of them equipped with a 20-μl external sample loop, which is described in detail elsewhere [12]. The SFC column was packed with Envisil (Dr. Molnar, Berlin, Germany) by Grom, Herrenberg (Envisil, C_{18}, 200 × 1 mm I.D., 5 μm, 300 Å). Connections between column and detector cells were made of fused-silica capillaries, 50 μm I.D. Data acquisition was done using Linear Instruments UVIS 206 PC Software (version 2.1) and Dionex AI-450 SFC chromatography software (version 3.32). SFC-grade carbon dioxide was purchased from Air Products (Hattingen, Germany). The test mixture (Polyaromatic Hydrocarbons Mixture) was obtained from Sigma-Aldrich and methanol for HPLC was purchased from Baker.

For UV detection a commercially available flow cell (volume 250 nl) was employed. The flow cell for fluorescence detection was built in-house. It is made of a short piece of fused-silica tubing (320 μm I.D.), from which a small section (ca. 6 mm) of polyimide coating was removed. Into one end a fused-silica capillary of 50 μm I.D., which is connected to the UV detector, was inserted. For pressure restriction a fused-silica capillary of 25 μm I.D. (total length ca. 70 cm) was placed at the other end. The resulting cell volume is approximately 500 nl. The mounting of the detector cell is made of aluminium and resembles the commercially available mounting of the HPLC cell. It is possible to cool the cell mounting using a circulating pump. An additional device allows adjustment of the detector cell in the focal path.

All SFC experiments were carried out using pure carbon dioxide as the mobile phase. The separations were performed employing a density gradient at 80°C as follows: 3 min at 0.15 g/ml, programmed to 0.35 g/ml at 1 g ml^{-1} min^{-1}, then programmed to 0.78 g/ml at 0.015 g ml^{-1} min^{-1}, then held at 0.78 g/ml for 8 min.

2.2. Standardised method

Sampling system

The sampling procedure for the reference measurements is following guideline VDI 3873 "Measurement of PAHs in stationary industrial plants — dilution method — gas chromatographic determination" [2] with minor modifications. Fibre glass filters and polyurethane foam plugs (25 cm diameter) took the place of paraffined fibre glass filters. The total sample volume was about 4.5 m^3 (see Table 1).

Sample preparation and analysis

For validation studies the entire filters and PUF plugs were extracted with toluene under reflux. After extraction a clean-up procedure was performed and for separation and quantification gas chromatography with FID was used [2].

3. Results and discussion

3.1. Development of a SFE method for PAH extraction from polyurethane foam

In a first step the optimum extraction conditions had to be determined. In this case (SFE of adsorbents) spike experiments were assumed to give extraction conditions that are transferable to real-world samples. An aliquot of 100 μl of a PAH solution in toluene (200 ng of each component) was spiked on the PUF plugs. After evaporation of the solvent the PUF plug was placed in the extraction cell. The cell was then connected to the SFE system in such a way that the PAHs had to be carried through the whole extraction cell and with this through the whole length of the PUF plug. The following extraction parameters were optimised: modifier and modifier concentration, fluid flow, pressure and oven temperature. In Table 2 the SFE recoveries using the optimised extraction conditions (CO_2 modified with 10% toluene, pressure 40 MPa, oven temperature 130°C, restrictor temperature 150°C, flow ca. 1200 ml/min) are shown. The total extraction time was 60 min. After an extraction time of half an hour the trapping vials were replaced and the extraction was continued for another 30 min. Each vial was analysed separately by HPLC with fluorescence detection. The lower mass PAHs are extracted within 30 min. For the other substances 60 min are necessary for quantitative recoveries.

During the development of a new SFE method it is very important to test the extraction conditions using real-world samples. Therefore three samples were taken in the crude gas of a sawdust-stoked boiler. Because a simultaneous sampling was not possible, the samples were taken successively. The sampling filters and PUF plugs were analysed in our laboratory. In order to compare the extraction results of the SFE method with conventional techniques, one of the samples was extracted using a Soxhlet apparatus. With the integrated clean-up system (ICUS) a further clean-up process in SFE becomes un-

Table 2
Percent recoveries of spiked PUF samples

	Recovery (%)	
	1st extraction	2nd extraction
Naphthalene	102	n.d.
Acenaphthene	91	n.d.
Fluorene	93	n.d.
Phenanthrene	98	n.d.
Anthracene	102	n.d.
Fluoranthene	105	n.d.
Pyrene	107	n.d.
Benz[*a*]anthracene	105	n.d.
Chrysene	100	n.d.
Benzo[*b*]fluoranthene	102	n.d.
Benzo[*k*]fluoranthene	100	1
Benzo[*a*]pyrene	101	4
Dibenz[*a,h*]anthracene	99	6
Benzo[*ghi*]perylene	94	11
Indeno[1,2,3-*cd*]pyrene	100	8
Anthanthrene	79	11
Coronene	80	20

Spiking level ΣPAHs 5.2 μg; extraction conditions CO_2–10% toluene, 40 MPa, 130°C oven temperature, 150°C restrictor temperature, 1200 ml/min flow of gaseous CO_2, 60 min total extraction time (2 × 30 min); chromatographic analysis was performed by HPLC (for detailed description see Section 2); number of replicate extractions $n = 3$ (standard deviations < 10%).

necessary. However, a clean-up had to be performed for the Soxhlet extract. The separation and quantification of the components were performed using HPLC and fluorescence detection. The extraction results are given in Table 3.

Table 3 shows that there are no significant differences between the two supercritical fluid extractions as well as between these and the Soxhlet extraction, in particular when it is taken into account that the sampling had to be performed successively. The experiments show that SFE is a promising alternative for conventional liquid extraction. SFE gives similar results in shorter analysis time and without further clean-up.

3.2. Supercritical fluid chromatography

One aim of this work was to develop a sensitive and efficient alternative for HPLC using packed column SFC.

Injection

To overcome the limitations caused by the relatively low injection volumes of conventional techniques we used a home-made solid-phase injector. With this system it is possible to inject 20 μl without any loss of chromatographic resolution. In Table 4 the detection limits of four PAHs obtained with direct injection (0.5 μl) are compared to those obtained using the new solid-phase injector.

Table 4
Comparison of detection limits (in units of concentration) of direct injection (0.5 μl) versus injection via solid-phase sample loop (20 μl), signal-to-noise ratio 3

Compound	Direct injection (ng/μl)	Solid-phase sample loop (ng/μl)
Fluorene	6	0.3
Fluoranthene	15	0.4
Chrysene	3.5	0.1
Benzo[*a*]pyrene	8	0.2

Separation

For the SFC separation of the priority PAHs we used a polymeric C_{18} column. With this column it is possible to separate 15 out of 16

Table 3
Extraction results of three real-world samples; comparison of Soxhlet and supercritical fluid extraction

	SFE1 (μg/m^3)	SFE2 (μg/m^3)	Soxhlet (μg/m^3)
Naphthalene	89.0	92.4	39.5
Acenaphthene	18.0	12.0	8.0
Fluorene	11.0	10.0	8.1
Phenanthrene	55.0	52.0	50.2
Anthracene	28.0	22.5	18.2
Fluoranthene	17.0	22.0	24.3
Pyrene	16.0	25.0	28.0
Benz[*a*]anthracene	2.8	5.6	5.9
Chrysene	2.3	4.0	6.3
Benzo[*b*]fluoranthene	3.9	6.1	6.1
Benzo[*k*]fluoranthene	1.1	1.2	1.6
Benzo[*a*]pyrene	1.9	2.4	2.6
Dibenz[*a,h*]anthracene	[a]	[a]	[a]
Benzo[*ghi*]perylene	1.9	2.0	2.2
Indeno[1,2,3-*cd*]pyrene	2.1	2.2	2.4
Anthanthrene	0.4	0.5	0.6
Coronene	0.7	0.9	1.1

[a] Not detected.

EPA-PAHs within 35 min. As far as we know this is the first separation of the 15 fluorescent EPA-PAHs using single-column SFC with pure carbon dioxide. These experiments demonstrate that it is possible to obtain satisfying SFC separations provided a suitable packing material is employed (Fig. 1).

Detection

To overcome the problems related to low selectivity in UV detection, the aim of this work was to use fluorescence detection in SFC. A commercially available fluorescence detector equipped with a home-made high-pressure flow cell assembly was employed. Although the fluorescence detector cell assembly is still in the stage of development, similar limits of detection and a significantly higher selectivity compared to UV-detection are obtained.

Our next aim is to combine the above-described extraction and separation steps based on supercritical carbon dioxide in order to form a PAH monitoring system. Therefore the suitability of the single components in the present state of development has to be tested.

3.3. Suitability test

In the following experiments the results obtained with the described off-line SFE–SFC monitoring system were compared with those of a reference method. The reference measurements were carried out by the RWTÜV Essen, an accredited institute for official emission control in Germany. During three successive sampling intervals, two samples were taken simultaneously in the crude gas of a fuel-oil-stoked industrial boiler plant. The sampling for both methods differed in size of the PUF plugs and waste gas volume. All relevant values are listed in Table 1.

One sample of every sampling interval was analysed by the reference laboratory (RWTÜV). Liquid extraction was accomplished using a Soxhlet apparatus (toluene). Following several clean-up steps, the analysis was performed using GC–FID. The results for the three sampling intervals are given in Table 5.

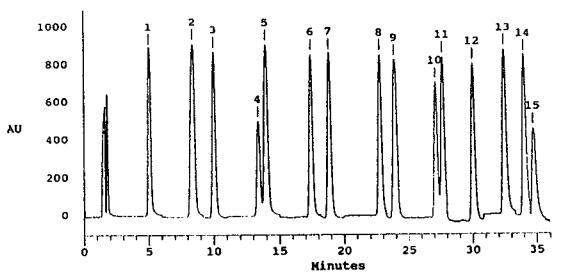

Fig. 1. SFC chromatogram using a polymeric C_{18} stationary phase. Mobile phase: carbon dioxide; oven temperature 80°C; density 3 min at 0.15 g/ml, programmed to 0.35 g/ml at 1 g ml^{-1} min^{-1}, then programmed to 0.78 g/ml at 0.015 g ml^{-1} min^{-1}, then held at 0.78 g/ml for 8 min. UV detection, wavelengths are given in brackets: 1 = naphthalene (212 nm); 2 = acenaphthylene/acenaphthene (220 nm); 3 = fluorene (208 nm); 4 = phenanthrene (240 nm); 5 = anthracene (240 nm); 6 = fluoranthene (230 nm); 7 = pyrene (232 nm); 8 = benz[*a*]anthracene (270); 9 = chrysene (240 nm); 10 = benzo[*b*]fluoranthene (240 nm); 11 = benzo[*k*]fluoranthene (240 nm); 12 = benzo[*a*]pyrene (258 nm); 13 = dibenz[*a*,*h*]anthracene (290 nm); 14 = indeno[1,2,3-*c*,*d*]-pyrene (244 nm); 15 = benzo[*ghi*]perylene (293 nm).

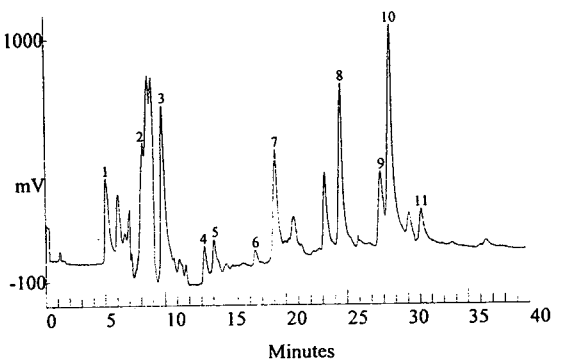

Fig. 2. SFC–fluorescence chromatogram. For chromatographic conditions see Fig. 1. Fluorescence wavelengths (excitation/emission) are given in brackets: 1 = naphthalene (210 nm/328 nm); 2 = acenaphthene (220 nm/338 nm); 3 = fluorene (200 nm/310 nm); 4 = phenanthrene (240 nm/372 nm); 5 = anthracene (240 nm/372 nm); 6 = fluoranthene (234 nm/432 nm); 7 = pyrene (236 nm/414 nm); 8 = chrysene (256 nm/380 nm); 9 = benzo[*b*]fluoranthene (240 nm/430 nm); 10 = benzo[*k*]fluoranthene (240 nm/430 nm); 11 = benzo[*a*]pyrene (252 nm/418 nm).

Table 5
Comparison of different analysis methods; for detailed description see text

Compound	Sample 1			Sample 2			Sample 3		
	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)
Naphthalene	1 754	n.d.	54 470	2 625	6 750	10 340	3 067	n.d.	27 940
Acenaphthene	10 088	710	1 750	8 831	800	820	6 444	820	1 170
Fluorene	2 083	1 030	1 220	2 076	900	960	1 689	840	810
Phenanthrene	1 820	1 010	1 360	1 766	790	1 060	1 511	740	990
Anthracene	n.d.[a]	230	230	n.d.	140	130	n.d.	80	50
Fluoranthene	175	320	340	47.7	70	230	44.4	[b]	200
Pyrene	88	430	490	14.3	340	410	67	350	370
Benz[*a*]anthracene	n.d.	n.d.	440	n.d.	n.d.	200	n.d.	n.d.	240
Chrysene	66	210	300	35.8	50	80	44.4	30	60
Benzo[*b*]fluoranthene	55	260	260	23.9	90	60	22.2	70	30
Benzo[*k*]fluoranthene	21.9	110	90	16.7	50	20	17.8	50	10
Benzo[*a*]pyrene	32.9	90	70	23.9	40	20	22.2	60	10

[a] n.d. = not determined, because of peak overlapping.
[b] = Not detected.

The smaller PUF plugs of the three sampling intervals were extracted with the described SFE method. In order to check the SFC results all extracts were analysed using both HPLC and SFC. Figs. 2 and 3 show the corresponding SFC and HPLC chromatograms of sample 1. The chromatograms and Table 5 show that the waste gas consists mainly of two- and three-ring PAHs. The agreement between SFC and HPLC results indicates that SFC using fluorescence detection may be a competitive way to analyse PAHs.

The results of the SFE–SFC monitoring system differ from those of the reference laboratory (Table 5). For naphthalene, acenaphthene, fluorene and phenanthrene the RWTÜV obtained higher concentrations than we did. For all other components the concentrations were lower. This fact is assumed to be caused mainly by differences in the sampling technique (gas volume and PUF size) and not by the extraction method. To verify this a comparison of both sampling techniques is under present investigation.

However, Table 5 illustrates that the PAH concentration pattern obtained with both methods correlates well. Thus the SFE–SFC method can now be used as a fast monitoring system for PAHs.

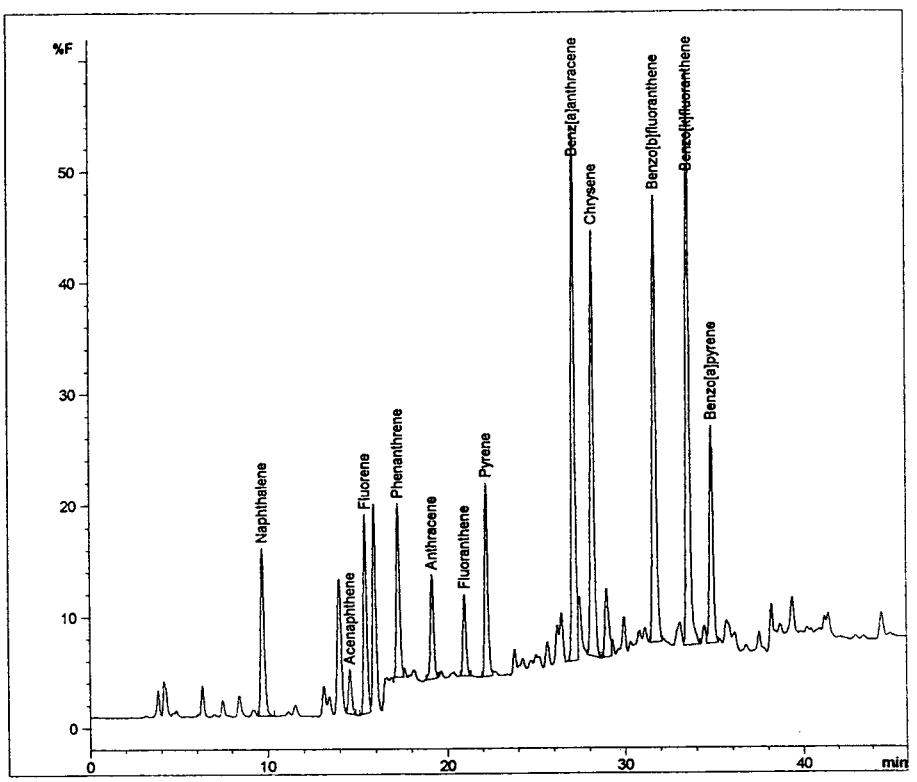

Fig. 3. HPLC–fluorescence chromatogram. Chromatographic conditions: flow-rate 0.5 ml/min, mobile phase acetonitrile–water (50:50, v:v), initially for 6 min, then programmed to 99:1 (v:v) in 29 min. Fluorescence wavelengths (excitation/emission) are given in brackets: naphthalene, acenaphthene (210 nm/320 nm); phenanthrene, anthracene (248 nm/384 nm); fluorene, pyrene (236 nm/430 nm); benz[*a*]anthracene, chrysene (270 nm/390 nm); benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (250 nm/440 nm); dibenz[*a,h*]anthracene, benzo[*ghi*]perylene (296 nm/405 nm); indeno[1,2,3-*c,d*]pyrene (245 nm/480 nm).

4. Conclusions

The aim of this work was to simplify the measurement of PAHs in exhaust gas emissions. Conventional methods are time-consuming and use relatively large quantities of potentially harmful organic solvents. The new off-line SFE–SFC system reduces both the analysis time and the amount of solvents. The latter aspect is of high importance with respect to the fact that a solvent-free method may be used in a mobile lab for on-site analysis. Fast on-site measurements for quasi-continuous monitoring of emission sources are important tools for the reduction of emissions.

The SFE–SFC system was compared with a standard method. The results of this comparison show that the PAH concentration patterns obtained with both methods correlate very well. However, there are some differences in the absolute concentration values. It is assumed that these are caused mainly by differences in the sampling techniques.

In conclusion these first results of the recently developed method show that methods using supercritical fluids are powerful technologies. Using SFE and SFC it is possible to reduce the quantity of toxic organic solvents and to shorten and simplify sample preparation. In a further step it may be possible to construct a fully automated monitoring system not attainable with classical methods.

Acknowledgements

The financial support of the German Bundesministerium für Forschung und Technologie (01 VQ 9003) and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged.

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Journal of Chromatography A, 710 (1995) 139–147

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Pentafluorobenzyl derivatives for the gas chromatographic determination of hydroxy-polycyclic aromatic hydrocarbons in urban aerosols

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Abstract

A method for the analysis of hydroxy-substituted polynuclear aromatic hydrocarbons (hydroxy-PAHs), using gas chromatography with electron-capture (ECD) and mass spectrometric (MS) detectors, is described. Pentafluorobenzyl bromide (PFBBr) was used as derivatizing agent for the hydroxy-PAHs. Optimization of the derivatization conditions was performed, and electron impact and negative ion chemical ionization mass spectra were studied. Detection limits ranged from 0.01 to 3.3 pg in ECD and negative ion chemical ionization mode (NICI)-SIM-MS values that allowed the determination of these compounds in environmental samples. Samples of air particulate matter were collected for the analysis of hydroxy-PAHs. The concentrations found for 5-hydroxyindol, 2-nitro-1-naphthol, 2-hydroxy-1,4-naphthoquinone and 2-hydroxy-9-fluorenone ranged between 5 and 189 pg/m^3.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are obtained in the incomplete combustion of fuel and they constitute an important environmental hazard. Polar functional groups can be introduced in polycyclic aromatic hydrocarbons by incomplete combustion in diesel engines or by chemical reactions with O_x, SO_x and NO_x in ambient air combustion [1–5]. Substituted PAHs have been identified in diesel exhausts and atmospheric aerosols [3,6–12]. For instance, nitro- and oxy- compounds have been found at ng/m^3 levels in aerosol samples [13–16], and the mutagenicity of certain extracts has been attributed to the presence of these compounds rather than to the PAHs themselves. In addition, more polar compounds have been identified in these samples such as hydroxy-PAHs [17], nitrated lactone derivatives [18], and aliphatic and aromatic carboxylic acids and their hydroxy derivatives [19].

Due to their low concentration levels, nitro- and oxy- compounds are currently determined by GC with electron-capture detection (ECD) or mass spectrometry in the negative ion chemical ionization mode (NICI-MS), but few methods have been proposed for the analysis of the hydroxy derivatives. Free phenolic compounds can be analyzed by GC, but the hydroxyl groups cause difficulties in their analysis. The transformation of the hydroxyl groups into less polar derivatives facilitated the use of GC for the analysis of these compounds. This increases the number of useful stationary phases, leads to an improvement in the peak shape and improves

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0021-9673/95/$09.50
SSDI 0021-9673(95)00263-4

separation and detection [20–23]. Thus, an increase in accuracy can be obtained.

Two of the most sensitive techniques for the determination of organic compounds at trace level are based on the process of gas-phase electron capture: the electron-capture detector in gas chromatography (GC–ECD) and the mass spectrometer in the electron-capture negative ion chemical ionization in the single ion monitoring (NICI-SIM-MS) [24]. In both cases, low detection limits (low femtogram) have been achieved [24,25].

Both the chromatographic behaviour and the relative response of electron-capture detectors can be enhanced by derivatization with halogen-containing reagents [20,26–28]. Phenols can be converted to pentafluorobenzyl ethers by reaction with pentafluorobenzyl bromide (PFBBr). These derivatives exhibit high electron affinity and, therefore, good response in ECD and NICI-MS [24,26,28–30]. Moreover, pentafluorobenzyl ethers have been shown to give NICI mass spectra with abundant analyte specific ions [24,31].

The aim of this study is to establish a simple and virtually quantitative derivatization procedure for hydroxy-PAHs. The method was optimized and quality parameters were established using ECD, NICI-MS and EI-MS operating in the positive mode as detectors. The procedure was applied to the analysis of hydroxy-PAHs in airborne particulate matter.

2. Experimental

2.1. Materials

5-Indanol (5-IOH), 5-hydroxyindol (5-HI), 2-nitro-1-naphthol (2N-1N), 2-hydroxy-1,4-naphthoquinone (2-H-1,4-NQ), 2-hydroxy-9-fluorenone (2-H-9-FLO) were purchased from Aldrich (Steinheim, Germany) and 1,8-dihydroxy-9,10-anthraquinone (1,8-DH-9,10-AQ) from Scharlau (Barcelona, Spain). Hexachlorobenzene (Aldrich) was used as internal standard. Pentafluorobenzyl bromide was purchased from Sigma (St. Louis, MO, USA), and 18-crown-6 (18c6) from Merck (Darmstadt, Germany). Potassium carbonate (Panreac, Barcelona, Spain) was washed with dichloromethane and acetone, and then stored at 110°C. Organic solvents (dichloromethane, acetone, hexane, methanol and toluene) were of HPLC-grade (Merck). Bond Elut silica cartridges were provided by Varian (Harbor City, OR, USA) and a Supelco Visiprep (Supelco, Gland, Switzerland) was used for the clean-up.

2.2. Capillary gas chromatography

High-resolution gas chromatography (HRGC) analyses were carried out with two different chromatographic systems. A Carlo-Erba (Milan, Italy) 5300 Mega Series equipped with a ^{63}Ni electron-capture detector, autosampler and split–splitless injector was used for the GC–ECD determinations. The injection port and the detector temperatures were 290°C and 330°C, respectively. Chrom-Card data system was used for data handling. For GC–MS analyses a Hewlett-Packard Model 5988A instrument coupled to an HP-5890 gas chromatograph was used. A Hewlett-Packard 59970MS Chemstation data system was used to record the data. The injection port temperature was 250°C, and the transfer line interface was kept at 280°C and the ion source at 250°C. Data were acquired using electron-impact (EI) mode (70 eV) and negative ion chemical ionization (NICI) with methane (1 Torr) as reagent gas.

The separation was carried out on a DB-17 fused-silica capillary column (J&W Scientific, Rancho Córdova, CA, USA), 30 m × 0.25 mm I.D., 0.25-μm film thickness. Helium at 30 cm/s was used as carrier gas.

For the chromatographic analysis of the derivatives two temperature programmes were used with the two detection systems: (a) GC–MS: initial 100°C, hold 1 min, rate 6°C/min to 280°C, hold 20 min; (b) GC–ECD: initial 100°C, hold 2 min, rate 25°C/min to 125°C, hold 1 min, rate 6°C/min to 240°C, hold 1 min, rate 30°C/min to 300°C, hold 20 min.

2.3. Derivatization procedure

Pentafluorobenzyl (PFB) ethers were prepared by the Claisen method [21,26,28,32,33]. The hydroxy-PAH mixture in acetone (1 ml) was introduced into a 2-ml screw top vial, and 10 μl of 10% PFBBr in acetone, 50 μl of an 18c6 solution (4000 ppm in acetone) and 10 mg of powdered K_2CO_3 were added. The vial was stoppered and shaken in a sonication bath for 60 min, at a temperature below 25°C. After the reaction, the solution was filtered, dried on anhydrous Na_2SO_4, evaporated under nitrogen to dryness and dissolved in 1 ml of hexane. To eliminate the by-products that strongly interfere in GC–ECD analyses a clean-up on a silica cartridge was required. Hexane (10 ml) was used to condition the cartridge. The sample was quantitatively transferred to the column, washed with 3 ml of hexane and eluted with hexane (5 ml), hexane–toluene (5 ml) and toluene–methanol (5 ml). The PFB ethers were eluted in the first and third fractions, which were pooled, evaporated to dryness and redissolved with 1 ml hexane containing the internal standard.

2.4. Sample collection

Airborne particulate matter samples were collected in one of the main avenues of Barcelona, 10 m above ground level. A large volume of heavy traffic passes through this area. Four atmospheric aerosols were collected in one year, one sample per season, on a 20.3 × 25.4 cm glass fibre filter paper (Whatman EPM-2000) thermally treated (300°C for 2 h), using a Sierra Misco Model 650 high volume sampler. After sampling filters were stored at −20°C.

2.5. Sample extraction and clean-up procedure

The sample was cut into four pieces and each piece was extracted ultrasonically with 75 ml dichloromethane for 30 min followed by 75 ml of methanol for 30 min at a temperature below 30°C. Both extracts were combined, dried over anhydrous sodium sulphate, passed through a Whatman GF/A glass microfibre filter, evaporated at 25°C in a rotary evaporator under reduced pressure to near dryness and redissolved in 1 ml of hexane for clean-up.

The extract was transferred onto the silica cartridge previously rinsed with 10 ml of hexane, and sequentially eluted with 3 ml of hexane and 2 ml of hexane–dichloromethane (80:20) to give fractions enriched in alkanes and PAHs, respectively. Then an alumina cartridge rinsed with 5 ml of hexane and 5 ml of hexane–dichloromethane (80:20) was coupled to the bottom of the silica cartridge. Both cartridges were eluted with 6 ml dichloromethane to obtain the oxy- and nitro- PAHs. The hydroxy-PAH fraction was obtained by eluting the alumina and silica columns with 5 ml of methanol. The methanol fraction was evaporated under reduced pressure to dryness and dissolved in 1 ml of acetone for derivatization.

3. Results and discussion

3.1. Optimization of the derivatization conditions

The derivatization reaction needs a basic medium, which was obtained using K_2CO_3. A large number of degradation products from the derivatizing agent were obtained when aqueous solutions of this salt were used. To avoid this problem, the derivatization procedure was performed using solid K_2CO_3 and 18c6 as catalyst, as recommended for derivatization of phenols with PFBBr [29,33]. To optimize the procedure, the amount of derivatizing agent, the temperature and the time were studied. High concentrations of derivatizing agent increased both the number and the abundance of interfering peaks. So, an excess of PFBBr equivalent to 30 times the total amount of the hydroxy compounds was used. Although degradation of the derivatizing agent was reduced under these conditions, and no interference was observed in the GC–MS analysis, a large number of interfering peaks appeared in the GC–ECD chromatogram, as can be seen in Fig. 1. These by-products, which strongly interfere in the gas chromatographic

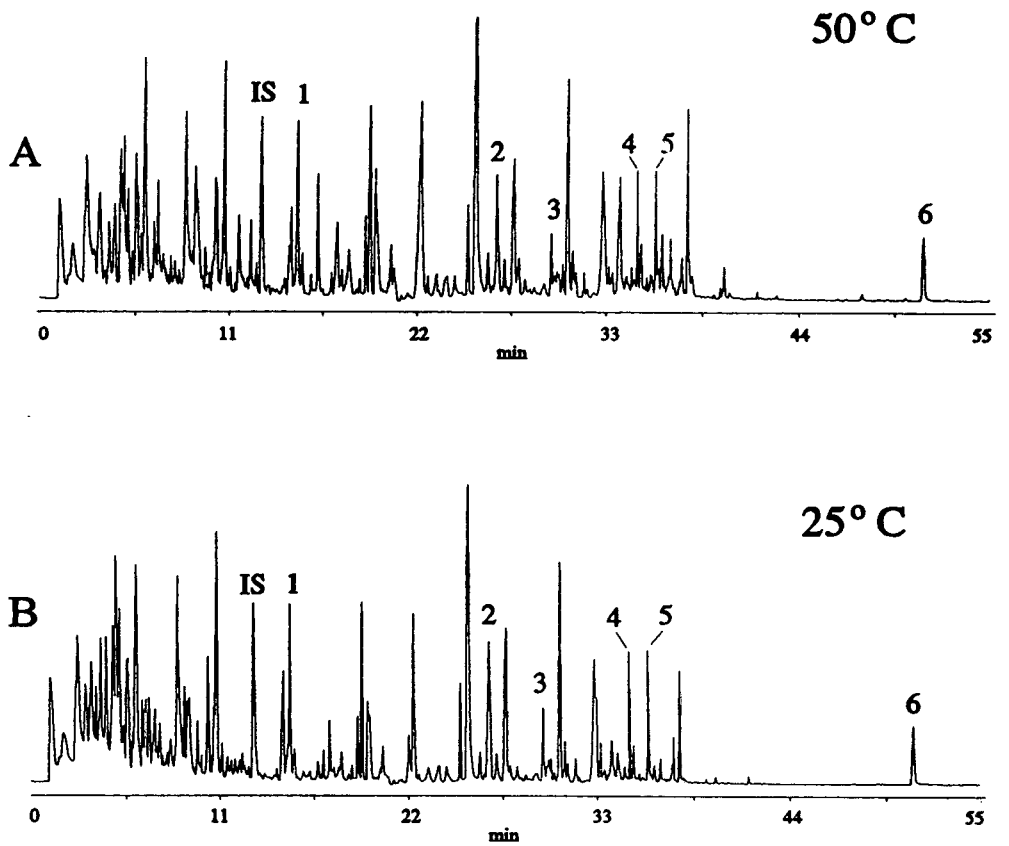

Fig. 1. GC–ECD chromatograms of a standard solution of hydroxy-PAHs (120 μg/l) after derivatization at different temperatures: (A) 50°C; (B) 25°C. Peaks: 1 = 5-IOH; 2 = 5-HI; 3 = 2N-1N; 4 = 2H-1,4-NQ; 5 = 2H-9-FLO; 6 = 1,8-DH-9,10-AQ. Chromatographic conditions as indicated in the text.

analysis with ECD, may originate from the decomposition of PFBBr, and probably have the structure $(C_6F_5CH_2O)_n$, as has been indicated by Davis [33].

Temperature also affects the decomposition of PFBBr. Derivatization at 80°C gave a larger number of interfering peaks in the chromatogram than derivatization at lower temperatures; the GC–ECD chromatograms of the PFB ethers obtained at 50°C and 25°C are given in Fig. 1.

Different derivatization processes were carried out with different reaction times, ranging from 15 to 120 min, to optimize reaction time, showing that reaction times of 60 min at 25°C are needed to obtain maximum responses. At higher temperatures a large decrease in the reaction time was observed: 15 and 35 min for 80°C and 50°C, respectively; however under such conditions a greater number of interfering peaks was obtained. The optimum conditions for the derivatization process were 25°C, 60 min and 10 μl of 2.5% derivatizing agent in acetone. Although these conditions gave a relatively clean chromatogram, an additional clean-up procedure was needed to eliminate most of the interferences and obtain a chromatogram with higher resolution, which would be suitable for the identification and determination of the hydroxy-PAHs. To clean the derivate solution a solid-phase extraction procedure was used. Silica was the adsorbent, as has been recommended for the derivatization of phenols [21,26,28]. The solvent

composition and the volume of each fraction were optimized. After a cleaning step with 3 ml hexane, in the second fraction eluted with 5 ml hexane the pentafluorobenzyl ether of 5-IOH was recovered. The third fraction eluted with 5 ml hexane–toluene (90:10) was discarded, and the rest of the compounds was eluted in the fourth fraction with 5 ml toluene–methanol (95:5). A GC–ECD chromatogram of a standard sample (120 μg/l) obtained after derivatization and clean-up is given in Fig. 2.

3.2. Gas chromatography–mass spectrometry

The PFB derivatives were studied by gas chromatography–mass spectrometry with EI and NICI. Mass spectra were recorded in both ionization techniques. The relative abundances of the main fragment ions are given in Table 1. The EI spectra of the ether derivatives showed two different patterns. Compounds such 5-indanol, 5-hydroxyindol and 2-hydroxy-9-fluorenone without electronegative groups in the aromatic rings or low electronegativity gave the phenoxyde ion $[ArO]^+$ as base peak and some fragment ions, such as the loss of CO group, characteristic of phenolic compounds. Compounds with electronegative groups such 2-nitro-1-naphthol, 2-hydroxy-1,4-naphthoquinone and 1,8-dihydroxy-9,10-anthraquinone gave the ion m/z 181 corresponding to the pentafluorobenzyl ion $[C_6F_5CH_2]^+$ as base peak, so no characteristic ions of the original hydroxy-PAH were observed. The derivative molecular ions generally showed low relative abundance, except for the 5-hydroxyindol, 2-hydroxy-9-fluorenone and 2-hydroxy-1,4-naphthoquinone, whose relative abundances were higher than for the other compounds.

Under NICI conditions the pentafluorobenzyl derivatives underwent a dissociative electron-capture process to produce the phenoxide anion $[ArO]^-$ as a sole peak in the mass spectrum. Low relative abundance of the ion at m/z 181 and other fragments were observed for all the compounds (Table 1). The 2-hydroxy-1,4-naphthoquinone gave ions at m/z 174 and 175 due to the quinone group. For the hydroxy compound 1,8-dihydroxy-9,10-anthraquinone the loss of a PFB group gave the base peak, although the loss of two PFB groups and the molecular ion were also observed.

3.3. Quality parameters

Linearity and reproducibility of the GC–ECD system were determined (Table 2). Linearity between 7 and 185 pg, and correlation coefficients better than 0.999 for all the PFB ethers were obtained. To determine reproducibility of

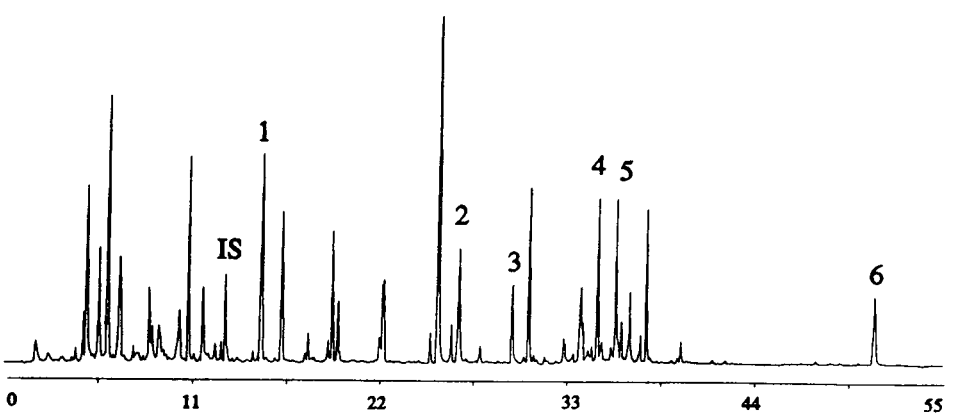

Fig. 2. GC–ECD chromatogram of a standard solution of hydroxy-PAHs (120 μg/l) after derivatization (25°C) and clean-up. Peaks: 1 = 5-IOH; 2 = 5-HI; 3 = 2N-1N; 4 = 2H-1,4-NQ; 5 = 2H-9-FLO; 6 = 1,8-DH-9,10-AQ. Chromatographic conditions as indicated in the text.

Table 1
Electron-impact and negative ion chemical ionization mass spectra data for the hydroxy-PAHs PFB derivatives

Compound	MW		*m/z* (relative abundance, %)								
	A	D	Electron-impact					Negative ion chemical ionization			
			$[M]^+$	$[ArO]^{+\cdot}$	$[ArO\text{-}CO]^+$	$[R]^+$	$[ArO\text{-}2CO]^+$	$[M]^-$	$[ArO]^-$	$[R]^-$	$[ArO\text{-}NO]^-$
Monohydroxy											
5-IOH	134	314	314(33)	133(100)	105(50)	181(69)	–	–	133(100)	–	–
5-HI	133	313	313(7)	132(100)	104(45)	181(18)	–	–	132(100)	–	–
2N-1N	189	369	369(3)	–	–	181(100)	–	–	188(100)	181(8)	158(23)
2-H-1,4-NQ	174	354	354(20)	173(9)	145(7)	181(100)	117(2)	–	173(100)	181(4)	–
2-H-9-FLO	196	376	376(23)	195(100)	167(21)	181(35)	139(45)	–	195(100)	181(5)	–
	A	D	$[M]^+$	$[ArOO]^{+\cdot}$		$[R]^+$		$[M]^-$	$[ArOO]^-$	$[R]^-$	$[ArOOR]^-$
Dihydroxy											
1,8-DH-9,10-AQ	240	600	–	239(49)		181(100)		600(17)	239(51)	181(26)	419(100)

A = hydroxy-PAH; D = PFB ether; M = PFB ether derivative; R = derivatizing agent; ArO = phenoxide ion [M − R].

Table 2
Linearity and reproducibility of the PFB ether of hydroxy-PAHs

Compound	Linearity (pg)	Reproducibility[a] (R.S.D., %)	Reproducibility of the method[b] (R.S.D., %)
5-IOH	7–92	0.94	2.04
5-HI	25–145	2.21	5.26
2-N-1-N	40–185	1.61	4.04
2-H-1,4-NQ	25–135	4.22	6.43
2-H-9-FLO	15–135	2.26	4.57
1,8-DH-9,10-AQ	15–180	3.17	5.04

[a] Three daily injections on four different days.
[b] Four derivatizing processes.

the chromatographic analysis three replicate injections of a derivatized hydroxy-PAH standard solution (120 pg each) were carried out on four different days. Relative standard deviations (R.S.D.) in the range of 0.94–4.22%, based on the peak area, were obtained. To determine the reproducibility of the entire method four independent derivatization processes of a standard solution of hydroxy-PAHs (120 μg/l of each compound) were carried out. The relative standard deviations ranged from 2.04 to 6.43%.

Detection limits of pentafluorobenzyl derivatives using ECD, EI-MS and methane NICI-MS based on a signal-to-noise ratio of 3:1 are shown in Table 3. Scan mode and selected-ion monitoring (SIM) using the base peak ions given in Table 1 were used to record the respective mass spectrometric responses. Detectors based on electron capturing (ECD and NICI-MS) gave low detection limits, ranging between 0.01 and 3.3 pg for ECD and 0.02 and 1 pg for NICI-SIM-MS. For NICI-MS, detection limits are higher for those compounds which showed higher fragmentation, such 1,8-dihydroxy-9,10-anthraquinone, 2-nitro-1-naphthol and 2-hydroxy-1,4-naphthoquinone. Values obtained with either technique are 10^2 times lower that those obtained with EI-SIM-MS for PFB ether derivatives.

3.4. Application

The analytical method studied in this paper was developed mainly to determine hydroxy-PAHs in airborne particulate matter. Four urban

Table 3
Detection limits of the PFB ethers of hydroxy-PAHs

Compound	Detection limits (pg)				
	ECD	MS			
		EI		NICI	
		SCAN	SIM	SCAN	SIM
5-IOH	0.01	20	5	0.5	0.02
5-HI	0.05	50	10	1	0.03
2-N-1-N	0.7	50	15	15	0.3
2-H-1,4-NQ	3.3	80	20	15	0.4
2-H-9-FLO	2	25	5	2	0.08
1,8-DH-9,10-AQ	3.3	400	100	25	1

aerosol samples, one in each season, were analyzed. A GC–NICI-MS chromatogram of an atmospheric aerosol is shown in Fig. 3. Only some of the hydroxy-PAHs studied were detected in the extracts. These compounds were identified from the NICI mass spectra and determined by GC–ECD, using hexachlorobenzene as internal standard. 2-Hydroxy-9-fluorenone was identified in all samples, at concentrations of 20, 5, 31 and 75 pg/m^3 in spring, summer, autumn and winter, respectively. Concentration in summer was the lowest probably due to the high temperatures which caused evaporation of the compounds. 2-Hydroxy-1,4-naphthoquinone was identified in winter and spring at concentrations of 13 and 14 pg/m^3, respectively. 2-

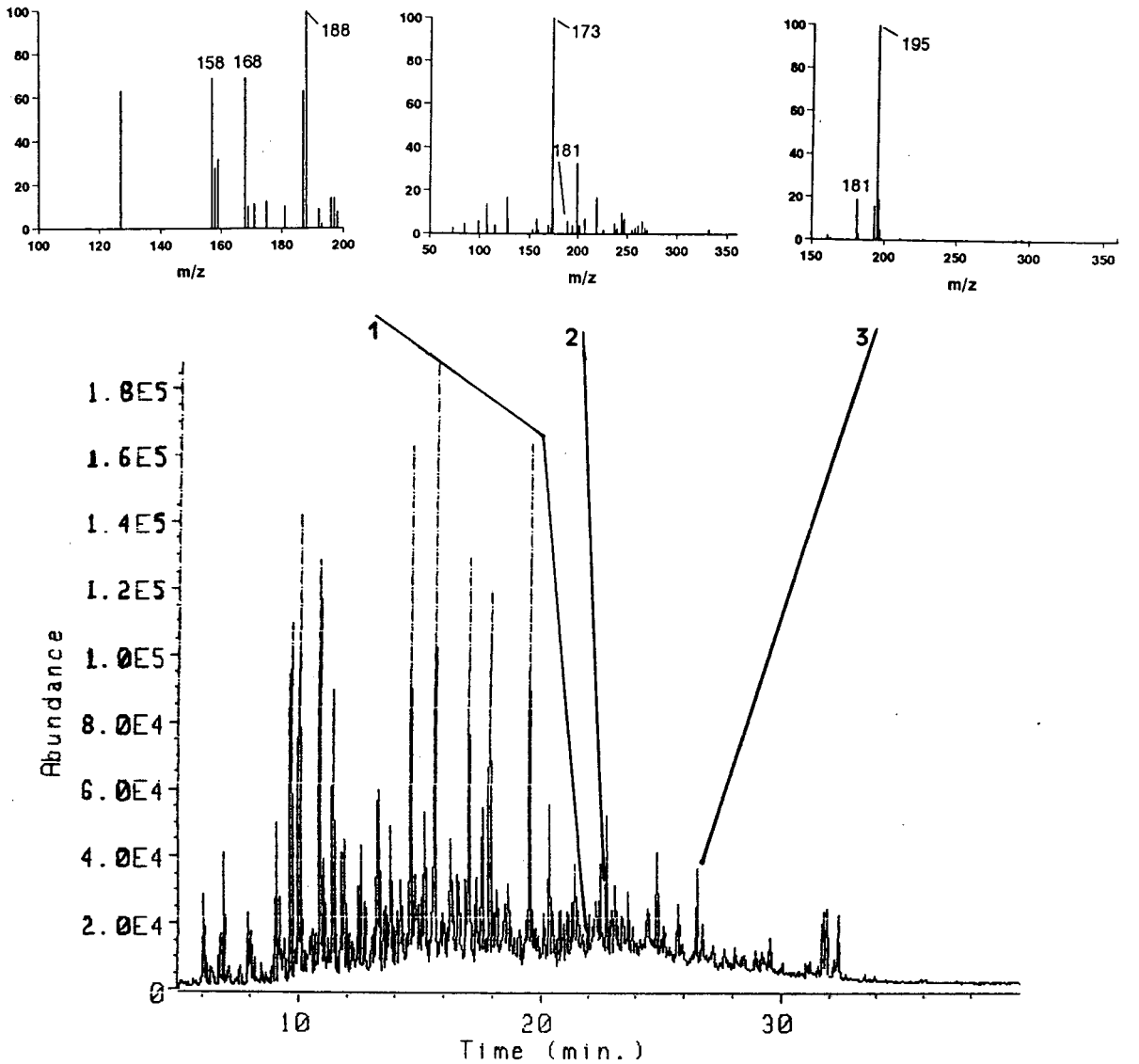

Fig. 3. Chromatogram (GC–NICI–MS) and mass spectra of the identified compounds of an atmospheric winter aerosol registred from m/z 100 to 250. Identified compounds: 1 = 2-N-1-N; 2 = 2-H-1,4-NQ; 3 = 2-H-9-FLO. Conditions as indicated in the text.

Nitro-1-naphthol was also identified in autumn and winter at levels of 24 and 189 pg/m^3, respectively. 5-Hydroxyindole was only identified in the autumn sample at very low levels (5 pg/m^3). Although very few studies deal with these compounds in atmospheric aerosols, our results agree with published values. For instance, Nishioka et al. [17] reported concentrations for hydroxy-nitro-PAHs in urban air particulate extracts between 10 and 600 pg/m^3. Bayona et al. [34] give similar values for nitronaphthol isomers (10–30 pg/m^3), and Tomingas and Mönch [35] reported 200 pg/m^3 for 9-hydroxyfluorene.

4. Conclusions

A procedure to obtain the PFB ethers of hydroxy-PAHs and the clean-up for the GC–ECD has been established. EI and NICI gas chromatography–mass spectrometry of the derivatives was used for the identification of these compounds in real samples. Electron-capture techniques (ECD and NICI) gave the best detection limits. The procedure proposed was used for the determination of some hydroxy-PAHs in urban aerosol samples.

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Journal of Chromatography A, 710 (1995) 149–157

JOURNAL OF CHROMATOGRAPHY A

Separation of ^{32}P-labeled 3′,5′-bisphosphate nucleotides of polycyclic aromatic hydrocarbon *anti*-diol-epoxides and derivatives ☆

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Abstract

^{32}P-Postlabeling-HPLC is a highly sensitive analytical method for identification of chemical-modified DNA adducts isolated from samples obtained from experimental animals or humans exposed to carcinogenic chemicals. To determine optimal ^{32}P-postlabeling-HPLC conditions for efficient separation, we report here the use of ten diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides derived from benzo[*a*]pyrene (BaP), nitrated BaP, and related compounds. After testing ODS-modified, C_4-modified, phenyl-modified, diphenyl-modified, and cyclodextrin-bonded reversed-phase HPLC columns, we found that the Vydac diphenyl-modified column can efficiently separate these 3′,5′-bisphosphate deoxynucleotides. The results suggest that ^{32}P-postlabeling-HPLC is a potentially useful methodology for detecting environmental carcinogens that can be metabolized to diol-epoxides. The relationships between the structures of *anti*-diol-epoxides and HPLC retention order are also discussed.

1. Introduction

In the USA about 95% of the current energy consumption is fossil fuel [1]. Combustion of fossil fuel is never complete and produces polycyclic organic matter (POM) as by-products. It has been well documented that POM causes air pollution and poses a threat to human health and the environment [2,3]. POM contains polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) [4–7], both of which are carcinogenic chemicals [4,5,8,9]. The POMs extracted from the ambient air, coal, chimney soot, diesel and gasoline engines, industrial carbon black, oil shale soot, coke oven emissions, and roofing tar emissions all induce tumors in experimental animals [4]. Consequently, it is important to assess human health risk posed by air pollution from different sources.

Benzo[*a*]pyrene (BaP) has been used as a biomarker for measurement of PAHs extracted from the POM. It has been found that POM extracted from diesel soot contains a relatively

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0021-9673/95/$09.50
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high concentration of nitro-PAHs compared to the parent PAHs [6,10]. For example, diesel soot extract contains 30 and 202 ppm pyrene and 1-nitropyrene, respectively, and contains BaP, 1-nitrobenzo[*a*]pyrene (1-NBaP), 3-nitrobenzo[*a*]pyrene (3-NBaP), and 6-nitrobenzo[*a*]pyrene in quantities of 6.4, 3, 6, and 14 ppm, respectively [6]. Both PAHs and nitro-PAHs require metabolic activation to covalently bind to DNA and to exert their mutagenic and tumorigenic activities [4,5,8,9,11]. It has been established that binding of the reactive *anti*-diol-epoxide metabolites to DNA, resulting in the formation of N^2-deoxyguanosinyl adducts, is the principal metabolic activation of PAHs in vivo [1,8]. ^{32}P-Postlabeling has been established as a sensitive analytical method for identification of chemical-modified DNA adducts isolated from samples obtained from experimental animals or humans exposed to carcinogenic chemicals [6,7,12–16]. Pfau and Phillips [16] developed an efficient ^{32}P-postlabeling-HPLC methodology for the separation of ten ^{32}P-labeled nucleoside 3′,5′-bisphosphate adducts derived from *anti*-diol-epoxides of PAHs, including benzo[*a*]pyrene (BaP) *anti*-diol-epoxide. The optimal HPLC conditions for separation of these adducts were discussed in detail. Recently, King et al. [7] reported the separation of several ^{32}P-labeled 3′,5′-bisphosphate adducts of *anti*-diol-epoxides of PAHs and a series of nitro-PAH derived adducts.

1-NBaP and 3-NBaP are potent mutagens in *Salmonella* [17,18]. In vitro microsomal metabolism of 1- and 3-NBaP-DE both produce the corresponding bay-region *anti*-diol-epoxides as metabolites [17,18], which upon interaction with calf thymus DNA result in the formation of N^2-deoxyguanosinyl adducts [19,20]. Since both BaP and NBaPs are present in diesel soot extract in substantial quantities [6], it is relevant to determine whether or not the ^{32}P-labeled nucleoside 3′,5′-bisphosphate adducts derived from *anti*-diol-epoxides of BaP and NBaPs are separable. We report in this paper the separation of the ^{32}P-labeled nucleoside 3′,5′-bisphosphate adducts derived from ten PAH and nitro-PAH *anti*-diol-epoxides. The relationships between the structures of *anti*-diol-epoxides and HPLC retention order are also discussed.

2. Experimental

2.1. Materials

BaP diol-epoxide, *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (BaP-DE), was prepared as previously described [21]. The following five *anti*-diol-epoxides were previously prepared in our laboratory: *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydro-1-nitrobenzo[*a*]pyrene (1-NBaP-DE) [22], *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydro-2-nitrobenzo[*a*]pyrene (2-NBaP-DE) [23], *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydro-3-nitrobenzo[*a*]pyrene (3-NBaP-DE) [19], *cis*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (*cis*-BaP-DE) [24], and *trans*-9,10-dihydroxy-*anti*-7,8-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (9,10-BaP-DE) [24]. Following the established procedures for synthesis of the diol-epoxides described above [19–22], *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydro-7-methylbenzo[*a*]pyrene (7-MBaP-DE) was synthesized by epoxidation of *trans*-7,8-dihydroxy-7,8-dihydro-7-methylbenzo[*a*]pyrene [25]. *Trans*-8,9-dihydroxy-*anti*-10,11-epoxy-8,9,10,11-tetrahydrobenz[*a*]anthracene (8,9-BA-DE), *trans*-10,11-dihydroxy-*anti*-8,9-epoxy-8,9,10,11-tetrahydrobenz[*a*]anthracene (10,11-BA-DE), and *trans*-10,11-dihydroxy-*anti*-12,13-epoxy-10,11,12,13-tetrahydrodibenz[*a,c*]-anthracene (DB[*a,c*]A-DE) were similarly prepared.

2.2. Chemical synthesis of DNA adducts

The DNA adducts of BaP-DE, 3-NBaP-DE, *cis*-BaP-DE, and 7-MBaP-DE were prepared according to previously described procedures [19,24,26]. The DNA adducts of 1- and 2-NBaP-DE were prepared in a manner similar to the 3-NBaP-DE DNA adduct [19]. The DNA adducts of the remaining diol-epoxides were prepared by a standard procedure: a solution of a

diol-epoxide (5.0 mg, dissolved in 200 μl of freshly distilled tetrahydrofuran) in 10 m*M* Tris buffer (20 ml, pH 7.5) was incubated with purified calf thymus DNA (20 mg) at 37°C for 4 h. The reaction mixture was extracted three times with an equal volume of *n*-butanol saturated with 10 m*M* Tris buffer (pH 7.5). The aqueous layer was extracted three times with 20 ml of water-saturated isoamyl alcohol. An amount of 2 ml of 5 *M* sodium chloride was added to the aqueous phase and the DNA was precipitated with 22 ml of ice-cold 95% ethanol. The DNA concentration was determined spectrophotometrically by measuring the UV absorbance at 260 nm.

For structural identification of the adducts, each of the modified DNA was enzymatically digested to nucleosides by incubating with DNase I, followed by incubation with alkaline phosphatase and snake venom phosphodiesterase I.

2.3. ^{32}P-postlabeling-HPLC identification of 3′5′-bisphosphates deoxyribonucleotides

The modified DNA (10 μg) suspended in 20 μl of 5 m*M* Bis-Tris, 0.1 m*M* EDTA, pH 7.1 buffer was hydrolyzed to deoxyribonucleoside 3′-monophosphate at 37°C for 4 h with 30 μl of a mixture containing micrococcal nuclease (125 U/ml) and spleen phosphodiesterase (12.5 U/ml) in 20 m*M* sodium succinate and 10 m*M* calcium chloride (pH 6.0) following the procedure of Gupta [27]. DNA adducts were enriched by the *n*-butanol extraction method. The resulting deoxyribonucleoside 3′-monophosphates were dissolved in 25 μl of water and [γ-^{32}P] phosphorylated with 5 μl of PNK mix containing 200 μCi [γ-^{32}P]ATP and 1 U/μg DNA of T4 polynucleotide kinase at 37°C for 40 min. The residual [γ-^{32}P]ATP was destroyed by the addition of 1.5 μl of potato apyrase (30 μU), followed by incubation at 37°C for 30 min.

To separate the modified 3′,5′-bisphosphate deoxyribonucleotides from the unmodified nucleotides, thin-layer chromatography was performed using Machery–Nagel PEI cellulose plates (3 × 5 cm, Alltech Associates, Deerfield, IL, USA) with 0.65 *M* sodium phosphate, pH 6.8, onto a 15-cm Whatman 1 paper wick that had been attached to the top of the plate (D_1 direction only). The material from the origin of the plates was scraped, transferred to 1.5-ml polypropylene microcentrifuge tubes, and extracted with 500 μl of 4 *M* pyridinium formate, pH 4.2 at room temperature for 4 h with stirring on a mechanical mixer. After centrifugation for 10 min, the supernatant was collected and centrifuged again for 10 min to remove fine particles. The supernatants were dried under reduced pressure and redissolved in 0.5 *M* sodium phosphate buffer (pH 2.0) for HPLC analysis. The radioactivity was determined by liquid scintillation counting.

2.4. HPLC analysis

HPLC analysis was performed with a Waters Associates instrument consisting of two Model 510 pumps, a Model 680 solvent programmer, a Model U6K injector, and in line with a Radiomatic FLO-ONE/Beta A-515 system with the samples measured in a 500-μl flow cell. Samples were eluted at 1.2 ml/min with a 3-step linear gradient as follows: (1) a linear gradient from 10% of solvent A (methanol–500 m*M* sodium phosphate buffer, pH 2.0, 9:1) in solvent B (500 m*M* sodium phosphate buffer, pH 2.0) to 30% of solvent A in solvent B for 10 min; (2) a linear gradient for 30 min from 30% of solvent A in solvent B to 35% solvent A in solvent B; and (3) a 20 min linear gradient from 35% solvent A in solvent B to 90% solvent A in solvent B. The columns used were: Zorbax ODS (250 × 4.6 mm I.D.); Zorbax phenyl (250 × 4.6 mm I.D.) (DuPont Medical Products, Wilmington, DE, USA); Vydac 201TP54 ODS (250 × 4.6 mm I.D.); Vydac 219 diphenyl (250 × 4.6 mm I.D.) (The Separations Group, Hesperia, CA, USA); MetaChem C4/E (250 × 4.6 mm I.D.) (MetaChem Technologies, Redondo Beach, CA, USA); Phenomenex IB-SIL 5 phenyl column (250 × 4.6 mm I.D.) (Phenomenex, Torrance, CA, USA); Waters μBondapak ODS (300 × 3.9 mm I.D.) (Waters Associates, Milford, MA, USA); Beckman ODS (250 × 4.6 mm I.D.) (Beckman Instru-

ments, San Ramon, CA, USA); Astec Cyclobond II (γ); Supelcosil LC-18-DB (250 × 4.6 mm I.D.) (Supelco, Supelco Park, Bellefonte, PA, USA); Hypersil ODS (250 × 4.6 mm I.D.) (Sigma-Aldrich, Aldrich, Milwaukee, WI, USA). All columns have a particle size of 5 μm. To eliminate the possible UV photolytic decomposition of the compounds, the laboratory was equipped with UV absorbing films placed above the light diffusion panels.

3. Results and discussion

3.1. Selection of diol-epoxides for study

To determine optimal ^{32}P-postlabeling-HPLC conditions for efficient separation of diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides derived from PAHs and nitro-PAHs, we employed ten structurally related PAH and nitro-PAH diol-epoxides and a number of different types of HPLC columns for study. The structures and abbreviations of the diol-epoxides used in this study are shown in Fig. 1. The reason for choosing these diol-epoxides is based on the following considerations: BaP-DE, 1-NBaP-DE, 3-NBaP-DE, and DB[*a*,*c*]A-DE are the ultimate metabolites of BaP, 1-NBaP, 3-NBaP, and DB[*a*,*c*]A [28], respectively. BA *trans*-8,9-dihydrodiol and BA *trans*-10,11-dihydrodiol are the predominant metabolites of BA in vitro [29]. Metabolism of these two BA dihydrodiols may result in the formation of 8,9-BA-DE and 10,11-BA-DE. 7-MBaP is a possible environmental contaminant, and metabolism of 7-MBaP forms

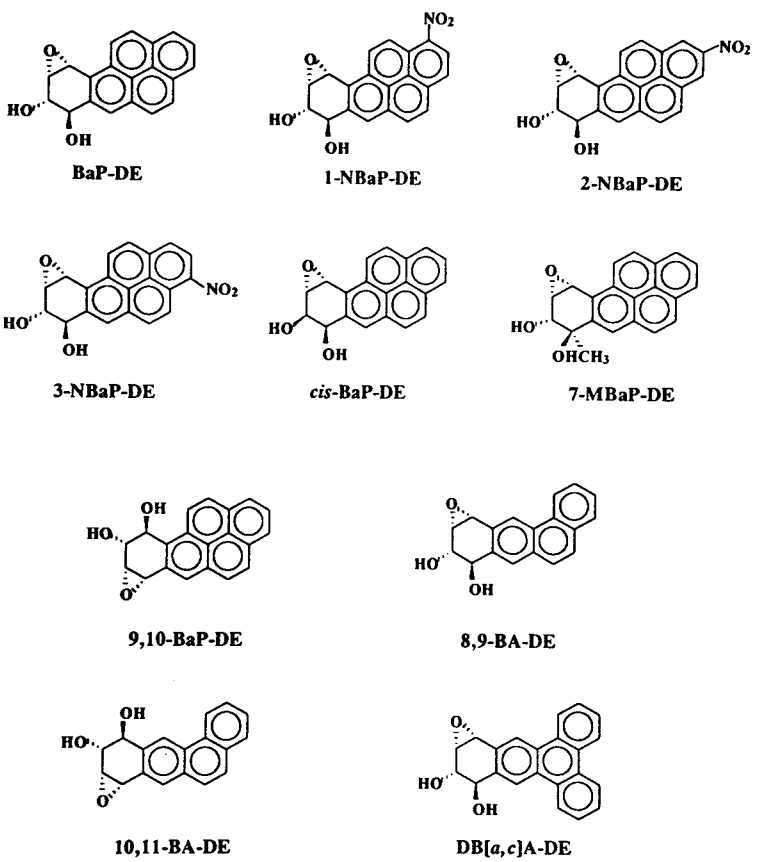

Fig. 1. Structures and abbreviations of *anti*-diol-epoxides of BaP, 1-NBaP, 2-NBaP, 3-NBaP, and related PAHs.

7-MBaP *trans*-7,8-dihydrodiol [30]. With an additional methyl group at the C_7 position compared with that of BaP-DE, study of this compound will enable us to determine the effect of a methyl group on HPLC retention. Since BaP *trans*-7,8-dihydrodiol is a metabolite of BaP, 9,10-BaP-DE is also possibly formed. The use of *cis*-BaP-DE will enable us to determine the effect of the *cis* configuration on elution order.

With the exception of 9,10-BaP-DE and *cis*-BaP-DE, all the other diol-epoxides employed for this study are *anti*-diol-epoxides. As reported previously, diol-epoxides of *cis*-BaP-DE and 9,10-BaP-DE are a mixture of the *syn*- and *anti*-diastereoisomers [24].

The diol-epoxide-modified DNA adducts, prepared by reacting diol-epoxides with purified calf thymus DNA, were hydrolyzed to deoxyribonucleoside 3′-monophosphates with micrococcal nuclease and spleen phosphodiesterase following the published standard procedure [12]. [5′-^{32}P]Phosphorylation of 3′-monophosphates resulted in diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides [12] which were enriched by the *n*-butanol extraction procedure [14] and analyzed by HPLC.

3.2. Separation of diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotide adducts by HPLC

To compare separation efficiency among different types of columns (monomeric and polymeric; octadecyl-modified and phenyl-modified etc.), eleven reversed-phase HPLC columns [six ODS columns (Zorbax, Vydac, μBondapak, Supelcosil LC-18-DB, Ultrasphere, and Hypersil), one C_4-modified column (MetaChem), two phenyl-modified columns (Zorbax and Phenomenex IB-SIL), one diphenyl-modified column (Vydac), and one cyclobond column (Astec Cyclobond II(γ))] were used. The Zorbax ODS, μBondapak C_{18}, and Vydac ODS columns have a conventional bonding between the silicate hydroxy groups and the substituents. However, the bonded phase of the Zorbax and μBondapak ODS columns is monomeric and the Vydac ODS is polymeric. The MetaChem C_4 column is packed with a uniform matrix of crosslinked polysiloxane functional groups. The phenyl and diphenyl columns, which are recommended for polypeptides, particularly those containing aromatic sidechains, have an aromatic phenyl or diphenyl group chemically bonded to silica that is capped with trimethylsilane to prevent adsorption of polar compounds. The Cyclobond II(γ) column consists of eight glucopyranose units arranged in the shape of a hollow truncated cone with the interior cavity of 9.5 Å in diameter. Separation of compounds by the Cyclobond column is in general governed by the molecule's ability to fit the cavity of the cyclodextrin, although the polarity of the molecule is also a factor. Thus, comparison of the separation efficiencies of the columns and the retention order of the compounds will provide a better understanding of the mechanisms of interaction between the bonded phase and the diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotide solutes.

After employing various solvent systems and HPLC conditions, it was found that, in general, the order of separation efficiency of these HPLC columns is: diphenyl-modified column ≥ phenyl-modified column > ODS column ≫ cyclobond column > C_4-modified column. Separation of each of the ten diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides on a Vydac diphenyl-modified reversed-phase HPLC column is shown in Fig. 2. The optimal HPLC conditions employed a solvent system similar to that reported by Pfau and Phillips [16], which consists of buffer A, 0.5 *M* sodium dihydrogen orthophosphate and 0.5 *M* orthophosphoric acid (pH 2.0) and buffer B, a mixture of methanol in buffer A (9:1, v/v). With the exception of 9,10-BaP-DE and *cis*-BaP-DE, all the diol-epoxides generated one major adduct. The major adducts account for the following percentages of total adduct formation: 10,11-BA-DE, 79%; 8,9-BA-DE, 78%; BaP-DE, 90%; 1-NBaP-DE, 56%; 2-NBaP-DE, 75%; 3-NBaP-DE, 73%; 7-MBaP-DE, 61%; and DB[*a*,*c*]A, 72%. Due to being a mixture of *syn*- and *anti*-diol-epoxides, both 9,10-BaP-DE and *cis*-BaP-DE generate multiple adducts (Fig. 2) and are not suitable to combine with other adducts for HPLC separation. There-

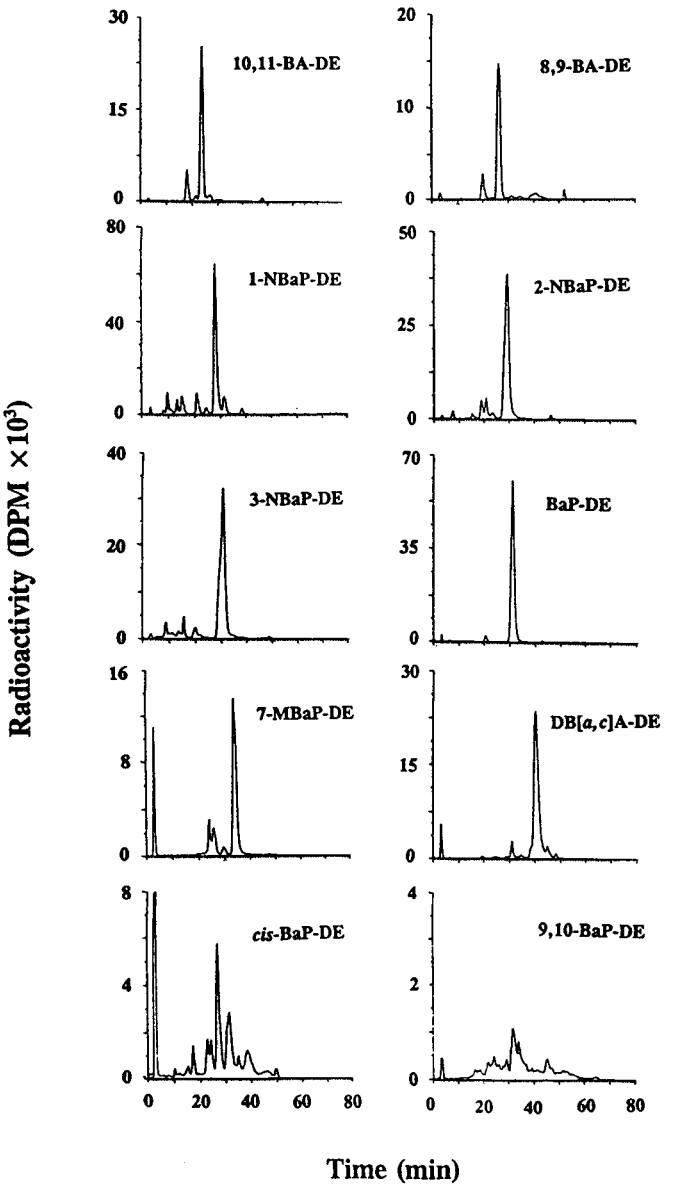

Fig. 2. Separation of each of the ten diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides on a Vydac diphenyl-modified reversed-phase HPLC column. For chromatographic conditions, see Section 2.4.

fore, only eight diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides were employed for determining HPLC separation efficiency (Fig. 3). For comparison, the retention times of the 9,10-BaP-DE and *cis*-BaP-DE adducts are marked in Fig. 3.

Two approaches are used to determine the relative HPLC retention times of each adduct. The first is to compare the retention time of the individual adduct. The second is to repeat the HPLC separation by increasing the concentration of one or two components. For example, as shown in Fig. 3B, when the quantities of the 10,11-BA-DE and BaP-DE adducts were in-

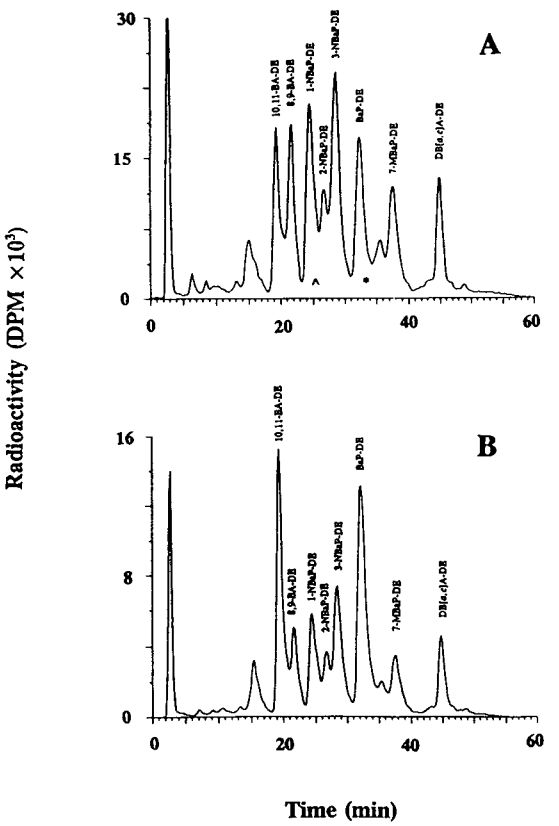

Fig. 3. (A) Separation of a mixture containing eight diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotides on a Vydac diphenyl-modified reversed-phase HPLC column. The retention times from the major adducts of 9,10-BaP-DE and *cis*-BaP-DE are marked (* and Λ, respectively). (B) The quantities of 10,11-BA-DE and BaP-DE adducts in (B) are increased compared to those in (A). For chromatographic conditions, see Section 2.4.

creased, the intensity of the corresponding chromatographic peaks increased (compared with those shown in Fig. 3A).

Pfau and Phillips [16] previously reported the use of a phenyl-modified Zorbax column for efficient separation of ten PAH *anti*-diol-epoxides, including the adducts of BaP-DE and DB[*a*,*c*]A that we also used. In our study of *anti*-diol-epoxide adducts, separation by Zorbax and another phenyl-modified HPLC column (Phenomenex IB-SIL) resulted in less satisfactory separation efficiency of 1-, 2- and 3-NBaP-DE, although the HPLC retention order is in general similar to that from the Vydac diphenyl-modified column (data not shown). The adducts of 1-NBaP-DE, 2-NBaP-DE, 3-NBaP-DE, and BaP-DE eluted within a very narrow range without having a baseline separation. Nevertheless, similar to the results reported by Pfau and Phillips [16], the adduct of DB[*a*,*c*]A eluted last (data not shown).

Separation of the adducts by the six ODS HPLC columns was less successful. The C_4 reversed-phase column provided the worst separation affording all the adducts eluted within a narrow range. The Cyclobond II column did not result in satisfactory separation either. Several of the diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotide adducts had a very short retention time, eluting closely with the unmodified deoxynucleotides (data not shown). Separation by the Cyclobond II(γ) column is in general governed by the molecule's ability to fit the cavity of the cyclodextrin, although polarity of the molecule can be considered as a secondary factor. Thus, these results indicate that part of the adduct molecules do not fit the cavity.

3.3. Relationships between structures of the adducts and HPLC retention order

We previously employed more than 100 PAHs, nitro-PAHs, and their derivatives for study of relationships between structures and HPLC retention order [31–33]. It is found that when a compound is eluted from an HPLC column, polarity and size of the molecule are important factors in determining the HPLC retention time. Polarity is largely related to the type, number, and location of the functional group(s) in the molecule. Thus, a functional group, such as a nitro, hydroxyl, or a methyl group, would also alter polarity and therefore affect HPLC retention times of nitro-PAHs. However, all diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotide adducts contain two highly polar phosphate groups attached to the deoxy ribose and three hydroxyl and one secondary amino groups linked to the saturated terminal benzo ring of the aromatic moiety. As a consequence, due to similar strong polarity, these adducts are not well

separated by the ODS reversed-phase HPLC columns. On the other hand, these adducts can be better separated by diphenyl- or phenyl-modified reversed-phase columns, which are recommended for separation of aromatic-ring-containing peptides. Therefore, it is evident that the determining factor in the separation of these adducts is the number of aromatic rings contained in the modified 3′,5′-bisphosphate deoxynucleotide adducts. This can well explain why 10,11-BA-DE and 8,9-BA-DE eluted first, followed by the NBaP-DEs, BaP-DE, and 7-MBaP-DE, and DB[*a*,*c*]A-DE last (Fig. 3).

We have found that, when a diphenyl-modified HPLC column is used, the elution order of the adducts, as shown in Fig. 3, is in accordance with those of the parent PAHs, nitro-PAHs, and their derivatives. Comparison of the retention times between the adducts of BaP-DE and 1-, 2-, and 3-NBaP-DEs indicates that the presence of a polar nitro functional group results in a shorter retention time (Fig. 3). This finding is similar to the results previously reported for the HPLC separation of the parent PAHs and nitro-PAHs [31]. On the other hand, the increase of retention time by adding an additional methyl group to the molecule (e.g. the adduct of 7-MBaP-DE vs. that of BaP-DE) is also consistent with our previous report [31]. Thus, the molecular size, the geometric shape of the molecule, and the substituted nitro and methyl groups should be factors in determining HPLC retention of the modified 3′,5′-bisphosphate deoxynucleotide.

3.4. Separation of diol-epoxide-modified 3′,5′-bisphosphate deoxynucleotide adducts derived from ambient air

Both PAHs and nitro-PAHs are contaminants present in ambient air, diesel soot extract, and other environmental sources. Since BaP, 1-NBaP, and 3-NBaP have been detected in diesel soot extract [7], it is highly possible that more bay-region-containing PAHs and nitro-PAHs are present in a variety of environmental samples. When humans are exposed to these compounds, these compounds may be enzymatically converted into the corresponding diol-epoxides. For hazard prevention, biomonitoring of their presence in the human is, therefore, timely and important. Our study indicates that the BaP-DE adduct can be separated from the other diol-epoxide adducts (Fig. 3). These results are in accordance with the findings by Pfau and Phillips [16] and by King et al. [7] that the BaP-DE is separable from the other adducts. Furthermore, our results also indicate that the diol-epoxide adducts derived from the mutagenic environmental 1-NBaP and 3-NBaP are also separable (Fig. 3). Thus, the results presented in this paper, together with those reported by others, also suggest that the ^{32}P-postlabeling-HPLC system is a potentially useful methodology for detection of environmental carcinogens that can be metabolized to diol-epoxides. Nevertheless, it is worthy to note that due to exposure to various environmental carcinogenic chemicals, a large number of chemical-modified DNA adducts are present in human tissues. It is possible that some of the diol-epoxide modified 3′,5′bisphosphate deoxynucleotide adducts may co-elute together, and may co-elute with the adducts derived from other chemicals. Therefore, it is essential to use more than one analytical technique for identification and quantitation of DNA adducts contained in human samples [34–36].

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Journal of Chromatography A, 710 (1995) 159–165

JOURNAL OF CHROMATOGRAPHY A

Review

Derivatization and chromatographic determination of aldehydes in gaseous and air samples

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Abstract

Various aldehyde derivatives were used for the determination of volatile aldehydes in gaseous or air samples in order to investigate the behaviour of aldehydes in air and their contribution to air pollution. Oxime derivatives of aldehyde are useful for gas chromatographic analysis because the reactions proceed under mild conditions and the derivatives give good separation. Aldehyde pentafluorobenzyloximes are especially superior to aldehyde 2,4-dinitrophenylhydrazones in volatility and sensitivity to GC detection. The technique was applied to the analysis of gaseous and air samples and a method for the determination of volatile aldehydes was developed. This review focuses primarily on the formation of aldehyde oximes, related reactions for GC analysis and other derivatization reactions for GC and HPLC analysis with selective detection.

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1. Introduction

Volatile aldehydes, such as formaldehyde, acetaldehyde, and acrolein, irritate the eyes and respiratory tract. These aldehydes have received attention as hazardous air pollutants. Aldehydes are present in exhaust gases during incomplete burning of organic compounds and are also formed by photochemical reaction with hydrocarbons in air. Aldehydes in air are recognized as contributors to photochemical oxidants that influence human health and plant growth.

Because of the environmental importance of

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0021-9673/95/$29.00
SSDI 0021-9673(94)01006-4

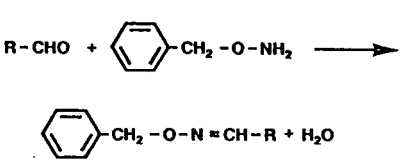
these compounds, sensitive and selective methods for the determination of volatile aldehydes in exhaust gas and/or air are needed. Recently, various derivatization methods and gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) methods for the determination of aldehydes have been reported. Derivatization is very useful in analyses for aldehydes using GC or HPLC with selective detection. This review describes (1) derivatization for sensitive GC analysis, i.e., alkyloxime methods including the pentafluorobenzyloxime method, bromination method with alkyloximes, cysteamine method and oxazolidine method, and (2) derivatization and HPLC methods and applications. We deal here particularly with selective and sensitive chromatographic methods for the determination of volatile aldehydes in gaseous or air samples.

2. Derivatization and gas chromatography

2.1. Oxime derivatization

2,4-Dinitrophenylhydrazone (DNPH) derivatives of aldehydes have been used classically in GC analysis [1–7]. However, the GC analysis of DNPH derivatives needs a high oven temperature because of the low volatility of these compounds. Oxime derivatives of volatile aldehydes show excellent volatility compared with that of DNPH derivatives.

Magin [8,9] reported a qualitative and semiquantitative GC method using benzyloxime derivatives to investigate volatile carbonyl compounds in cigarette whole smoke. The reaction procedure of aldehyde is as follows:



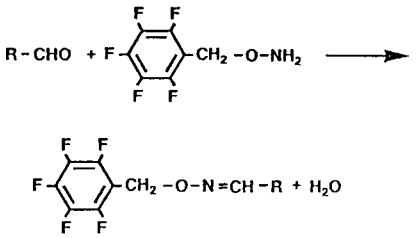
Aldehydes and ketones were trapped on silica gel, eluted with water and derivatilized with benzyloxyamine to form the corresponding oxime. The derivatives were determined by GC with nitrogen-selective detection (NPD). A short free fatty acid phase (FFAP) glass capillary column (12 m) was used for the separation of these compounds. The column oven temperature programme was from 100 to 180°C at 2°C/min. Good separation of many carbonyls was achieved. However, the method is not suitable for the determination of volatile aldehydes because the collection efficiency and detection limit were not reported.

Levine et al. [10] combined several methods to permit the collection, derivatization and determination of low-molecular-mass aldehydes in air samples. The O-benzyloxime derivatization was accomplished by using benzyloxyamine hydrochloride in methanol solution with 0.5 *M* sodium acetate buffer, and was compared with O-methyloxime derivatization as follows:

$$R\text{–}CHO + CH_3\text{–}O\text{–}NH_2 \rightarrow CH_3\text{–}O\text{–}N = CH\text{–}R + H_2O$$

The aldehyde O-benzyloximes were separated by GC. They could be detected with picogram-level sensitivity by NPD. The reaction efficiencies were over 90%. O-Methyloximes of low-molecular-mass aldehydes have high volatility. The technique permits the determination of carbonyls with widely differing volatilities and identification of these compounds from their mass spectra. The detection limit for each aldehyde in air was about 40 ppb (v/v). These methods are adequate for application to automotive exhausts and stationary sources, but not for ambient air measurements.

The O-pentafluorobenzyloxime (PFBO) method is good for the determination of trace levels of volatile aldehydes in air samples. O-Pentafuluorobenzylhydroxylamine (PFBOA) was first synthesized as a derivatization reagent for the GC of keto steroids by Nambara et al. [11]. The reagent was used for carbonyl compounds [12], and was applied to the determination of formaldehyde in clothes [13] and also to the indirect determination of uric acid in serum [14]. The reaction of aldehyde and PFBOA proceeds as follows:



Nishikawa et al. [15] applied the method to the determination of trace amounts of formaldehyde in air. A 1–5-l volume of air was collected in distilled water at a flow rate of 1 l/min. PFBOA solution was added to a portion of the absorption solution and the mixture was allowed to stand for 40 min. Formaldehyde PFBO derivative was extracted with *n*-hexane and determined by GC with electron-capture detection (ECD). Sub-ppb levels of formaldehyde in air could be determined at a sample size of 5 l. The recovery of formaldehyde in air samples was 94% and the calibration graph showed good linearity in the range 10–80 ng in 25 ml of absorption solution. A similar method was reported later by Wolfel et al. [16]. In the analysis of gaseous samples with a complex matrix, such as exhaust gas and emission gas, flame thermionic detection (FTD) or NPD is more effective.

Nishikawa et al. [17] combined a capillary column for the complete separation of aldehydes from ketones and FTD for the sensitive and selective determination of aldehyde PFBO derivatives. As a result, low-molecular-mass aliphatic aldehydes in exhaust gas or thermal degradation emissions could be determined. Aldehydes in sample gas (2–30 l) were collected by passing the gas at a flow-rate of 0.5 l/min through two impingers connected in series. A 10-ml volume of ethanolic PFBOA solution was contained in each impinger. After sampling, the absorption solution was diluted with ethanol and allowed to stand for 80 min. A 10-ml portion of the solution and 20 ml of distilled water were mixed and the mixture was passed through a Sep-Pak C_{18} cartridge. The derivatives in the cartridge were eluted with hexane and determined by GC–FTD. Formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde were determined selectively without interference from ketones. The determination limits were 14 ppb for formaldehyde, 10 ppb for acetaldehyde, 67 ppb for propionaldehyde and 38 ppb for butyraldehyde with 30 l of sample gas. The reaction efficiencies of these aldehydes were over 88% and the collection efficiencies were over 89%.

The PFBO method was applied to the determination of saturated and unsaturated aliphatic aldehydes in environmental water [18], and aldehyde PFBO derivatives were identified by GC–MS. Takino and Yamaguchi [19] reported sample preparation of aldehydes by solid-phase extraction with PFBO derivatization to determine trace amounts of aldehydes in water.

2.2. Bromination of unsaturated aldehyde oxime

Acrolein, a typical unsaturated aldehyde, is an irritant of the skin, eyes and nasopharyngeal membranes. A spectrophotometric method with 4-hexylresorcinol [20] and a fluorimetric method with *m*-aminophenol [21,22] have commonly been used for the determination of acrolein. However, these methods show poor selectivity. Although a GC method based on bromination of acrolein has been reported [23,24], the brominated product of acrolein was unstable and the reproducibility was poor. Nishikawa et al. [25,26] established an improved method based on the bromination of acrolein O-methyloxime to determine trace amounts of acrolein in environmental samples. The reaction procedure is as follows:

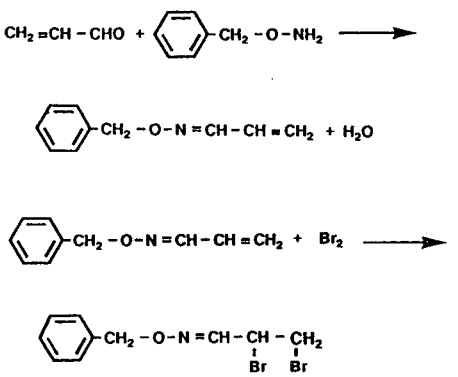
$$CH_2=CH-CHO + CH_3-O-NH_2 \rightarrow CH_3-O-N=CH-CH=CH_2 + H_2O$$

$$CH_3-O-N=CH-CH=CH_2 + Br_2 \rightarrow CH_3-O-N=CH-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

The reaction proceeds at room temperature. The reaction product was identified as 2,3-dibromopropionaldehyde O-methyloxime by GC–MS

measurement. The overall reaction efficiency was 92%. The detection limit (signal-to-noise ratio = 2) was 0.4 ng/ml of acrolein in rain water by GC–ECD and the recovery obtained was in the range 90–101%. The method was applied to the determination of acrolein in air samples, i.e., urban air, air in a road tunnel and automobile exhaust [26]. Acrolein in sample gas (3–40 l) was collected at a rate of 0.5–1.0 l/min in two impingers containing ethanol. The collection efficiency was >81%. No interference from co-existing ions, such as chloride, nitrate, nitrite and sulphate ion, was found. The overall detection limit of acrolein in air was about 0.5 ppb with a 40-l air sample.

Another method for the bromination of unsaturated aldehyde oximes was developed. Bromination of the O-benzyloximes was investigated to determine acrolein and crotonaldehyde simultaneously [27]. This method was preferable to the bromination of O-methyloxime derivatives for the determination of acrolein and crotonaldehyde because the reaction efficiency (98% for acrolein and 88% for crotonaldehyde) was higher. The reaction for acrolein proceeds as follows:



The method was applied to the determination of acrolein and crotonaldehyde in automobile exhaust gas, and was suitable for the simultaneous determination of these compounds without any interferences, as shown in Fig. 1. The detection limits were 13 ppb for acrolein and 8 ppb for crotonaldehyde in air samples. The recoveries of these compounds from standard

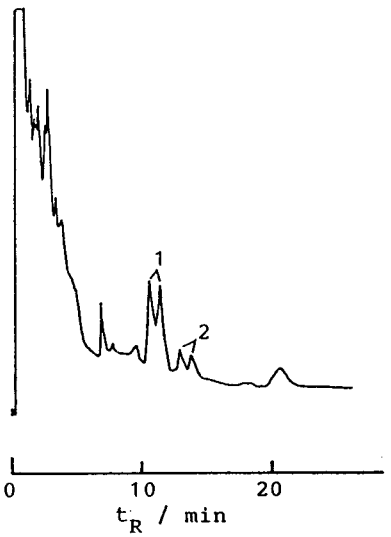


Fig. 1. Typical gas chromatogram of automobile exhaust gas sample. Peaks: 1 = acrolein (*syn/anti* forms); 2 = crotonaldehyde (*syn/anti* forms).

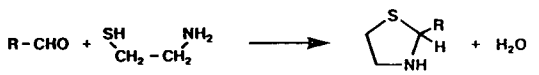
gases were >90% and the relative standard deviations were <5%.

2.3. Other methods

Kennedy and Hill [28] developed a reagent-coated sampling technique for the determination of formaldehyde. Formaldehyde in air reacted with N-benzylethanolamine coated on Chromosorb 102 sorbent to produce 3-benzyloxazolidine. The product was eluted from the sorbent with isooctane determined and by GC–FID. The determination range was 0.55–4.71 mg/m^3 of formaldehyde. The method seems not to be suitable for the determination of formaldehyde in ambient air because the sensitivity was low. A similar approach was demonstrated for acrolein determination [29]. Acrolein in an air sample was collected with 10% 2-(hydroxymethyl)piperidine coated on XAD-2 sorbent to produce 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane. The derivative was eluted from the sorbent with toluene and determined by GC with nitrogen-specific detection. The determination range was 0.13–1.50 mg/m^3 of acrolein. The overall relative standard deviation was 11.1%.

Dimethone derivatives of aldehyde were investigated. Dimedone (5,5-dimethyl-1,3-cyclohexanedione) is a specific reagent for aldehydes [30–32]. Peltonen et al. [33] reported a method for the separation and determination of the dimedone derivatives of aldehyde by capillary GC–ECD. The recoveries of acetaldehyde and *m*-tolualdehyde were >73%. Eight aldehydes were detected in an air sample from thermally degraded epoxy plastic. Acetone, acrolein and propionaldehyde were successfully separated with this method.

Hayashi and co-workers [34,35] developed a method for the determination of formaldehyde and methyl glyoxal in foods and beverages. The method is well known as the cysteamine method. Volatile aliphatic aldehydes react with 2-aminoethanethiol (cysteamine) to form thiazolidine compounds [36]. The reaction proceeds as follows:



The method has the following characteristics, as described by Yasuhara and Shibamoto [36]: only one derivative is formed from one aldehyde; the reaction proceeds rapidly under mild conditions; derivatives can be separated well with a capillary column; and derivatives can be detected selectively with NPD. Yasuhara and Shibamoto reported the physical properties, mass spectra and NMR spectra of thiazolidines [37], and applied the method to the determination of formaldehyde in air samples [38]. The reaction efficiency of formaldehyde with cysteamine was >90.5%. The detection limit was 5.8 pg of formaldehyde and the recovery efficiency of trace gaseous formaldehyde in air was >90%. They reported that the cysteamine method could be used in the range 1 ppb–10 000 ppm of formaldehyde in air and also reported analytical data for aldehydes and ketones in the headspace of heated pork fat [39]. Recently, the cysteamine method was applied to the determination of C_1–C_6 aldehydes in automobile exhaust using GC–NPD by Yasuhara and Shibamoto [40]. The chromatogram showed a good separation of these aldehydes without interferences.

Yasuhara et al. [41] developed a method using N-methylhydrazine to determine acrolein in air. Acrolein reacts with N-methylhydrazine to form 1-methyl-2-pyrazoline. The derivative was determined by GC–NPD. The calibration graph showed good linearity in the range 150 ng–150 μg in 10 ml of dichloromethane. The detection limit was 5.9 pg of acrolein and the recovery efficiency of gaseous acrolein was >98%. The method was applied to the headspace of corn oil and to the exhaust air from a kitchen ventilator [42].

Kashihira et al. [43] reported a simple method for the determination of acrolein in gas samples by GC with chemiluminescent detection. The method is based on the chemiluminescence reaction between ozone and ethylene, which is produced via catalytic decomposition of acrolein on reduced copper in a stream of hydrogen. The determination limit was about 50 ng of acrolein. Acrolein in automobile exhaust could be determined without interference from other hydrocarbons.

3. Derivatization and high-performance liquid chromatography

3.1. DNPH method

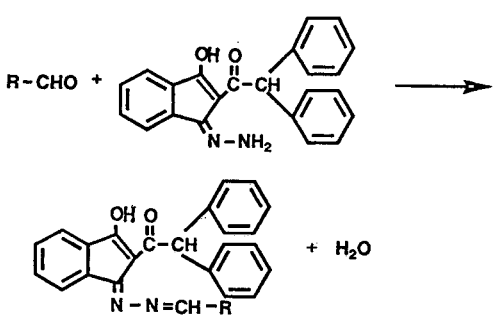
DNPH derivatives of aldehydes are often used in HPLC analyses. The derivatives show strong absorbance of UV radiation. The separation of aldehydes and ketones of identical molecular mass was achieved by HPLC with a reversed-phase μBondapak C_{18} column [44]. One of the sampling techniques for aldehydes in air samples is the impinger method, which uses an absorbing solution containing the reagent 2,4-dinitrophenylhydrazine [45–47]. On the other hand, an absorption column coated with the reagent was used to trap trace levels of aldehydes in air samples. Beasley et al. [48] used a convenient silica column coated with the reagent and hydrochloric acid to determine formaldehyde in air. Grosjean and Fung [49] used a glass cartridge packed with glass beads impregnated with the reagent in phosphoric acid-saturated poly-

(ethylene glycol) to determine volatile aldehydes in air samples. Kuwata et al. [53] applied a Sep-Pak C_{18} cartridge coated with the reagent and phosphoric acid to the determination of C_1–C_4 aliphatic aldehydes in air. The recoveries of the derivatives from the cartridge were >95% and the determination limits were sub-ppb levels of aldehydes for a 100-l air sample. The relative standard deviation was <8.7%. The method may be useful for the routine analysis of air samples.

Lipari and Swarin [51] used a 2,4-dinitrophenylhydrazine-coated Florisil cartridge to determine formaldehyde in air. The determination limit was ppb levels of formaldehyde. Olson and Swarin [52] reported a method for DNPH derivatives of carbonyl compounds by LC–MS. However, in these DNPH methods the reagent blank and contamination from the laboratory atmosphere and water used in analysis must be considered. Karst et al. [53] investigated the interferences of nitrogen dioxide in sampling using a 2,4-dinitrophenylhydrazine-coated solid sorbent. They showed that the products of the nitrogen dioxide–2,4-dinitrophenylhydrazine reaction were 2,4-dinitrophenylazide and 2,4-dinitrochlorobenzene and that only large amounts of nitrogen dioxide would interfere in the determination of formaldehyde.

3.2. Other methods

Swarin and Lipari [54] determined formaldehyde and other aldehydes in automobile exhaust by HPLC with fluorescence detection. The reagent used was 2-diphenylacetyl-1,3-indandione-1-hydrazone, which forms fluorescent derivatives with aldehydes. The reaction proceeds as follows:



The sample collection and derivatization were performed in impingers containing the reagent solution. The mean collection efficiency for aldehydes was 96% and the detection limits were from sub-ppb to ppb levels of aldehydes in the exhaust. Osaki et al. [55] determined acetaldehyde and acrolein in environmental and waste water by HPLC with this reagent. Groemping and Cammann [56] also used this reagent to determine ppb levels of formaldehyde in the atmosphere.

Suzuki [57] reported an HPLC method for the determination of aliphatic aldehydes using cyclohexane-1,3-dione as a fluorescent derivatizing reagent. The determination limit was about 30 pg of each aldehyde. The method was applied to the determination of aldehydes in whisky and it should be applicable to the trace determination of aldehydes in rain water.

Nondek and co-workers [58,59] developed an HPLC technique with fluorescence and chemiluminescence detection using dansylhydrazine [5-(dimethylamino)naphthalene-1-sulfohydrazide]. Sample collection was performed in microcartridges containing porous glass beads coated with the reagent and on-line analysis was used. The detection limits were 0.1 ppb for formaldehyde and acetaldehyde in air. This method was applied to the measurement of sub-ppb levels of aldehydes in a forest atmosphere.

Acknowledgement

We are grateful to Dr. Akio Yasuhara, National Institute for Environmental Studies, Japan, for constructive advice.

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Journal of Chromatography A, 710 (1995) 167–173

JOURNAL OF CHROMATOGRAPHY A

Application of solid sorbents to the trace analysis of alkyl esters of acrylic acid in air

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Abstract

Ten sorbents (Tenax GC, Porapak R and S, Chromosorb 102 and 105, DVB–1,4-DMN, Separon SE, CHN and SDA, and Synachrom E5) were tested for (pre)concentration of acrylates present in air. From a study on the applicability and the conditions to be used for both thermal desorption and GC separation, as well as evaluation on the factors influencing these two steps, optimum conditions for both concentration and separation have been estimated. Practical applications of the method for the analysis of the working atmosphere are demonstrated.

1. Introduction

Preconcentration is a basic step in the trace analysis of organic substances in the surrounding air. Trapping of the substances of interest on solid sorbents, especially on porous chromatographic polymers, is of considerable importance [1]. A survey of sorbents used for this purpose has been published by Namieśnik [2]. Based on hygiene criteria, methods have to be developed for the determination of gaseous pollutants in the working environment within the concentration range either of 10^{-3}–10^{-7} g m^{-3}, or of 1–10^{-4} g m^{-3}, depending on the type of the pollutant.

For the selection of the sorbent to be used for the preconcentration of gaseous organic contaminants, a high sorption capacity, which determines the maximum sample volume, is not the only criterion. Factors influencing both the course of the sorption process together with the method and results of the analytical determination should also be taken into account [2,3].

Recently, gas chromatography combined with mass spectrometry has become the method of choice for the analysis of acrylic acid esters, when preconcentration is needed [4–7]. The effect of the conditions of the exposure to acrylates and the sorption capacities of Tenax GC [8,9], other polymer sorbents [10,11] and silica gel [12,13] have been studied in actual working environments. Moreover, the determination of low concentrations of acrylic acid esters in air, trapped on chromatographic sorbents covered with a liquid phase, has been described in Refs. [14–17]. Recently a new sorption–derivatization–concentration technique has been described for C_1–C_8 acrylic acid esters [10].

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0021-9673/95/$09.50
SSDI 0021-9673(95)00004-6

2. Experimental

2.1. Apparatus

A Chrom 5 gas chromatograph equipped with a flame ionization detector (Laboratorní přístroje, Prague, Czech Republic), an Apex chromatographic integrator (DataApex, Prague, Czech Republic), a glass-packed column, 2.5 m × 3 mm I.D., with 10% SP-1000 on Supelcoport 80–100 mesh (Supelco, Bellefonte, PA, USA), a 50-μl gas-tight microsyringe (Hamilton Reno, NE, USA), Series 222 personal air sampler/low-flow pumps (SKC, PA, USA), thermal desorption equipment (University Pardubice) [18], glass sample tubes (61 × 3 mm I.D.), and U-shaped glass test columns, 3 mm I.D., were used throughout this study.

2.2. Chemicals

The specifications and suppliers of the sorbents and chemicals used are as follows: Tenax GC, 60–80 mesh, Chromosorb 102, 100–120 mesh, Chromosorb 105, 80–100 mesh (Serva Feinbiochemia, Heidelberg, Germany); Porapak R, 80–100 mesh, Porapak S, 120–150 mesh (Waters, Milford, MA, USA); DVB–1,4-DMN copolymer of divinylbenzene with 1,4-di-(methacryloyloxymethyl)naphthalene [19], 200–250 μm (Institute of Chemistry, M.C.S. University, Lublin, Poland); Separon SE, 200 μm, Separon CHN, 200–300 μm, Separon SDA, 90–125 μm (Tessek, Prague, Czech Republic); Synachrom E5, 125–160 μm (Lachema Brno, Czech Republic).

The acrylates were synthesized at the Faculty of Chemical Technology, University of Pardubice.

2.3. Procedure

The U-shaped test columns (TC) and the sample tubes (ST) of identical I.D. differed only in their lengths. The mass of the sorbent filling and the length of its bed are given in Table 1. All sorbents were conditioned. Their thermal stability was investigated by recording the ionization current at the programmed increasing temperature. The maximum sample volumes (V_{max}) of the tested sorbents were determined by an indirect method [3,18,20,21], based on the specific retention volumes and the number of theoretical plates, followed by extrapolation and calculation. The tested acrylates were fed as calibrated vapours using a gas-tight syringe.

Retention volume measurements were performed by determination of the number of theoretical plates using the test U-column; the height equivalent to the theoretical plate was calculated as well. The plate number of the trapping tube thus found was confirmed actually on the trapping tube at 50°C, a flow-rate of 60 ml min^{-1} and a load of $4.5 \cdot 10^{-7}$ g g^{-1}.

Table 1
Parameters of test columns and sampling tubes, thermal stability of sorbents, and desorption temperature, BA specific retention volumes at TD, extrapolated specific retention volumes and maximum BA sample volumes at 20°C

	TC m (g)/l (cm)	ST m (g)/l (cm)	TS/TD (°C)	V_g^{TD} (1 g) BA (ml)	V_g^{20} (1 g) BA (l)	V_{max}^{20} (1 g) BA (l)	V_{max}^{20} (ST) BA (l)
Tenax GC	0.7170/61.8	0.0661/5.7	>380/200	9.3	1638.9	1583.4	71.2
Porapak R	1.2847/60.5	0.1210/5.7	250/200	99.7	6669.4	6367.3	591.1
Porapak S	0.9540/37.6	0.1446/5.7	250/200	79.3	2151.7	2011.3	220.6
Chromosorb 102	1.5633/57.0	0.1562/5.7	235/200	46.8	1185.4	1122.9	139.7
Chromosorb 105	1.5087/59.0	0.1457/5.7	235/190	91.8	1475.1	1307.5	130.0
DVB–1,4-DMN	1.1395/61.7	0.1053/5.7	250/200	36.0	2495.2	2321.9	166.5
Separon SE	1.5004/53.2	0.1608/5.7	230/190	19.8	1146.8	1032.6	118.4
Separon CHN	0.6005/48.0	0.0713/5.7	225/190	86.3	4828.8	4633.6	223.0
Separon SDA	1.3400/62.0	0.1231/5.7	220/190	21.2	509.4	479.7	43.8
Synachrom E5	0.59225/40.2	0.0840/5.7	195/170	313.3	37637.0	36388.0	2232.3

For trapping of acrylates in real samples from the surrounding air, Tenax GC (0.0661 g) and Separon SE (0.1608 g) were used at a flow-rate of 20 ml min^{-1}. The sample volume was 250–750 ml, at 20 ± 2°C, and the desorption temperature was 190°C.

3. Results and discussion

The sorbents were selected on the basis of experience and literature data with respect to parameters influencing the sorption capacity and their desorption properties, i.e. particularly with respect to polarity, specific surface area and chromatographic background.

From the many commercially available sorbents, Tenax GC was selected, being the most frequently used sorbent with a low chromatographic background, useful for thermal desorption, together with Porapak R and S, Chromosorb 102 and 105 and DVB–1,4-DMN. The locally produced sorbents Separon SE, CHN and SDA and Synachrom were also investigated.

The thermal stability of the sorbents is given in Table 1. It was verified that, with insufficient conditioning, the plot of $\log V_g$ versus the reciprocal of the absolute temperature is not linear and the values of V_g are lower; at the same time the level of the chromatographic background is higher.

For preliminary testing of the properties of the sorbents used, butyl acrylate (BA) was selected from its homologous series. Retention volumes were measured at temperatures between 120 and 220°C (Fig. 1). By extrapolation to the sampling temperature, i.e. 20°C, values for the specific retention volume, V_g^{20}, were obtained. Comparison of the sorbents in terms of V_g^{20} as measured under comparable conditions for flow-rate and sorbent loading is given in Table 1.

As the specific retention volume is significantly affected by the quantity of gaseous sorbate, a factor known as loading of the sorbent, Z (g g^{-1}), was applied, expressing the mass of a sorbate sorbed by the unit mass of the sorbent. The retention volumes were measured on all

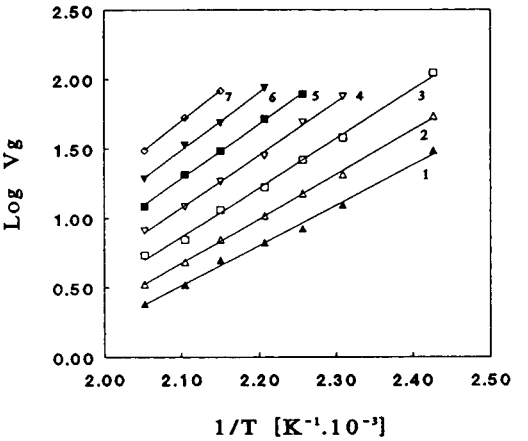

Fig. 1. Plot of $\log V_g$ versus the reciprocal of the absolute temperature for methyl acrylate (1), ethyl acrylate (2), propyl acrylate (3), butyl acrylate (4), pentyl acrylate (5), hexyl acrylate (6) and heptyl acrylate (7) on Separon SE.

sorbents at different sample volumes and, consequently, for different quantities of sorbate in the gas phase (Figs. 2 and 3, Table 2).

The results show that the V_g^{20} values are almost constant up to $Z = 10^{-5}$ g g^{-1}; however, with Z increasing beyond this value the specific retention volume on all sorbents significantly decreases (Fig. 3).

The dependence of $\log V_g$ on the boiling points of the homologous series of acrylates is linear

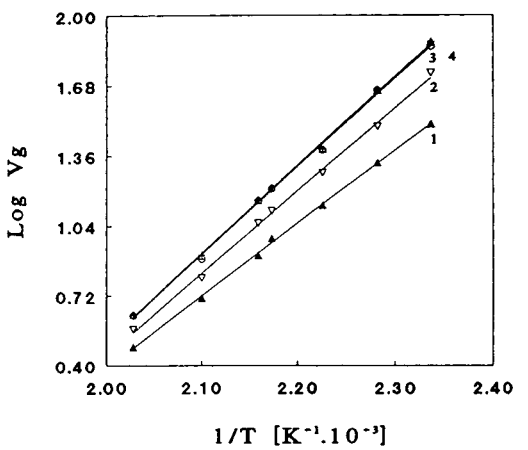

Fig. 2. $\text{Log } V_g = AT^{-1} + B$ for BA on Tenax GC as a function of sorbent loading factor (Z, g g^{-1}). Z-values: $3.80 \cdot 10^{-4}$ (1), $1.27 \cdot 10^{-4}$ (2), $1.27 \cdot 10^{-5}$ (3) and $8.16 \cdot 10^{-7}$ (4).

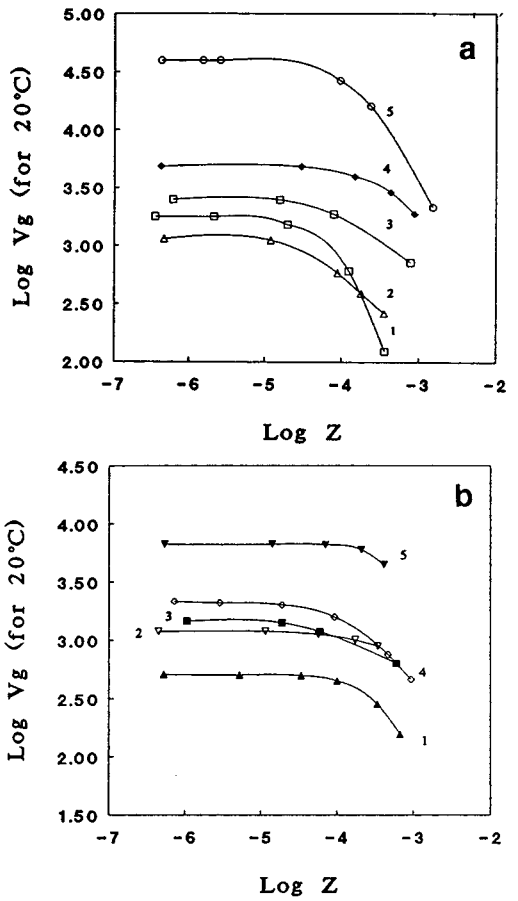

Fig. 3. (a) BA specific retention volume V_g^{20} as a function of sorbent loading factor Z for test sorbents Tenax GC (1), Separon SE (2), DVB–1,4-DMN (3), Separon CHN (4) and Synachrom E5 (5). (b) BA specific retention volume V_g^{20} as a function of sorbent loading factor Z for test sorbents Separon SDA (1), Chromosorb 102 (2), Chromosorb 105 (3), Porapak S (4) and Porapak R (5).

(correlation coefficient $r > 0.9965$), and this can be used to check and estimate the retention volume of the sorbents. The dependencies for Tenax GC, Separon SE and Separon CHN are shown in Fig. 4.

Maximum sorption is obtained at the "optimum linear flow-rate". The minimum of the Van Deemter dependence corresponds to low flow-rates and in all sorbents investigated it was less than 5 cm s^{-1}. Flow-rates in the range 10–100 ml min^{-1} did not affect the retention volumes significantly. The selected flow-rate of 60 ml min^{-1} permitted measurements under comparable conditions for all sorbents investigated, also for the higher members of the homologous series of acrylates, which had very long retention times with low flow-rates.

For the determination of V_{max}, a method based on measuring V_g and n [2,20–22] was selected. V_{max} values were determined for a completely filled sampling tube (ST) and for identical amounts of the sorbents (1 g; Table 1).

The number of theoretical plates of the sampling tube [n(ST)] and of the column containing 1 g of sorbent [n(1 g)] was determined in a similar way. First of all, n was determined for the test column [n(TC)], followed by measuring V_g^{20}, and the height equivalent to the theoretical plate, H. On this basis [n(ST)] and [n(1 g)] values were determined.

The number of theoretical plates of the sampling tube [n(ST)], with EA and BA as samples on Tenax GC and Separon SE, was verified by means of measurements on a bed of sorbent corresponding to that of the sampling tube. When identical conditions (sorbent load and carrier gas flow) were employed in the two procedures, the corresponding mean values for n(ST) showed differences within the limits of 10 and 20%.

To verify the calculated V_{max} values the maximum sample volumes of the sampling tube were measured using direct gas chromatographic measurement in the systems Tenax GC vs. EA and Separon vs. EA. Measurement was carried out at 50°C, because at lower temperatures chromatography was very slow due to the long retention times, and it was not possible to determine the exact breakthrough point. The calculated maximum sample volume for Tenax GC was 400 ml, as compared to a measured value of 535 ml; for Separon SE these values were 950 and 850 ml, respectively. If the maximum sample (breakthrough) volume is defined as the volume at which the sorbate starts to penetrate through the sorbent bed, then at a 10% breakthrough for EA the volume passed through corresponds to 1.7 times the V_{max} for Tenax GC and 1.5 times the V_{max} for Separon SE. Brown [10] gives a safe

Table 2
Number of plates of test column n(TC), height equivalent to a theoretical plate H, number of plates of sampling tube n(ST), number of plates of sampling tube with 1 g of sorbent n(1 g), their maximum sample volumes V_{max}(ST), V_{max}(1 g) at 20°C, specific retention volume V_g^{20} and these parameters as a function of sorbent loading Z for BA

Z (g g^{-1})	n(TC)	H (mm)	n(ST)	n(1 g)	V_g^{20} (l)	V_{max}(ST) (l)	V_{max}(1 g) (l)
Tenax GC							
$3.56 \cdot 10^{-7}$	288.2	2.14	26.6	402.0	1638.9	71.2	1583.4
$2.12 \cdot 10^{-6}$	286.5	2.16	26.4	399.6	1632.5	70.7	1576.7
$2.51 \cdot 10^{-5}$	257.8	2.40	23.8	359.6	1515.4	63.4	1454.8
$1.25 \cdot 10^{-4}$	226.2	2.73	20.9	315.5	606.7	24.2	577.8
$3.76 \cdot 10^{-4}$	197.9	3.12	18.2	276.0	123.0	4.6	116.1
Separon CHN							
$4.25 \cdot 10^{-7}$	214.2	2.24	25.4	356.7	4828.8	223.0	4633.6
$3.00 \cdot 10^{-6}$	186.9	2.57	22.2	311.2	4810.0	211.8	4577.0
$1.50 \cdot 10^{-4}$	156.3	3.07	18.6	260.3	3950.1	161.9	3713.8
$4.49 \cdot 10^{-4}$	123.7	3.88	14.7	206.0	2879.8	105.4	2660.0
$8.99 \cdot 10^{-4}$	92.1	5.21	10.9	153.4	1872.7	56.6	1685.2

sampling volume per gram of Tenax GC for MA (32 l) and EA (120 l). The values measured in our laboratories are lower: 22.7 l for MA and 80 l for EA (Table 3).

For comparison of sorbents with respect to their suitability for thermal desorption, specific retention volumes were determined for BA at the recommended desorption temperature, which ranged from 30 to 50°C below the value of the thermal stability (Table 1). Before heating is started, air should be removed from the sorbent since, in the presence of oxygen, rapid degradation of otherwise thermally stable polymer sorbents occurs. The efficiency of desorption depends not only upon the type of the desorbed substances, but also on the quantity of analytes entrapped in the sorbent bed.

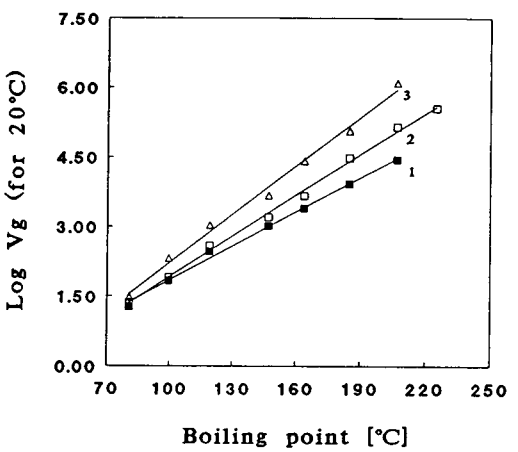

Fig. 4. Log V_g for Separon SE (1), Tenax GC (2) and Separon CHN (3) as a function of boiling point.

For liberating acrylates concentrated upon Synachrom E5, carbon disulphide desorption is preferable because of the high chromatographic background at thermal desorption. By using the method described, concentrations of 2-ethylhexyl acrylate [V_{max}^{20}(ST) >2232.3 l] in the air above unhardened floors (20–50 mg m^{-3}) and above hardened and mature floors (0.005–0.060 mg m^{-3}) were estimated. The relative standard deviation of the determination in five parallel samples was 15%.

The method was used in practice for checking ethyl acrylate concentrations in monomer storage facilities. With Tenax GC and Separon SE and thermal desorption, concentrations varying between 0.01 and 0.48 mg m^{-3} were obtained under various trapping conditions.

Sorption of acrylates from gas-phase trapping tubes filled with polymer sorbents with subsequent thermal desorption is also suitable for

Table 3
Maximum sample volumes of acrylates for 1 gram of sorbent and sampling tube; the upper value is V^{20}_{max}(1 g) (l) and the lower value is V^{20}_{max}(ST) (l)

	MA	EA	PrA	BA	PeA	HexA	HepA	OcA
Tenax GC	22.7	80.0	386.2	1583.4	4540.1	30075	139916	350722
	1.2	4.1	18.9	71.2	196.4	1243.0	5720.7	13754
Separon SE	18.7	64.4	293.8	1032.6	2458.9	8204.2	27385	
	2.3	8.2	35.2	118.4	252.9	815.4	2555.8	
Separon CHN	30.3	207.9	1075.6	4633.6	25741	116219		
	1.7	11.7	58.7	223.0	1165.2	4745.7		

Experimental conditions: $F = 60$ ml min^{-1}, Z (10^{-7}; 10^{-6}) g g^{-1}.

head-space analyses of aqueous acrylates solutions.

Acknowledgements

This work was accomplished with the financial support of the Grant Agency of the Czech Republic, reg. number 203/93/2157.

List of symbols and abbreviations

BA butyl acrylate
EA ethyl acrylate
F flow-rate (ml min^{-1})
H height equivalent to a theoretical plate (mm)
HepA heptyl acrylate
HexA hexyl acrylate
l length (cm)
m mass of sorbent (g)
MA methyl acrylate
n number of theoretical plates
OcA octyl acrylate
PeA pentyl acrylate
PrA propyl acrylate
ST sampling tube
T temperature (K)
TC test column
TD maximum recommended desorption temperature (°C)
TS thermal stability (°C)
V^{20}_{g} specific retention volume at 20°C (l)
V^{20}_{max} maximum sample (breakthrough) volume at 20°C (l)
Z sorbent loading factor (g g^{-1})

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Journal of Chromatography A, 710 (1995) 175–180

JOURNAL OF CHROMATOGRAPHY A

Laboratory validation of a diffusive sampler for the determination of glutaraldehyde in air

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Abstract

A diffusive sampling method has been validated for determination of glutaraldehyde in air. The sampler consists of a filter impregnated with 2,4-dinitrophenylhydrazine, mounted in a polypropylene housing. The uptake rate was determined to be 11.8 ml/min, with a relative standard deviation of 13%. The effect of glutaraldehyde concentration, sampling time and relative humidity on uptake rate was undetectable or small. The temperature effect was significant, about 1.5%/°C. The samplers are stable for at least two weeks at 22°C. The detection limit is about 0.03 mg/m^3 for a 15-min sample.

1. Introduction

Glutaraldehyde is used in the drug and polymer industry, as a fixative for tissues, as a tanning agent in the leather industry and as a cold sterilizer for medical equipment. The substance is irritating to the respiratory tract, eyes and skin and can cause allergic contact dermatitis [1]. Occupational exposure limits are low because of health effects. The current Swedish ceiling value as well as the ceiling value of the American Conference of Governmental Industrial Hygienists (ACGIH) is 0.8 mg/m^3 [2,3].

Glutaraldehyde in air can be sampled by passing the air through a liquid absorber, but impingers or gas wash bottles makes personal sampling laborious. A solid sorbent would be preferable for field measurements.

For pumped sampling of glutaraldehyde, various adsorbents, such as alumina [4] or XAD-4 [1], have been used but the samples are not stable and have to be analysed the same day. The use of 2,4-dinitrophenylhydrazine (DNPH) as chemosorbent gives a stable derivative that allows selective and sensitive analysis with HPLC and UV detection. For pumped sampling of glutaraldehyde, DNPH-coated XAD-2 [5] or DNPH-coated glass-fiber filters have been used [1].

In recent years, diffusive sampling has become important as an efficient alternative to pumped sampling in occupational hygiene [6]. The theory of diffusive sampling is described by Fick's first law, i.e.

$$m/t = DA(C - C_0)/L$$

where m = mass collected on the sorbent (ng); t = sampling time (s); D = diffusion coefficient (cm^2/s); A = cross sectional area of the opening of the monitor (cm^2); C = external concentration (ng/cm^3 = mg/m^3); C_0 = concentration of the analyte above the surface of the sorbent (ng/

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0021-9673/95/$09.50
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$cm^3 = mg/m^3$); L = length of the diffusive zone of the monitor (cm). With an ideal adsorbent or a chemosorbent with no reverse reaction the assumption can be made that $C_0 = 0$, which reduces the Fick's law relationship to:

$$m/t = DAC/L = SC$$

where S = sampling rate, DA/L (cm^3/s). The diffusion coefficient (D) is a physical parameter of the sampled analyte and independent of the sampler construction whereas A and L are parameters associated with the sampler construction and independent of analyte. The sampling rate can be theoretically calculated from the diffusion coefficient and the geometry of the sampler, but these theoretical values often differ from measured values. An experimentally determined sampling rate is calculated after analysis of diffusive samplers exposed in atmospheres of known concentration.

The most important protocol describing how to test a diffusive sampling method has been proposed by the European Committee for Standardisation (CEN) [7]. This protocol describes how tests should be performed to examine effects on sampling rate from parameters such as sampling time, concentration, relative humidity, temperature, storage, wind velocity, etc. These tests must be performed under laboratory conditions with accurate control of the above-mentioned parameters.

We have previously reported the development of a diffusive sampler, designed to contain a reagent-coated filter for the sampling of reactive compounds [8]. The sampler, with a DNPH-coated filter, has been validated for formaldehyde [9]. It has also been validated for sampling of primary and secondary amines with 1-naphthyl isothiocyanate-impregnated filter [10,11]. We have now validated the sampler for the determination of glutaraldehyde with the use of DNPH-impregnated filters.

2. Experimental

2.1. Diffusive sampler

The diffusive sampler is shown in Fig. 1. The housing, measuring 60 × 30 × 5 mm, is made of polypropylene. The impregnated filter, 20 × 45 mm, is placed beneath a 2.9-mm thick screen of the same size. Within an area 20 × 20 mm, the screen has 112 holes with a diameter of 1.0 mm. The filter part beneath the holes is used for sampling (sampling filter) and the other half is used to quantitate the filter blank (control filter). The tape is marked into the two sections by a small ridge on the back of the screen plate. A sliding cover is used to seal the holes when the sampler is not in use. The sampler is available from GMD Systems (Hendersonville, PA, USA).

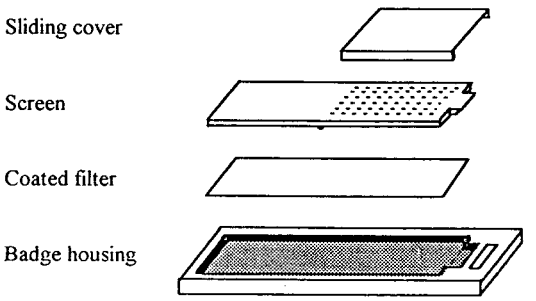

Fig. 1. Diffusive sampler for reactive compounds.

2.2. Chemicals

Solvents used for the HPLC analysis were acetonitrile (HPLC grade, Rathburn, Walkerburn, UK) and water (purified by use of Milli-RQ system, Millipore, Bedford, MA, USA). 2,4-Dinitrophenylhydrazine (DNPH) (Fluka p.a.) was recrystallized twice with 4 *M* HCl. For coating filters, phosphoric acid (Merck, p.a.), glycerol (May and Baker, p.a.), ethanol (99.99%) and acetonitrile (Rathburn, HPLC grade S) were used. For the dynamic generation, glutaraldehyde (TAAB, 24.8%, purified for electron spectroscopy, Reading, UK) was used. Glutaraldehyde–2,4-DNPH was prepared from DNPH, glutaraldehyde and concentrated HCl and recrystallized twice from ethanol [5].

2.3. Filters for diffusive sampling

A solution for coating the filters was made from 160 mg recrystallized DNPH, 0.3 ml con-

centrated phosphoric acid, 0.7 ml 20% glycerol in ethanol and 20 ml acetonitrile. Glass fiber filters (2 × 2 cm), were cut from round filters (Type AE, 0.3 μm pore size, diameter 25 mm, SKC, PA, USA). These were then dipped into the coating solution and allowed to dry on a glass surface. One filter was placed under the sampling part of the sampler and another under the control part.

2.4. Reference method

As a reference method, pumped sampling with a 13-mm glass-fiber filter impregnated with DNPH was used. This method has been described previously [12].

2.5. Generation of glutaraldehyde

The glutaraldehyde was diluted in water to obtain concentrations ranging from 6.4 to 32 mg/ml. These solutions were injected with a syringe pump (Carnegie Medicine, Stockholm, Sweden) into a glass nebulizer (J.E. Meinhard Assoc., CA, USA). The syringe pump flow varied from 2 to 10 μl/min and the air flow though the nebulizer was 0.9 l(N)/min. The aerosol from the nebulizer was mixed with air (5 l(N)/min) and evaporated in an evaporation chamber with an internal volume of about 0.5 l (Fig. 2.) [13]. The air mixture was then further diluted and transported to an exposure chamber that has been described earlier [12]. The air flow in the exposure chamber was 40 l/min. The air was controlled in respect of relative humidity and temperature. The wind velocity in the exposure chamber was 0.3 m/s for all experiments.

2.6. Sample analysis

The glutaraldehyde–DNPH was eluted from the filter by shaking for 1 min with 2.0 or 3.0 ml acetonitrile. A volume of 10 μl was injected into the liquid chromatograph. An HPLC system consisting of two Waters M-6000 A pumps, a Waters M-710 B auto sampler and a Shimadzu adsorbance detector was used. The system was controlled from a computer with a Waters Maxima data system which also served as the tool for evaluating the chromatograms. The column was a Cosmosil 5 NPE Waters 4.6 × 150 mm (Nacalai Tesque, Kyoto, Japan). The mobile phase was 80% acetonitrile in water and the flow-rate was 0.8 ml/min. The hydrazone was detected at 365 nm.

The glutaraldehyde hydrazone can exist as three different isomers (*cis–cis*, *cis–trans* and *trans–trans*). From the analysis, two of these can be seen with a major isomer of about 85–90% of the total area of the isomers (Fig. 3.). In a fresh standard solution the major isomer is about 90% or more of the total area, but decreases to about 85% after storage. As the relation between the peaks can alter, both have to be taken into account in the analysis. The extinction coefficient at 365 nm for different low molecular aliphatic dinitrophenylhydrazones are about the same which gives the assumption that the extinction coefficients of the glutaraldehyde–hydrazone isomers are equal. This assumption and the fact that two peaks have to be summed up can give some uncertainty to the method, but this is within the measured overall uncertainty of the method.

The analytical system detection limit of the main peak was about 70 pg (signal-to-noise ratio

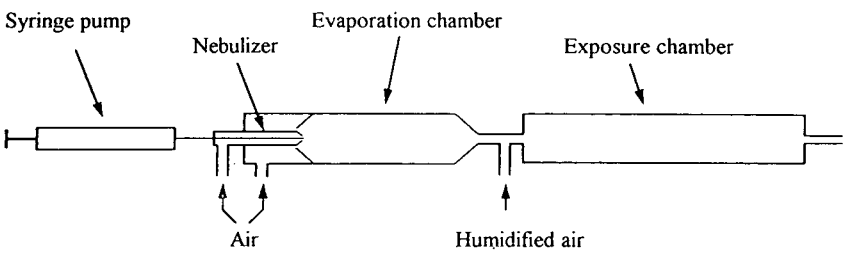

Fig. 2. Evaporation chamber with nebulizer for generation of gaseous glutaraldehyde.

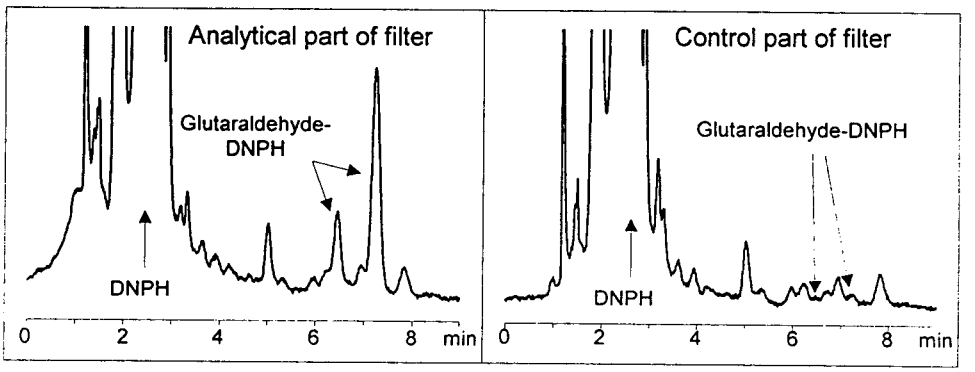

Fig. 3. HPLC chromatogram showing glutaraldehyde–DNPH from a diffusive sampler exposed to 0.08 mg/m^3 glutaraldehyde for 8 h. The concentration in the analytical part of the filter was 1.08 μg/ml and in the control part 0.053 μg/ml of glutaraldehyde–DNPH corresponding to 0.47 and 0.023 μg glutaraldehyde per sample, respectively.

3:1). However, because of isomers and impurities, the smallest detectable amount for the method was about 5 ng glutaraldehyde per sample.

3. Results and discussion

The diffusive sampler was validated according to the protocol proposed by European Committee for Standardisation (CEN) [7]. The effects of sampling time, concentration, relative humidity, temperature, zero exposure and storage were investigated. The effects of wind velocity and sampler orientation were previously studied in connection with validation of the sampler for formaldehyde [9]. In that study the uptake rate was constant with a wind velocity at the sampler face varying between 0.02 and 1.0 m/s. Most personal sampling conditions give wind velocities of about 0.1 m/s [6]. A slight increase in the uptake rate at high wind velocities was observed with the sampler in an orientation perpendicular to the air stream. The sampler has been compared with pumped sampling in office and home environments. These tests were performed without active ventilation and without any people present. The wind velocities were less than 0.02 m/s. The sampler performed well at these very low wind velocities, allowing static area sampling of indoor air [8,9]. As wind velocity and sampler orientation are parameters associated with the sampler and not the analyte, these effects were not studied further in this work.

The sampler is manufactured with a cellulosic material filter tape. This original tape contained some contaminants that made the detection limit too high for short-time sampling of low levels of glutaraldehyde. The use of a glass-fiber filter material gave detection limits that were close to the analytical detection limit. In this study we used our own coated glass-fiber filters in all the experiments.

The concentration in the exposure chamber was calculated from the amount delivered through the nebulizer and the total air flow. The concentration was confirmed by the reference method. The experimentally determined values were generally within $\pm$ 10% of the calculated values. In all experiments the calculated value was taken as the true value of the delivered concentration.

The effect of sampling time, concentration and relative humidity (RH) was investigated by a three-factor factorial design. The individual results from each experiment are shown in Table 1. The statistical analysis was performed with the use of multiple regression [14]. This analysis gives information on the influence of the different parameters on sampling rate. As can be seen in Table 2, there is a small positive influence by time and a small negative influence by concen-

Table 1
Sampling rate of diffusive sampler at various glutaraldehyde concentrations, sampling times and relative humidities

Time (min)	Concenration (mg/m^3)	RH (ml/min)	Uptake	RSD	n
15	0.16	20%	11.8	13%	6
17	0.16	80%	12.1	6%	6
434	0.08	20%	13.5	4%	6
15	1.6	20%	11.6	3%	6
17	1.6	80%	9.3	8%	6
479	1.6	20%	10.6	3%	6
481	1.6	80%	13.5	2%	6
288	0.84	50%	12.7	1%	6
Mean			11.8	13%	48

Face velocity 0.3 m s^{-1}. RH = relative humidity, RSD = relative standard deviation, n = number of determinations.

tration. These effects give deviations less then 10% from the mean. There was no influence by relative humidity. The mean was 11.8 ml/min, with a relative standard deviation of 13%. This gives a relative overall uncertainty of 26%, calculated according to the European Standard EN 482 [15].

With a diffusion coefficient of 0.0718 cm^2/s, calculated according to Hirschfelder et al. [16], the theoretically calculated uptake rate is 13.1 ml/min. This deviation from the measured value by only 11% is well within accepted limits.

The hydrazone derivative stability was evaluated in a zero exposure test. Glutaraldehyde exposure for 30 min was followed by a zero concentration (clean air) exposure for 7.5 h.

As Table 3 shows, the result obtained from the test was 11.6 ml/min. This shows that there is no decomposition of the glutaraldehyde hydrazone.

The temperature tests showed a significantly lower uptake rate (8.6 ml/min) at 12°C, and a significantly higher uptake rate (13.5 ml/min) at 40°C (Table 3). The effect is about 1.5% per degree Celsius. A temperature dependence of $T^{1.75}$ on the diffusion coefficient from temperature is given by Fuller et. al. [17]. This diffusion coefficient variation of about 0.6% per degree can only partly explain the temperature effect on uptake rate. Possibly there is also a reaction rate effect.

Two storage tests were performed, one with the filter cut into two pieces and one with the filter uncut (2 × 4 cm). This was done in order to detect possible hydrazone migration on the filter. The filters were stored for 14 days at 22°C. No difference between the two experiments could be seen which shows that there is no migration within the filter (Table 3). The storage tests also confirm the assumption based on the zero exposure test that there is no decomposition of the hydrazone.

Table 2
Multiple regression analysis of the influence of sampling time, concentration and relative humidity

Variable	Parameter estimate (ml/min)	Standard error	
Intercept (uptake rate)	11.8	0.42	
Time	$3.9 \cdot 10^{-3}$	$8.4 \cdot 10^{-4}$	S
Concentration	−1.1	0.25	S
RH	$6.0 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	NS

S = significant; NS = not significant.

4. Conclusions

The diffusive sampler tested in the study has been designed for use with reagent-coated filter

Table 3
Tests on zero exposure, temperature and storage

	Time (min)	Concentration (mg/m^3)	RH	Uptake rate (ml/min)	RSD	n
Zero exposure[a]	30	1.6	20%	11.6	6%	5
Exposure at 12°C[b]	200	1.6	50%	8.6	2%	6
Exposure at 40°C[b]	250	1.6	50%	13.5	3%	6
Storage, filter uncut[c]	240	1.6	50%	12.7	3%	6
Storage, filter cut[c]	240	1.6	50%	12.9	1%	5

[a] Exposure for 30 min followed by a zero concentration (clean air) exposure for 7.5 h.
[b] Calculated against normalized volume (22°C, 1013 bar).
[c] Storage at 22°C for 14 days.

tape. For sampling of glutaraldehyde, 2,4-dinitrophenylhydrazine is used. The determined sampling rate was 11.8 ml/min, with a standard deviation of 13%. The influence of concentration, time and humidity on uptake rate was undetectable or small. The effect of temperature was significant, and about 1.5%/°C. No decomposition could be seen in the storage test. The sampler can be used for short-time sampling (15 min) with a sensitivity of about 0.05 mg/m^3 as well as for 8 h sampling.

The sampler has been shown to perform well at extremely low wind velocities which makes the method suitable both for static and for personal monitoring.

Acknowledgement

The authors wish to thank the European Commission, Measurement and Testing Programme (BCR) for financial support.

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Journal of Chromatography A, 710 (1995) 181–190

JOURNAL OF CHROMATOGRAPHY A

Environmental and biological monitoring of chloroform in indoor swimming pools

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Abstract

The presence of chloroform as the result of disinfection with sodium hypochlorite was demonstrated in the water and ambient air of indoor swimming pools. Environmental monitoring was performed in 12 indoor swimming pools in northern Italy and the level of human exposure was assessed. Biological monitoring performed by gas chromatography on human plasma and alveolar air samples evidenced that the uptake of chloroform in swimmers varies according to the intensity of the physical activity and age. The elimination of chloroform in alveolar air in one subject showed a very short half-life (from 20 to 27 min) and a complete clearance within 10 h after the end of exposure.

1. Introduction

Surveys from all over the world have reported the presence of trihalomethanes in swimming pools as by-products of treatment with chlorine and its derivatives [1–7]. The most common of these trihalomethanes is chloroform, which is a volatile substance released at the surface of the water and which can be inhaled by swimmers.

Since chloroform is classified in the 2B group by the International Agency for Research on Cancer (IARC), it is worthwhile studying the conditions under which exposure is likely, as well as the amount of chloroform in the environment, in order to assess the risk, if any, for exposed subjects [8,9].

The problem was approached in three ways:

–analysis of chloroform in the water and in the ambient air above the pools,

–biological monitoring of chloroform exposure by means of blood samples and exhaled air (alveolar air) samples,

–study of the kinetics of chloroform elimination from the lungs.

2. Environmental monitoring in indoor swimming pools

Sodium hypochlorite and, more recently, sodium dichloroisocyanurate are the substances most commonly used for the disinfection of swimming pool water. The concentration of active chlorine, and hence that of chloroform (the main by-product of chlorination), is usually higher than in treated drinking water.

Since 1980 we have been monitoring levels of

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0021-9673/95/$09.50
SSDI 0021-9673(95)00432-7

chloroform in indoor swimming pools in a region of northern Italy (Emilia Romagna). Concentrations in water and ambient air samples have been measured in 12 indoor swimming pools, several sampling sessions sometimes being performed in the same pool over a period of time. Eighty-eight data sets have been collected.

During each sampling session we took into account variables which could be associated with the release of chloroform from water to ambient air, namely, water and air temperature, pH, and free and combined chlorine residual.

The number of swimmers present in the pool was also noted, as turbulence caused by their movement could influence the release of chloroform into the air.

During each session, three samples of water were collected at a depth of 20 cm at three different positions near the edge of the pool; the mean value was considered as representative of the chloroform concentration in the water. Water samples were collected in screw-capped glass vials (40 cm^3) with silicone-faced septa. The vials were treated just before sampling with 5 mg of sodium thiosulfate to quench residual chlorine reactions.

2.1. Determination of chloroform in water

Samples were analyzed by a head-space gas chromatographic (GC) technique. A Dani HSS 3950 autosampler and a Varian 3400 gas chromatograph equipped with a ^{63}Ni electron-capture detector and a Vocol capillary column [30 m × 0.53 mm I.D., film thickness 3.0 μm (Supelco)] were used. Parameters were: carrier gas (He) flow-rate 8 ml/min; make-up gas, 20 ml/min; initial column temperature, 50°C (1 min); rate. 6°C/min; final temperature, 100°C (7 min); injector temperature, 150°C; detection temperature, 260°C; detector, electron-capture detection (ECD); range, 10; attenuation, 32. Calibration was performed by the external standard method, which is preferred by most workers when studying the presence of chloroform in waters by head-space GS [10,11]. Precision, calculated from five duplicate determinations on five different days, was 2.8% (coefficient of variation, C.V.). The limit of detection was calculated from 30 different series of chloroform determinations of blank value (vials with chloroform-free water). The mean blank concentration was 0.35 μg/l with a standard deviation of 0.04 μg/l. Based on 2.5 times the standard deviation, the limit of detection was 0.1 μg/l.

Chloroform was also measured in the ambient air: during the first session, the sampling of environmental air was performed by collecting spot samples every 15 min at different levels at the edge of the pool, using the same vials as before. As only slight variations were found between chloroform levels at the surface of the pool and those 150 cm above it, we decided to take samples only at 150 cm in order to avoid contamination by splashing. The mean values were considered to be representative of the environmental chloroform concentrations.

Environmental air samples used as controls were collected inside the Department of Hygiene of the University of Modena.

2.2. Determination of chloroform in environmental air

Samples were injected directly into the GC using a gas-tight syringe (Hamilton). Calibration was performed by the external standard method. Precision, calculated as before, was 3.5% as C.V.

The limit of detection was calculated from 30 different series of chloroform determinations of blank value (vials with environmental air). The mean blank concentration was 5.0 $\mu g/m^3$, with a standard deviation of 0.4 $\mu g/m^3$. Based on 2.5 times the standard deviation, the limit of detection was 1 $\mu g/m^3$. Quantitative analysis was performed by a Merck-Hitachi chromato-integrator D2000.

The identity of the chloroform was confirmed by GC–mass spectrometry (GC–MS) as follows: some ambient air samples were collected inside the swimming pools in Carbotrap 300 multibed thermal desorption tubes (Supelco) and injected using a thermal desorption cold-trap injector (Chromopack) into a GC–MS system (GC: HP 5990, MS: 5989A, Hewlett-Packard); identification was based on retention times measured on a

Table 1
Chloroform in water and environmental air samples collected in indoor swimming pools in northern Italy

Swimming pool	No. sampling sessions	Chloroform in water (μg/l)		Chloroform in environmental air (μg/m^3)	
		Arithmetic mean	Range	Arithmetic mean	Range
1	26	88.08	14–167	216.23	16–533
2	26	30.77	9–94	189	60–682
3	9	56.33	31–85	97.56	41–223
4	8	97.38	23–179	338.63	135–656
5	2	36.50	24–49	96	53–139
6	3	77.33	62–96	279.33	104–378
7	2	19.50	13–26	48	44–52
8	2	114.50	84–145	459.50	66–853
9	2	47.50	45–50	302.50	85–520
10	1	23[a]		80[a]	
11	1	56[a]		131[a]	
12	6	99.33	84–113	421.50	67–675

[a] One spot sample.

total ion-current chromatogram and on mass chromatograms of the molecular ion and of the most significant fragments of chloroform (m/z 47–50, 82–87, and 117–124).

The mean levels of chloroform in water and air in 12 indoor swimming pools are reported in Table 1. Chloroform in water ranges from 9 to 179 μg/l, which is in accordance with previous studies [4,12]. Levels in environmental air vary widely, from 16 to 853 μg/m^3.

Correlations among the variables taken into account during each sampling session are reported in Table 2.

The chloroform concentration in water correlates with that in air; the number of swimmers appears to be negatively correlated with the chloroform level in the water and positively with the concentration in air as a consequence of the turbulence induced in the water. Moreover, chloroform in water appears to be significantly correlated with the free and combined chlorine residuals, as all these variables are associated with the process of chlorination. No correlation appears between chloroform in water and the temperature of the water, and between chloroform in air and the temperature of the ambient

Table 2
Spearman's Rank correlation coefficients

	r	p
Chloroform in water (μg/l)/chloroform in air (μg/m^3)	0.2785	0.009
No. of swimmers/chloroform in water (μg/l)	−0.3451	0.001
No. of swimmers/chloroform in air (μg/m^3)	0.3555	0.001
Chloroform in water (μg/l)/free chlorine residual (mg/l Cl)	0.3255	0.002
Chloroform in water (μg/l)/combined chlorine residual (mg/l Cl)	0.2905	0.009
Chloroform in water (μg/l)/water temperature (°C)	0.1931	ns
Chloroform in water (μg/l)/water pH (unit)	0.2135	0.046
Chloroform in air (μg/m^3)/air temperature (°C)	0.0101	ns

Table 3
Multiple regression analysis. Chloroform in environmental air: dependent variable

Independent variable	Variables in the equation				
	B	SE *B*	Beta	*T*	Sig *T*
No. of swimmers	0.010928	0.002071	0.519178	5.277	<0.001
Chloroform in water	0.003532	8.3556×10^{-4}	0.415942	4.227	<0.001
Constant	1.694997	0.096278		17.605	<0.001

air, while a weak correlation exists between the pH and the amount of chloroform in water. It must be noted that in our data sets the values of water and air temperature and pH were within very narrow ranges.

Multiple regression analysis was performed by taking the level of chloroform in ambient air as the dependent variable, while chloroform in water and the number of swimmers were considered independent variables. Both independent variables influence the dependent one (after log transformation): the model accounts for 26.8% of the observed variance (R^2 adjusted: 0.268). The variables in the equation are reported in Table 3.

3. Biological monitoring in indoor swimming pools

People, particularly swimmers, visiting indoor swimming pools are exposed to chloroform by three routes: (1) inhalation of chloroform volatilized into indoor air from chlorinated water; (2) ingestion of chloroform from the water (particularly with children); (3) dermal contact with the water.

As indoor swimming pool visitors are exposed to chloroform for a precise period of time at a known environmental concentration, they form an experimental group from which more detailed information about chloroform exposure can be obtained.

The possibility of exposure via drinking water was excluded, as Modena is supplied with drinking water treated with chlorine dioxide (ClO_2) and is free from chloroform and other halogenated organic compounds. Nevertheless, we analyzed drinking water samples before, during, and after this study to confirm the absence of chloroform.

Chloroform is readily absorbed into the body mainly through the lungs and intestinal mucosa. However, when subjects take a bath or swim in chlorinated water, skin absorption may also be significant. In fact, the skin, the largest organ of the body, acts as a lipid sink for lipid-soluble contaminants [13].

Few data are available on the pharmacokinetics of absorption and excretion of chloroform in humans, particularly at the low rates of exposure normally found in ambient air and drinking water. Some studies show that absorption in man is rapid and complete, occurring by first-order passive absorption processes. Pulmonary uptake and elimination also occur by first-order diffusion processes, with three distinct components, with rate constants corresponding to tissue loading or desaturation of at least three major body compartments (vessel-rich tissues, lean body mass, adipose tissue).

Elimination of chloroform from the body occurs by two major simultaneous processes: pulmonary elimination of unchanged chloroform by first-order kinetics and metabolism. Chloroform is metabolized in the liver and to a lesser extent in the kidneys and other tissues. Metabolism is dose-dependent and saturable, with a greater proportion of small doses being metabolized. The predominant pathway for chloroform is oxidation, which produces phosgene and other active metabolites and may result in an alteration of cellular integrity and viability [14].

Up to now, no by-products have been found in

human fluids which could aid biological monitoring, so we decided to evaluate chloroform concentrations in human plasma. An original head-space GC technique, suitable for determining chloroform in human plasma, was developed in order to obtain a direct measurement in subjects exposed to low levels of chloroform [15].

3.1. Determination of chloroform in plasma

The analysis was performed on plasma aliquots. Samples were analyzed by a head-space GC technique. A Dani HSS 3950 autosampler and a Varian 3400 GC equipped with a ^{63}Ni electron-capture detector and a glass steel column packed with 10% OV-1 on Chromosorb WAW were used. The carrier gas (nitrogen) flow-rate was 30 ml/min; make-up gas, 30 ml/mm; oven temperature, 70°C; inlet temperature, 150°C; detector temperature, 280°C; sensitivity, $8 \cdot 10^{-11}$ AUFS. Calibration was performed by the external standard method.

The identity of the chloroform was confirmed by GC–MS. We examined both standard samples of chloroform in *n*-pentane and standard samples of chloroform-fortified human plasma at increasing concentrations (0.1–1000 mg/l) after extraction with *n*-pentane. The identification of chloroform is based both on retention times measured on a total ion-current chromatogram and on mass chromatograms of the molecular ion and the most significant fragments of chloroform (*m/z* 47–50, 82–87, and 117–124).

Plasma chloroform was evaluated in samples of 127 volunteer subjects (81 men and 46 women) who regularly attended three swimming pools in Modena (Emilia Romagna, Italy). The pools were visited over a period of six months (Nov. 1987–April 1988), and samples were collected in 18 sampling sessions [16].

The kind of activity practised in the swimming pool was recorded, and the subjects were classified into three main groups: competitive swimmers ($n = 102$) in daily training for competitions, non-competitive swimmers ($n = 16$) who were attending swimming courses twice a week, and visitors ($n = 9$) who were present but did not swim. Every subject was asked about frequency of attendance and length of time spent at the swimming pool in the course of a week. The length of the swimming session was noted, as was the time elapsing between the end of the session and blood sampling (only for swimmers). Data were gathered regarding the possibility of exposure outside the swimming pool (e.g. occupational exposure or handling of solvents at home).

A control group of 40 volunteers with no known occupational or environmental exposure and who had never visited an indoor swimming pool were also examined: none of them exhibited plasma chloroform at levels above the limit of detection.

On the other hand, chloroform was always present in all samples collected from exposed subjects, as shown in Table 4, where the levels of plasma chloroform recorded in 18 sampling sessions in the 127 subjects who habitually frequented the swimming pools are shown, together with the chloroform levels found in air and water samples.

Table 4
Chloroform in water, in environmental air, and in plasma samples collected from 127 subjects during 18 sampling sessions

	Geom. mean	Arith. mean	Median	Range
Chloroform in water ($n = 18$) ($\mu g/l$)	30.90	32.67	30.50	17–47
Chloroform in air ($n = 18$) ($\mu g/m^3$)	178.65	213.61	172.00	66–650
Chloroform in plasma ($n = 127$) ($\mu g/l$)	0.82	1.06	0.90	0.1–3.0

Chloroform was never found in the blood samples taken from the 127 investigated subjects before entering the premises; however, after a period of exposure in the swimming pool, their blood samples invariably revealed concentrations of between 0.1 (detection limit by the analytical method) and 3 μg/l, with a geometric mean of 0.82 μg/l and a median of 0.90 μg/l.

The plasma chloroform concentrations correlated significantly ($p < 0.001$) with those in the water and the ambient air, with the number of swimmers in the pool, and with the length of time spent swimming, but not with the number of visits to the pool during the week (Table 5).

Another variable that had a significant influence on plasma chloroform levels was the type of physical activity undertaken in the pool. Comparison by means of the Student Neuman Keuls test, with significance set at $p < 0.05$, of the mean values for competitive swimmers, swimmers attending swimming courses, and non-swimmers present at the sampling sessions showed that the competitive swimmers had significantly higher values (1.22 ± 0.68 μg/l) than either the non-competitive swimmers (0.40 ± 0.15 μg/l) or the non-swimmers (0.29 ± 0.20 μg/l).

Covariance analysis, performed for blood concentration, physical intensity, age of subject, and concentration of chloroform in the ambient air, showed that this model was able to account for 67.88% of the phenomenon: 48.16% of the plasma value was linked to the concentration of chloroform in the ambient air, 4.72% to the intensity of physical activity, and 1.47% to the subject's age, with which it showed a weak negative correlation depending on the amount of time spent in the covered pool.

Since it is not easy to collect numerous blood samples in a broad survey of this type, and as alveolar air sampling is a recognized technique for determining occupational exposure [17,18], we decided to take the alveolar chloroform level as the indicator of exposure for biological monitoring. Accordingly, in a subsequent phase of our study, we studied 163 subjects, comprising swimmers and non-swimming visitors, and 77 control subjects [19].

The exposed subjects, 98 male and 65 female, aged between 5 and 44 years, were classified into three groups, depending on their activity in the pool, namely, learners (12), competitive swimmers (120), and visitors (31). A sample of alveolar air was taken from each subject before entering the premises to check whether chloroform was present before exposure; a second sample was taken at the end of the session, together with a sample of ambient air. Alveolar air samples were collected in 34 cm^3 one-way glass tubes with two valves. Subjects were asked to breath normally into the tube with open valves. At the end of expiration, the valves were closed. For analysis the tubes were heated to 37°C to recreate the conditions at the time of sampling.

3.2. Determination of chloroform in alveolar air

This determination was performed by injecting samples directly into the GC (Varian 3400) using a gas-tight syringe (Hamilton). The analytical procedure has been described previously and was the same as used for the determination of chloroform in the ambient air. Calibration was performed by external standard methods.

Chloroform was found at the detection limit

Table 5
Spearman's Rank correlation coefficients

	r	p
Chloroform in plasma (μg/l)/no. of swimmers	0.322	<0.001
Chloroform in plasma (μg/l)/time spent swimming (min)	0.573	<0.001
Chloroform in plasma (μg/l)/chloroform in water (μg/l)	0.478	<0.001
Chloroform in plasma (μg/l)/chloroform in environmental air (μg/m^3)	0.739	<0.001

value (1 $\mu g/m^3$) in some samples before exposure, while after exposure all the samples of alveolar air revealed varying concentrations of chloroform.

Of the 77 subjects not known to have been exposed to chloroform and therefore serving as controls, it was nevertheless found, albeit in traces, in 53% of the total.

The chloroform concentrations found in the samples of alveolar air taken from the 163 subjects at the end of exposure in the pool are reported in Table 6. Chloroform was always present in the samples of alveolar air collected in the pool, with values ranging between 14 and 312 $\mu g/m^3$.

Our findings show a positive correlation between alveolar chloroform and the concentration of chloroform in the ambient air ($r = 0.907$, $p = 0.002$) and a weak negative correlation with the age of the subjects ($r = -0.310$, $p < 0.001$).

As in the case of plasma chloroform, the nature of the physical activity undertaken in the pool seems to have a considerable influence on the level of alveolar chloroform concentration.

Student Neuman Keuls test, carried out to compare average levels in the three groups (competitive swimmers, learners, and visitors), again showed a significant difference between the last two groups (learners, 74.61 $\mu g/m^3$ and visitors, 58.71 $\mu g/m^3$) and the first (competitive swimmers, 104.35 $\mu g/m^3$).

Covariance analysis was performed on the whole sample (swimmers and visitors) including alveolar concentration as a dependent variable, the intensity of physical exertion as a factor, and ambient air concentrations and age as covariates. The total explained variance by this statistical model was 73.05% ($F = 107.09$, $p < 0.001$), of which 58.36% was due to chloroform in ambient air ($F = 342.14$, $p < 0.001$), 13.13% to the age of the subjects ($F = 78.20$, $p < 0.001$), and 5.11% to the intensity of physical exertion ($F = 14.98$, $p < 0.001$).

4. Kinetics of chloroform elimination

In order to ascertain whether chloroform exposure through swimming in chlorinated water has any injurious effects on health, the pharmacokinetics of this compound needs to be understood. Various studies have been carried out to determine the uptake and elimination of different chemicals in occupationally exposed subjects; the pharmacokinetics of a compound in subjects who are not occupationally exposed, however, is not well documented.

For this reason we decided to study the kinetics of chloroform elimination in exhaled breath following the typical exposure of a swimmer in an indoor swimming pool. We report here the results of a first study carried out in the winter of 1993–1994.

A competitive swimmer (male, non-smoker, 34 years old, weight 104 kg, height 186 cm) who usually swims three times a week was monitored at four swimming sessions, and alveolar air samples were taken at intervals for 10 h after each session.

On each occasion he trained intensively for 45 min, from 20.00 to 20.45, and during this period water and ambient air samples were collected

Table 6
Chloroform in water, in environmental air, and in alveolar air samples collected from 163 subjects during six sampling sessions

	Geom. mean	Arith. mean	Median	Range
Chloroform in water ($n = 6$) ($\mu g/l$)	–	35.97	29.95	19–94
Chloroform in air ($n = 6$) ($\mu g/m^3$)	–	140.33	129.85	49–280
Chloroform in alveolar air ($n = 163$) ($\mu g/m^3$)	78.05	94.09	83	14–312

following the same procedures as reported before. A pre-exposure sample was taken just before the swimmer entered the swimming pool premises; a first post-exposure sample was taken as soon as the swimming session had finished and a second one 15 min after he had left the premises. Further samples were taken every 30 min for the following 3 h while the subject was at home resting, and a final sample was taken the following morning, about 10 h after the end of exposure.

At the same time ambient air samples were collected in the swimmer's house in order to ascertain the background level of any chloroform concentration.

The levels of chloroform in the swimming-pool water ranged between 106 and 144 μg/l, while ambient air values ranged from 92 to 208 $\mu g/m^3$, with a mean value of 139 ± 24.6 $\mu g/m^3$.

The ambient air levels in the swimmer's house were always below the limit of detection by our method.

In the pre-exposure samples of alveolar air, chloroform was not detected; the levels measured after the end of exposure and the corresponding time of collection are reported in Table 7.

Chloroform concentrations in alveolar air as a function of time after exposure found in the four sampling sessions are shown in Fig. 1. The figure shows that the elimination of chloroform in alveolar air after these exposure levels usually stops within 10 h; in the samples collected at the end of this time, chloroform was detected in all the samples but one, where it was measured at a very low concentration.

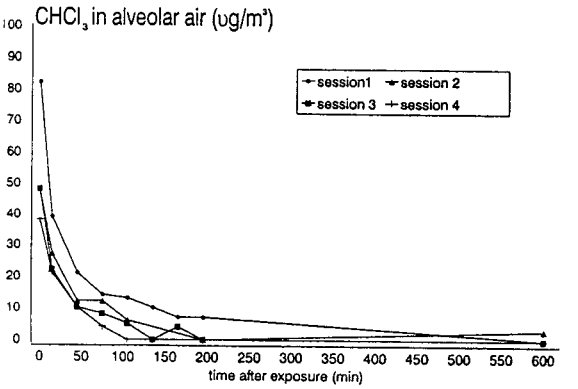

Fig. 1. Chloroform in alveolar air ($\mu g/m^3$) as a function of time after exposure in four sampling sessions.

According to our data, the elimination of chloroform follows first-order, one-compartment pharmacokinetics, and the equation describing breath decay is

$$C = C_0 e^{-kt}$$

where C is the concentration of chloroform at time t, C_0 the concentration of chloroform at time 0, and k is the first-order rate constant of the overall elimination of chloroform.

Table 7
Chloroform in alveolar air samples collected during four sampling sessions after exposure

Time after exposure (min)	Chloroform in alveolar air in sampling session ($\mu g/m^3$)			
	1	2	3	4
0	82	48	48	38
15	39	27	22	21
45	21	12	10	10
75	14	12	8	4
105	13	6	5	0
135	10	–	0	0
165	7	–	4	–
195	7	0	0	0
600	0	3	0	0

Table 8
Pharmacokinetics parameters of chloroform pulmonary elimination

Pharmacokinetics parameters	Sampling session			
	1	2	3	4
C_0 ($\mu g/m^3$)	75	45.4	45.7	37.3
k (min^{-1})	0.026	0.025	0.035	0.033
r^2	0.92	0.95	0.96	0.99
$t_{1/2}$ (min)	26	27	20	21
AUC ($\mu g/m^3$)	2815	1777	1269	1136

The pharmacokinetic parameters derived from the best-fit curves are reported in Table 8, together with the value of r^2, the biological half-time ($t_{1/2}$), and values of the area under the curve (AUC), which were calculated from the end of exposure to the last time at which data were available, 10 h after the end of exposure; r^2 values range between 0.92 and 0.99, which suggests that our model fits our data reasonably well.

The biological half-times ($t_{1/2}$) are very short and range from 20 to 27 min; our data are not sufficient to link this variable to specific factors.

The AUC values can be utilized to obtain information on the total amount of chloroform eliminated in alveolar air; considering a respiratory rate of 1 m^3/h the total amount of chloroform eliminated by the lungs in 10 h after these four swimming sessions was 28.150, 17.770, 12.690, and 11.360 mg, respectively.

5. Discussion

Throughout our investigations in covered swimming pools, chloroform was always present in the water and air at levels corresponding to the number of swimmers present in the pool. It was thus possible to identify an exposure factor of a non-occupational nature that affects subjects frequenting the pool, including those who do not swim but who remain on the premises for varying periods of time.

This population was therefore used for biological monitoring, and the findings show that the swimmers, particularly the competitive swimmers, were more heavily exposed to chloroform. The levels of concentration in the blood and alveolar air were in fact higher, the greater the degree of physical exertion; also, there was a negative correlation between chloroform levels and age, which suggests that younger subjects absorb chloroform more readily.

To complete our study we investigated the kinetics of chloroform elimination from the lungs after a period of exposure in the swimming pool under controlled conditions. Our findings point to single-stage clearance, at variance with that observed by other authors. Research conducted on subjects exposed to chloroform while showering revealed a dual-compartment model featuring a rapid initial phase of clearance from arterial blood followed by a slower second phase connected with the release of chloroform from the body tissues [20–22].

Another study conducted on a subject exposed for 30 min in the swimming pool showed two clearance peaks from the lungs, probably due to two different absorption routes: the first peak was thought to correspond to a very rapid absorption phase, most probably through inhalation, while the second, appearing 60–90 min after exposure, was linked to a slower, probably transdermal, process of absorption [6].

It is likely that the frequency of sampling in our study did not allow two distinct clearance phases to be detected. In two sessions we did in fact detect a slight increase in the amount of chloroform cleared in the 60–100 min interval, but it was statistically insignificant.

Our findings demonstrate that the clearance of chloroform absorbed after a period of exposure in the swimming pool is rapid and is complete after about 10 h from exposure–unlike other volatile halogenated substances such as trieline and perchloroethylene, which take longer to clear. It should be borne in mind, however, that the time taken by the same volatile substance to clear from the lungs may vary considerably from subject to subject [23].

As stated above, chloroform has been identified as a possible carcinogen in man and, as such, classified in group 2B by IARC. We therefore believe that all possible measures should be taken to reduce exposure as far as possible. Covered swimming pools represent a particular situation in which exposure can occur along three routes, absorption taking place through the lungs and the skin, and also by ingestion. Research should therefore be directed at reducing the generation of chloroform during the chlorination process and controlling the concentration of chloroform in the ambient air.

Acknowledgements

Our studies were supported by grants from the Italian Ministry of University and Scientific and Technological Research (40% and 60%). We are indebted to Prof. Sergio Fonda for consulting about pharmacokinetic models.

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ELSEVIER

Journal of Chromatography A, 710 (1995) 191–228

JOURNAL OF CHROMATOGRAPHY A

Denuder tubes used with gas chromatographic instrumentation to measure rate coefficients and equilibrium constants

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Abstract

To provide a scientific basis for conservation of objects of cultural heritage from air pollution, the use of denuder tubes in conjunction with gas chromatographic instrumentation is described. This leads to the determination of deposition velocities, reaction probabilities, adsorption isotherms and other physico-chemical parameters for the action of air pollutants on solid surfaces. Cylindrical, annular, parallel plate and wet effluent denuders are theoretically described, in addition to simple cylindrical without air flowing through them. The latter are combined with the reversed-flow gas chromatographic technique.

1. Introduction

One important effect of air pollution is damage to historic buildings and monuments, and generally to cultural heritage. This damage starts with the deposition of air pollutants, such as sulfur dioxide, nitrogen oxides, hydrocarbons and other air-dissolved pollutants or suspended particulate matter, followed by physical and/or chemical processes on the solid, which lead to permanent corrosion and damage. The air pollutants may arrive at the solid surface either by wet deposition (dissolved in rain or fog droplets, e.g., SO_4^{2-}, HNO_3) or by dry deposition, signifying deposition in particle form, e.g., NH_4HSO_4, or in gaseous form, e.g., SO_2. This means that deposition of gases on a wet stone surface is termed dry deposition.

The deposition of pollutants on solids is the first step of the mechanism for the degradation of stones, mainly calcareous, in the environment. In particular, SO_2 deposition on $CaCO_3$ of various forms (calcite, marble, etc.) gives gypsum as the final product, the mechanism of its formation being suggested for the first time by Skoulikidis et al. [1]. This mechanism still has some unresolved issues pertaining to the details of the reaction. For example, working with Carrara marble, Johansson et al. [2] concluded that at least two forms of tetravalent sulfur were present on marble exposed to SO_2 in humid air, namely $CaSO_3 \cdot \frac{1}{2}H_2O(s)$ and a more loosely bound form. Based on these observations, it is suggested that SO_3^{2-} (ads) is the first S(IV) species formed:

$$SO_2(g) + H_2O \rightleftharpoons SO_3^{2-}(ads) + 2H^+(ads) \quad (1)$$

This explains [2,3] the time-dependent desorption of SO_2. It is then shown that $CaSO_3 \cdot \frac{1}{2}H_2O(s)$ is formed according to the reaction

$$CaCO_3(s) + SO_3^{2-}(ads) + 2H^+(ads) \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O(s) + CO_2(g) + \tfrac{1}{2}H_2O \quad (2)$$

0021-9673/95/$09.50
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$CaSO_3 \cdot \frac{1}{2}H_2O(s)$ and $SO_3^{2-}(ads)$ are then oxidized to $CaSO_4(ads)$ and $SO_4^{2-}(ads)$, respectively, followed by the formation of gypsum:

$$CaSO_4(ads) + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) \quad (3)$$

$$SO_4^{2-}(ads) + CaCO_3(s) + 2H^+(ads) + H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) + CO_2(g) \quad (4)$$

It is expected and has been confirmed [2,3] that the rate of sulfite oxidation is increased in the presence of oxidants such as O_3 and NO_2.

The example described above indicates that, in order to help the conservation of cultural heritage, measurements must not be confined to pure chemical analysis, leading only to an empirical collection of data concerning an object of cultural heritage. The measurements should aim at providing a scientific basis for conservation, and for this purpose the first aspect to extract from the measurements is the mechanism of the action. This mechanism may consist of various steps in series, which are usually rate processes, with the deposition velocity as the first step, or sometimes equilibrium states, such as the distribution of a pollutant between the solid and the nearby atmospheric environment.

To study the rate processes, one has to measure their rate coefficients, such as the rate constant of a chemical reaction, while equilibrium states need a measurement of their equilibrium constants, preferably through the adsorption isotherm. These coefficients and constants should be as far as possible invariant with respect to the geometrical characteristics of the object parts, such as their shape, volume and external surface area. Such physico-chemical parameters may already exist in the physical sciences, but new concepts may be necessary to describe the mechanism. By organizing the experimental observations in a scientific manner, one transforms the protection and conservation of cultural heritage into a science.

The simplest way to approach the mechanism of a natural phenomenon is to formulate a model consisting of various physical and/or chemical processes and then use an experimental arrangement simulating this model and permitting the measurement of the rate coefficients and equilibrium constants mentioned above. One obvious model for the action of air pollutants on buildings and monuments is shown in Fig. 1. It is based on the general concept of an open system consisting of the exposed surface, over which convection and diffusion currents cause the movement of the gaseous pollutants, say A(g) and B(g), both, parallel and perpendicular to the surface, while a simultaneous interaction between them giving C(g) is possible [4]. When reaching the surface, pollutants are adsorbed on it, and this is followed either by a reaction with the solid of the adsorbed species A(ad) and B(ad) giving the products D and E, or by desorption back to the gaseous phase.

An experimental arrangement to simulate this simple model is of course possible, but the theoretical analysis is very difficult, if not impossible, with the existing methods. If convection currents perpendicular to the solid surface are ignored, one can use diffusion denuders, mostly being employed by environmental scientists for another purpose, i.e., to solve the problem of selective sampling of ambient air pollutants. They usually consist of an open cylinder, the internal surface of which is covered with a material capable of adsorbing a species under study from a gaseous stream through the denuder containing this species. Of course, the internal covered surface may simulate the solid surface, and the gaseous stream containing species A(g) and B(g) may resemble the convective current parallel to the surface. Cylindrical denuders have certain limitations, the most important of which are: an extreme length at high

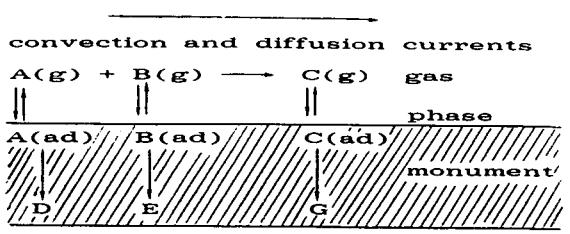

Fig. 1. Model for the mechanism of action of two gaseous pollutants A(g) and B(g) on a monument.

air flows to achieve considerable sorption efficiency; and low absorptive capacity on account of the reduced surface area. In order to overcome these drawbacks and achieve the highest possible efficiency and capacity, annular denuders were introduced by Possanzini et al. [5], consisting of two coaxial cylinders, so that air is forced to pass through the annular space.

Recently, parallel plate denuders [6] have been employed for physico-chemical measurements pertaining to air pollution, consisting of two parallel flat briquettes 3 mm apart of the material under study enclosed in a polyethylene box. Air is drawn into the box and flows parallel to the plates.

Another experimental arrangement is the wet effluent denuder [7], which involves an absorber liquid flowing down the inner walls of a tube while sample gas flows countercurrent upward. The design and construction of high-efficiency wetted denuders of annular and parallel plate geometries have been described [8].

Finally, the catalogue of cylindrical, annular, parallel plate and wet effluent denuders, operating at volumetric flow-rates ranging up to 40 dm^3 min^{-1}, is completed with a simple cylindrical denuder through which no air flows. The only carrier of pollutants parallel and perpendicular to the solid surface is gaseous diffusion. No convective current is operative.

Although classical denuders are virtually gas flow reactors, they can be combined with chromatography for determining inlet and outlet concentrations. To the best of our knowledge, a chromatographic column has never been used as a reactor to measure deposition velocities, reaction probabilities, etc. However, the simple cylindrical denuder without air flowing through it has been combined with reversed-flow gas chromatography (RF-GC) to measure, not only rate coefficients of pollutant deposition on solids, but also adsorption isotherms, and orders and rate constants of reactions between pollutants in the gas phase while they are depositing on solid surfaces.

In this review, denuders for measuring rate coefficients and equilibrium constants in conjunction with chromatography will be examined.

2. Theory of cylindrical denuders

If by $c_g = c_g(t, z, r)$ one denotes the gaseous concentration of a pollutant A (mol cm^{-3}) as a function of time t (s), length coordinate z along the cylindrical denuder (cm) and radial coordinate r, i.e., distance from the cylinder axis (cm), the general mass balance equation of A in the denuder is

$$\frac{\partial c_g}{\partial t} = -v\frac{\partial c_g}{\partial z} + D_A\frac{\partial^2 c_g}{\partial z^2} + D_A\left(\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right) - r_A \quad (5)$$

where

v = axial flow velocity of air (cm s^{-1}) given by the laminar flow field as $v = 2\bar{v}(1 - r^2/R^2)$, $\bar{v}$ being the mean axial flow velocity and R the cylinder radius;

D_A = diffusion coefficient of A into air (cm^2 s^{-1});

r_A = rate of a gaseous chemical reaction of A (mol cm^{-3} s^{-1}).

Obviously, Eq. 5 describes the rate of change of the pollutant as due to four causes, namely: (1) convective movement along the cylinder (first term on the right-hand side); (2) longitudinal diffusion along the cylinder axis (second term); (3) radial diffusion (third term); and (4) homogeneous chemical reaction (last term). The solution of Eq. 5 naturally depends on the initial conditions ($t = 0$), and the boundary conditions with respect to z (for $z = 0$ and $z = L$, where L is the length of the cylinder), and also with respect to r (for $r = 0$ and $r = R$). The initial conditions at $r = R$ may require a change of sign of the third term on the right-hand side of Eq. 5, as was done in a recent paper [9]. The boundary conditions at $r = R$ take into account any heterogeneous chemical reaction of A with the material covering the internal wall.

However, even an exact knowledge of the initial and boundary conditions does not permit an analytical solution of Eq. 5, unless drastic approximations are employed. The first of these, termed steady-state solution, is to set the left-hand side equal to zero, $\partial c_g/\partial t = 0$, and this

approximation has been adopted by all workers in the field, except those combining cylindrical denuders with the RF-GC technique. The second approximation is to omit the term for longitudinal diffusion on the right-hand side, $D_A(\partial^2 c_g/\partial z^2)$, assuming that the axial diffusion velocity is small compared with the bulk transport velocity, $v(\partial c_g/\partial z)$. This happens when the Peclet number $2Rv/D_A$ is >10. Papoutsakis et al. [10] gave a solution that takes into account axial diffusion. Finally, the last term r_A is omitted on the assumption that homogeneous chemical reactions do not create or destroy the pollutants in the cylinder. An analytical solution tried by Dang [11] included axial diffusion and homogeneous first-order reactions.

After the above three approximations, almost universally applied, only two terms of Eq. 5 remain, the first and third on the right-hand side, thus giving

$$v\frac{\partial c_g}{\partial z} = D_A\left(\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right) \tag{6}$$

Some additional assumptions lead to the best-known solutions of Eq. 6, namely the Gormley–Kennedy (GK) [12] and Cooney–Kim–Davis (CKD) [13] solutions. These assumptions are that pollutant A is a trace gas, laminar flow is developed with constant viscosity, the temperature is constant, and the amount collected on the tube wall is small compared with the tube's capacity.

The GK solution is

$$\begin{aligned}\bar{c}/c_0 = {} & 0.8191\exp(-7.314z^*) \\ & + 0.0975\exp(-44.61z^*) \\ & + 0.0325\exp(-113.9z^*) + \cdots\end{aligned} \tag{7}$$

where c_0 is the gas concentration entering the tube, $\bar{c}$ is the average gas concentration leaving the tube and z^* is a dimensionless length given by the relation

$$z^* = \frac{\pi}{2}\cdot\frac{D_A L}{\dot{V}} \tag{8}$$

with L denoting the actual length of the tube and $\dot{V}$ the volumetric flow-rate at the temperature and pressure of the denuder. Most workers have used only the first term of Eq. 7, an approximation that is valid to 1% when $z^* > 0.1$. As shown by Eqs. 7 and 8, the collection efficiency $(1-\bar{c}/c_0)$ of a cylindrical denuder increases with increase in the tube length and diffusion coefficient, whilst it decreases with increase in flow-rate. It is noteworthy that the GK solution does not depend on tube radius or pressure.

The analytical solution expressed by Eq. 7 has been derived with the boundary condition $c_g = 0$ at $r = R$. However, McMurry and Stolzenburg [14], and Murphy and Fahey [15] demonstrated a fundamental limitation in the GK model in that this boundary condition at the denuder wall is equivalent to the assumption of an infinite reaction rate of the species being removed with the wall covering material. A more realistic assumption would be that the wall reaction rate is given by some fraction γ (wall reaction probability) of the wall collision rate. This new boundary condition leads to an improvement of GK equation, which is the CKD solution. Murphy and Fahey [15] developed a mathematical model based on this approach of Cooney et al. [13] for calculating the effect of non-unitary γ in open cylindrical denuders. According to this, the boundary condition is written by equating the flux of molecules to the wall with the number removed by reaction at the wall:

$$-D_A\left(\frac{\partial c_g}{\partial r}\right)_{r=R} = c_R\frac{\langle\nu\rangle}{4}\frac{\gamma}{1-(\gamma/2)} \tag{9}$$

where $c_R = (c_g)_{r=R}$, $\langle\nu\rangle$ is the mean molecular velocity given by $(8R_gT/\pi M)^{1/2}$, R_g being the gas constant and M the molar mass of the analyte, and γ is the wall reaction probability, i.e., the constant fraction of the wall collisions resulting in reaction of the analyte with the wall coating material. We can write Eq. 9 in terms of a Sherwood number by letting $r^* = r/R$ and substitute it into the left-hand side. The result, after rearrangement, is

$$\begin{aligned}-\left(\frac{\partial c_g}{\partial r^*}\right)_{r^*=1} &= \left[\frac{\langle\nu\rangle R}{4D_A}\cdot\frac{\gamma}{1-(\gamma/2)}\right]c_R \\ &= N_{Shw}c_R\end{aligned} \tag{10}$$

the dimensionless Sherwood number being given in the brackets [ ].

Solving Eq. 6 numerically by the method of Cooney et al. [13], one finds the CKD solution, expressed by a series of exponential terms, equivalent to the GK solution, as

$$\bar{c}/c_0 = B_1 \exp(-\Lambda_1^2 z^*) + B_2 \exp(-\Lambda_2^2 z^*) + \cdots \quad (11)$$

where z^* is given by Eq. 8, Λ_n are eigenvalues of a dimensionless characteristic equation and both Λ_n and B_n are functions of the Sherwood number given in Eq. 10. For large values of z^*, the residual error is smaller than the third term. For $n = 1, 2, 3$, Murphy and Fahey [15] give the values of Λ_n and B_n for a range of N_{Shw} values between 0.001 and 100. By using these in Eq. 11, we can calculate the concentration of an analyte leaving the denuder.

The GK solution is an asymptotic one, valid at high N_{Shw}. Obviously this happens when γ and R are large, and D_A becomes small (cf., Eq. 10).

Based on the CKD solution, McMurry and Stolzenburg [14] determined reaction probabilities with the tube walls from penetration measurements, i.e., from the ratio $\bar{c}/c_0$, in fully developed laminar tube flow. The ratio $\bar{c}/c_0$ was related to the reaction probability of the pollutant species through Eq. 10, the Sherwood number given without the correction $\gamma/2$ in the denominator [15] and named the uptake parameter S:

$$S = \gamma \cdot \frac{\langle \nu \rangle}{4} \cdot \frac{R}{D_A} \quad (12)$$

The γ value can be determined from the penetration data if the value of S is substantially smaller than 10, a condition which is obviously met when

$$\gamma < 40 D_A / \nu R \simeq 1.3 \cdot 10^{-4} / R \quad (13)$$

where typical values for D_A (at $P = 1$ atm) and ν of 0.2 $cm^2\ s^{-1}$ and $6 \cdot 10^4$ $cm\ s^{-1}$, respectively, are assumed with R in cm. To measure γ approaching unity, tubes of exceedingly small radius would be necessary. As the surface uptake parameter becomes very small, surface resistance becomes the dominant limiting process in transport to the wall. Deposition velocities are then independent of diffusion. Otherwise, e.g., for large values of γ and/or small values of D_A, the deposition velocities becomes diffusion limited.

The relative contributions of γ and D_A in the overall deposition velocity V_d, as given by Cano-Ruiz et al. [16], are given by

$$\frac{1}{V_d} \approx \frac{1}{\gamma(\langle \nu \rangle / 4)} + \frac{\delta_c}{D_A} \quad (14)$$

where δ_c is the thickness of concentration stationary layer existing on the solid.

Analogous relationships and arguments were used by Volpe and Peterson [17] to measure deposition velocities and reaction probabilities of H_2S with silver in a circular tube lined with silver foil. Also, more recently, Cano-Ruiz et al. [16] corrected the uptake parameter S according to Hickman's asymptotic analysis [18].

The references cited so far by no means constitute a complete list of contributions to the theory of cylindrical denuders. Several other workers could be mentioned, such as Judeikis and Stewart [19], who claim that their model accounts for diffusive transport in the system, with the result that deposition velocities measured were independent of diffusion processes and represented the maximum values that would be encountered in the environment under turbulent atmospheric conditions. Actual deposition velocities will range from the maximum values in turbulent atmospheres to those determined by molecular diffusion in quiet atmospheres.

Febo et al. [20] developed a thorough theoretical approach for the evaluation of laboratory and field performances of denuder tubes. They described a differential technique, an asymptotic differential technique and an absolute differential technique as solutions to the problem of measuring a reactive species in real conditions. They proposed a procedure for relating the analyte distribution on the denuder tube to the concentration of parent species in the atmosphere, and also for understanding anomalous deposition patterns.

3. Theory of annular denuders

As already mentioned, these denuders consist of two coaxial cylinders, so that air is forced to pass through the annular space. Possanzini et al. [5] developed the first relationships governing annular denuders, based on the classical GK Eq. 7. They started by retaining only the first term of this equation, which is the most significant one for $z^* \geq 0.1$. For example, at $z^* = 0.1$, $\bar{c}/c_0 = 0.394$, with less than a 0.3% contribution from the second term. In an annular denuder an equation of the same form can express $\bar{c}/c_0$, if Eq. 8 is corrected to give

$$z_a^* = \frac{\pi D_A L}{2\dot{V}} \cdot \frac{d_1 + d_2}{d_2 - d_1} \tag{15}$$

where the subscript a means annular, d_1 and d_2 being the inside and outside diameters of the annulus, respectively. Then, the one-term Eq. 7 is

$$\bar{c}/c_0 = A \exp(-\alpha z_a^*) \tag{16}$$

where A and α have to be determined experimentally. It is seen from Eq. 15 that, in a laminar flow through the annulus, z_a^* may be optimized by varying not only the tube length L and the air flow-rate $\dot{V}$, but also the width of the annular section and the diameter of the inner tube. By reducing $d_2 - d_1$ and increasing d_1, values of z_a^* much larger than those corresponding to z^* of Eq. 8, at a given ratio $\dot{V}/L$, are obtained. By comparing the first term of Eq. 7 with Eq. 16, determined experimentally as regards A and α, Possanzini et al. [5] found the relationship

$$(\dot{V}/L)_a = 1.54 \cdot \frac{d_1 + d_2}{d_2 - d_1} \cdot \frac{\dot{V}}{L} \tag{17}$$

De Santis and Allegrini [21] applied annular denuders for the study of the reaction of $CaCO_3$ with SO_2 alone or in the presence of NO_2. They used two ways to calculate deposition velocities. The first was based on the equation $V_d = F/c$, where F is the flux rate of a pollutant with concentration c at a reference height. A direct estimate of V_d was made by the amount of sulfate measured after the experiment by using the equation $V_d = Q/cS_a t$, where Q is the amount of pollutant transferred to the walls, S_a the surface of the flow reactor and t the time of exposure. Their second way to find V_d was based on the mathematical model of Coutant et al. [22], which assumes that the pollutant reacts with a non-unitary reaction probability γ. Their calculations illustrate the importance of the collisional reaction efficiency in both design and use of the annular denuders. De Santis and Allegrini [21] found good agreement between the two ways of calculating V_d.

The theoretical background developed by Febo et al. [20] was used with annular denuders by Perrino et al. [23] for the selection of the best denuder coating and sampling set-up in the determination of HNO_2 and HNO_3 in the atmosphere.

4. Theory of parallel plate denuders

As pointed out before (cf. Section 2), surface resistance becomes the dominant limiting process in transport to the denuder wall if the surface uptake parameters S (cf. Eq. 12) is very small. Then deposition velocities V_d (cm s^{-1}) are independent of diffusion, as Eq. 14 shows, then being given by

$$V_d = \gamma \cdot \frac{\langle v \rangle}{4} \tag{18}$$

In this case, the fractional penetration $\bar{c}/c_0$ can be calculated with the following equation, derived from kinetic theory:

$$\bar{c}/c_0 = \exp(-4Sz^*) = \exp(-4V_d L/vd) \tag{19}$$

where S and z^* have been substituted from Eqs. 12 and 8, respectively, and V_d from Eq. 18. Here v is the axial flow velocity of air (cf. Section 2) and $d = 2R$ the equivalent channel diameter.

Eq. 19 has been applied to parallel plate denuders [6], the far right-hand side taking the form

$$\bar{c}/c_0 = \exp[-2V_d L(2a + b)/\dot{V}] \tag{20}$$

a corresponding to the half-depth and b to the long dimension of the denuder channel.

With high reaction probabilities, i.e., when walls are considered a perfect sink, the process becomes diffusion controlled as before, and penetration can be expressed by the first term of the GK solution, Eq. 7, with a slightly different pre-exponential factor and exponential coefficient of z^*:

$$\bar{c}/c_0 = 0.91 \exp(-15.08z^*) \quad (21)$$

Or, using a and b of Eq. 20,

$$\bar{c}/c_0 = 0.91 \exp[-15.08D_A L(2a + b)^2/4\dot{V}ab] \quad (22)$$

Eqs. 20 and 21 have been derived [6] from the work of Winiwarter [24], as outlined at the end of the next section.

5. Theory of wet effluent denuders

This type of denuder tube was introduced by Simon et al. [7] and is based on the idea that the analytes under study are absorbed by a liquid running down the inner walls of the tube while the sample gas flows countercurrent upward. The liquid is aspirated at the bottom and injected, along with small amounts of air, periodically into a chromatographic system. Four distinct designs of the wet denuder are described, namely, an internally threaded glass-filled PTFE, a porous-wall, a wettable membrane-lined and a silica-coated denuder.

The collection efficiencies are judged from semilogarithmic plots of the fractional penetration against the reciprocal flow-rate. By comparing them with the theoretical plots according to the GK equation (cf., Eq. 7), it was found [7] that for short, wet denuders and high flow-rates ($\geq$2.5 dm^3 min^{-1}) the data closely correspond to the theoretical predictions, but at lower flow-rates the collection efficiency is greater than the theoretical value. The longer wet denuder shows greater than theoretical collection efficiency for all flow-rates. In all cases near-theoretical y intercepts are observed.

The geometry of the wet effluent denuders has not been confined to simple cylindrical denuders, but extended to annular and parallel plate denuders, which were claimed to be of high efficiency by Simon and Dasgupta [8]. They evaluated their experimental results according to a theoretical treatment of Ali et al. [25], who expressed the collection efficiency $1 - \bar{c}/c_0 = f$ as

$$1 - f = 0.91 \exp(-3.77\alpha D_A L/\dot{V}) \quad (23)$$

which is similar to Eq. 21, α being given by the ratio b/a of the long and short dimensions, respectively, of the parallel plate denuder cross-section. The annular denuder was considered as an extension of the parallel plate geometry with

$$\alpha = \pi(d_1 + d_2)/(d_2 - d_1) \quad (24)$$

the reaction probability being assumed to be unity. Simon and Dasgupta [8] found no explanation for the supertheoretical collection efficiencies exhibited by their parallel plate denuders, but De Santis [26] explained that by pointing out that in the relation $\alpha = b/a$, used in Eq. 23 for a parallel plate denuder, a corresponds to the half-depth of the rectangular channel and not to its depth. Therefore, the numerical exponential coefficient should be multiplied by 2, becoming 7.54. The same applies for Eq. 23 when α is defined by Eq. 24. Thus, for the annular denuder, Eq. 23 becomes

$$1 - f = 0.91 \exp\left[-7.54 \frac{\pi(d_1 + d_2)}{(d_2 - d_1)} \cdot \frac{D_A L}{\dot{V}}\right] \quad (25)$$

De Santis suggested [26] that the Winiwarter equation [24]:

$$\bar{c}/c_0 = B_{(k)} \exp[-\beta_{(k)}^2 X] \quad (26)$$

be employed for any geometry of a denuder. Here, $k = d_1/d_2$ and $X = 2LD_A/d^2v$, d being the hydrodynamic equivalent diameter. The $B_{(k)}$ and $\beta_{(k)}$ values are obtained by numerical integration. Parallel plate and cylindrical geometry represents an upper ($k = 1$) and lower ($k = 0$) limit, respectively, whereas annular denuders have $k = 0.7$. Eqs. 21 and 22, given previously for a parallel plate denuder, are limiting cases of

the general Eq. 26. For a cylinder X coincides with z^* given by Eq. 8.

Summarizing the theory on denuders so far, all is based on Eq. 6, i.e., it neglects the rate of change $\partial c_g/\partial t$ (steady-state), the longitudinal diffusion $D_A(\partial^2 c_g/\partial z^2)$, and the rate r_A of homogeneous chemical reactions from the mass balance Eq. 5 for the pollutant species. Then, by measuring the penetration or tube transmittance $\bar{c}/c_0$, or the collection efficiency $f = 1 - \bar{c}/c_0$, as functions of tube length L and flow rate $\dot{V}$, one can calculate two important physico-chemical parameters, deposition velocities and reaction probabilities on denuder wall coatings. However, the first can provide sensitive information about the second only when surface reactions are the rate-limiting step and the return flux of accommodated molecules back to the gas phase is much less than the forward flux, i.e., irreversible reactions are assumed.

Diffusion-limited deposition velocities are not often reported, but reasonable values may be estimated and used in Eq. 14 to obtain reaction probabilities, as long as there are order of magnitude differences between the measured deposition velocities V_d and the estimated diffusion-limited values D_A/δ_c. Independently measured values of γ are rarely available, particularly reversible ones. The next section, however, offers such possibilities.

6. Theory of cylindrical denuders used with the RF-GC technique

Gas chromatographic instrumentation can be combined with simple cylindrical denuders, so that the complete mass balance Eq. 5 is used, without adopting any of the three approximations described so far and leading to the simpler Eq. 6. First, non-steady-state conditions can be used, thus retaining the left-hand side term $\partial c_g/\partial t$. Second, the longitudinal (axial) diffusion term $D_A(\partial^2 c_g/\partial z^2)$ on the right-hand side is retained by separating it physically from the bulk transport term $v(\partial c_g/\partial z)$. This separation can easily be achieved by arranging the air stream to flow perpendicularly to the denuder tube, as shown in Fig. 2. This leaves axial diffusion as the only carrier of substances along the denuder,

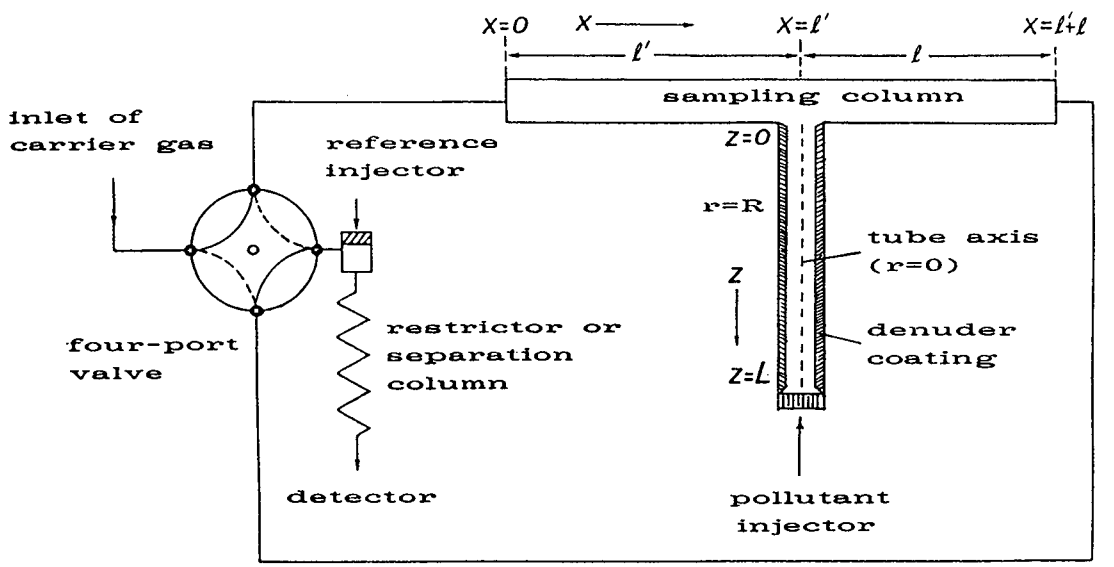

Fig. 2. Schematic representation of columns and gas connections for studying deposition velocities and reaction probabilities by reversed-flow gas chromatography. From Ref. [9] with permission.

"appointing" the air flow as carrier gas, to sample the junction point $x = l'$ and $z = 0$ as far as concentrations of analyte gases, emerging from the denuder tube, are concerned. These analyte pollutant concentrations are carried to an appropriate chromatographic detector through the four-port valve, an additional chromatographic column being inserted to separate analytes, if more than one exists.

Naturally, this sampling procedure will give continuous asymmetric chromatographic signals, even in the absence of the empty (of solids or liquids) sampling column, owing to the slow diffusion of the pollutant species out of the denuder tube. Theoretical work based on the height of the continuous detector signal is possible, but there is a better, simpler and more accurate sampling procedure, the well known reversed-flow gas chromatographic (RF-GC) technique [27–32]. It consists in reversing the direction of the air flow through the sampling column for a short time interval (usually 10–60 s), repeatedly by turning the valve from one position (cf., Fig. 2, solid lines) to the other (broken lines), and vice versa. If the reversal time above is smaller than the dead time in the sampling column, each flow reversal creates one extra chromatographic peak (or more than one, depending on the number of constituent analytes), which is a measure (its height or its area under the curve) of each analyte concentration at $x = l'$, at the time when the reversal was made. An example is shown in Fig. 3.

It is seen that each *sample peak* is fairly symmetrical and narrow, its width at half-height being equal to the reversal duration (ca. 10–60 s) and "sitting" on the asymmetric continuous signal. From this, considered as the baseline, the

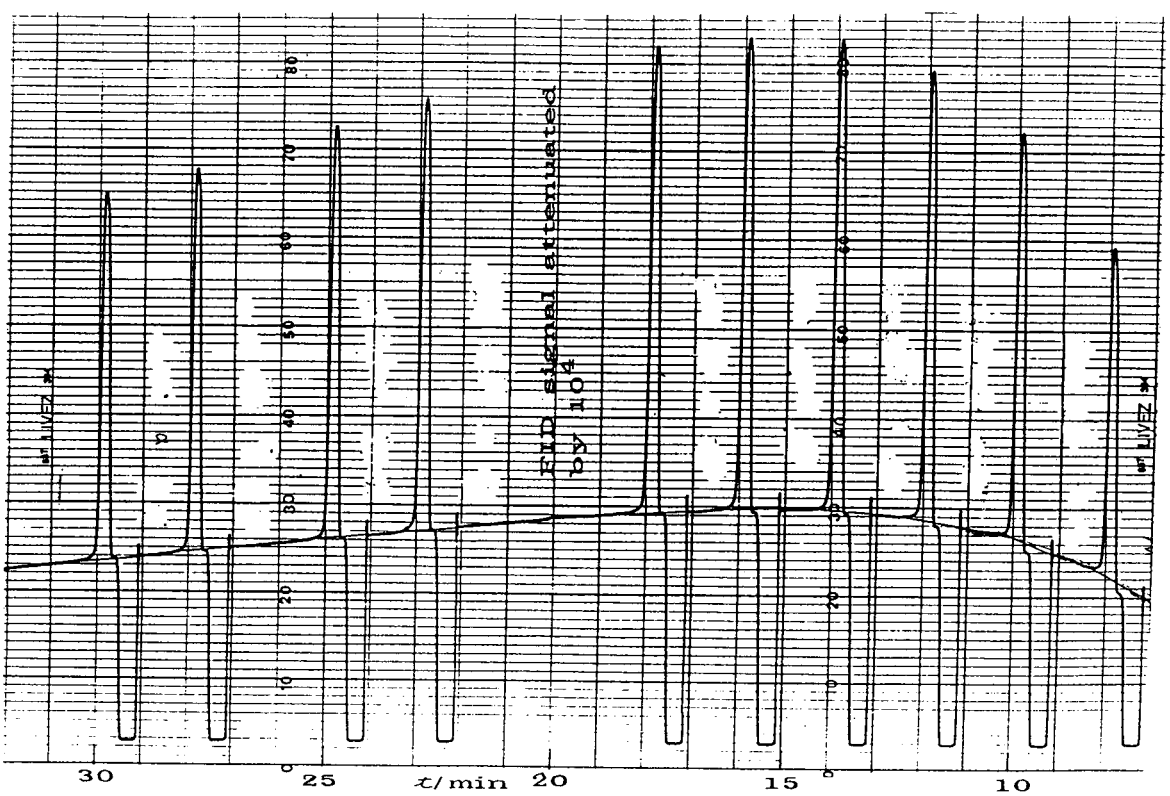

Fig. 3. Sample peaks of C_3H_6 in air due to flow reversals of 12 s. From Ref. [9] with permission.

height H or the area of the sample peaks is measured, giving the concentration $c(l', t)$ of the pollutant at $x = l'$ and time t:

$$H^{1/M} \approx gc(l', t) \tag{27}$$

where M is the response factor of the detector, e.g., $M = 1$ for a flame ionization detector, and g is a proportionality constant, usually being omitted because it is not needed in the mathematical analysis. These sample peaks are the source of all physico-chemical information which can be obtained from the set-up in Fig. 2. It should be noted that no correction due to the usual broadening factors of chromatography is needed for these peaks, as is the case when the usual elution bands are used. No retention time measurement, no flow-rate measurement and therefore no temperature and pressure correction of it are necessary. The whole work can be carried out without even knowing what the flow-rate was.

The equivalent of the elution band here is the so-called *diffusion band*, due to the axial diffusion along the denuder tube, and having various appearances depending on the phenomena taking place inside the tube and at its walls. Examples are shown in Fig. 4. They are simply plots of the height H or $H^{1/M}$ or $(1/M) \ln H$ vs. the time when the respective flow reversal was made. It is the mathematical function $H = f(t)$, describing the diffusion bands, which is sought when theoretical analysis is undertaken, to determine the rate coefficients and equilibrium constants, mentioned in Introduction and pertaining to the steps of the mechanism of air pollutants acting on solids.

6.1. Axial diffusion in the absence of wall coating and no homogeneous reaction

This is the simplest case of the experimental set-up in Fig. 2 and that of Eq. 5, reading

$$\frac{\partial c_g}{\partial t} = D_A \frac{\partial^2 c_g}{\partial z^2} \tag{28}$$

with initial condition

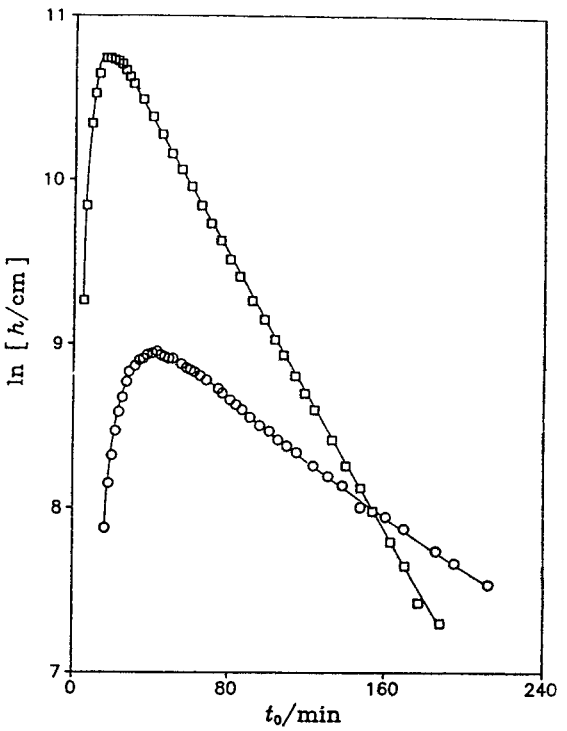

Fig. 4. Diffusion bands obtained with 0.5 cm^3 C_3H_6, injected into (□) an empty denuder or (○) a denuder coated with marble powder. From Ref. [9] with permission.

$$c_g(0, z) = \frac{m}{a_z} \delta(z - L) \tag{29}$$

or

$$c_g(0, z) = c_i \tag{30}$$

where m is the amount (mol) of analyte injected as a small volume instantaneous pulse (delta function) at $z = L$ (Eq. 29), or as a larger gaseous volume to fill the whole denuder tube initially with concentration c_i (Eq. 30), and a_z the cross-sectional area (cm^2) of the tube. There are two important boundary conditions, namely

$$(\partial c_g / \partial z)_{z=L} = 0 \tag{31}$$

since there is no flux of analyte across the closed boundary $z = L$, and

$$c_g(t, 0) = c(l', t) \quad \text{and} \quad D_A(\partial c_g / \partial z)_{z=0} = vc(l', t) \tag{32}$$

where $c(l', t)$ is the concentration in the sampling column at $x = l'$ and time t and v is the mean linear velocity of air in the same column. No reference is made here to the radial coordinate r of c_g, since the two relevant boundary conditions are $\partial c_g/\partial r = 0$ at both $r = 0$ and $r = R$, i.e., at the cylinder axis and at its wall, respectively.

Eq. 28 has been solved in the past [27,28] using certain approximations with the results

$$c(l', t) = N_2 \exp(-\alpha_A t) - 3N_2 \exp(-9\alpha_A t) + \cdots \quad (33)$$

$$c(l', t) = N_3 \exp(-\alpha_A t) + N_3 \exp(-9\alpha_A t) + \cdots \quad (34)$$

where

$$N_2 = \pi m D/\dot{V}L^2 \quad \text{and} \quad N_3 = 2D_A c_i a_z/\dot{V}L \quad (35)$$

and α_A is the diffusion parameter:

$$\alpha_A = \pi^2 D_A/4L^2 \quad (36)$$

The first solution, Eq. 33, applies to the initial condition in Eq. 29, whereas the second, Eq. 34, applies to the condition in Eq. 30. Both solutions describe the behaviour of the carrier phenomenon, i.e., axial diffusion along the cylinder axis, in the absence of any other physical or chemical process. They have been confirmed experimentally by measuring gas diffusion coefficients of binary and ternary mixtures at various temperatures [27], and comparing them with those reported by other workers or calculated theoretically.

Naturally, Eqs. 33 and 34 describe the experimental diffusion bands, such as that in Fig. 4 obtained with an empty denuder (top curve), given by Eq. 27.

6.2. Axial diffusion in the presence of a wall coating and no homogeneous reaction

In this case the mass balance Eq. 5 reads

$$\frac{\partial c_g}{\partial t} = D_A \frac{\partial^2 c_g}{\partial z^2} - D_A\left(\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right) \quad (37)$$

The minus sign in front of the radial term is due to the initial conditions in the coating, $c_s = 0$, where c_s (mol g^{-1}) is the adsorbed analyte concentration, and also to the fact that here the solution assumes a non-steady-state condition ($\partial c_g/\partial t \neq 0$) and a non-zero longitudinal diffusion ($D_A \partial^2 c_g/\partial z^2 \neq 0$). If one tries to solve Eq. 37 with a positive sign, a final result not supported by experimental measurements is obtained, namely, negative deposition velocities and reaction probabilities are calculated.

For the solution of Eq. 37, the standard method of separation of variables can be tried or an even simpler and more direct method [9] can be applied, leading to the same result. The latter is based on taking the double Laplace transforms of each term of Eq. 37 with respect to time t and the length coordinate z, resulting in a second-order differential equation of the independent variable r along the tube radius. This is easily solved with respect to r.

Then, a flux boundary condition at the gas–solid interface is written as

$$-D_A\left(\frac{\partial c_g}{\partial r}\right)_{r=R} = \frac{k_{-1}}{S_a}(c_s^* - c_s) \quad (38)$$

where c_s^* is the equilibrium concentration (mol g^{-1}) of the adsorbed analyte on the denuder coating, k_{-1} (s^{-1}) the rate constant for desorption from the solid coating and S_a ($cm^2\ g^{-1}$) the specific surface area of solid exposed to the gaseous analyte.

The above boundary condition is combined with the rate of change of the adsorbed analyte:

$$\frac{\partial c_s}{\partial t} = k_{-1}(c_s^* - c_s) - k_2 c_s \quad (39)$$

where k_2 (s^{-1}) is the rate constant of a possible first-order or pseudo-first-order surface reaction of the adsorbed analyte, and also with a linear adsorption isotherm

$$K = c_s^*/c_R \quad (40)$$

c_R being $(c_g)_{r=R}$. The combination of Eqs. 38, 39 and 40 is made after having taken their double Laplace transforms (with respect to t and z), with initial condition $(c_s)_{t=0} = 0$. The result is now used with the solution of initial Eq. 37 with respect to r, mentioned before.

A crucial parameter appearing in the last calculations is

$$\lambda_0^2 = \frac{4k_1(p+k_2)}{2D_A(p+k_{-1}+k_2)+R^2k_1(p+k_2)} \quad (41)$$

where k_1 (s^{-1}) is an adsorption rate constant, defined as

$$k_1 = k_{-1}\cdot\frac{K}{RS_a} = k_{-1}K' \quad (42)$$

K' being a dimensionless equilibrium distribution constant ($K' = k_1/k_{-1}$), and p is the Laplace transform parameter with respect to time.

Finally, the double inverse Laplace transformation with respect to z and t gives the function measured experimentally, i.e., the height H of the sample peaks:

$$\begin{aligned} H^{1/M} = {} & N_2\left(1-\frac{Z_1}{Y_1}\right)\exp\left[-\left(\frac{X_1-Y_1}{2}+k_2\right)t\right] \\ & + N_2\left(1+\frac{Z_1}{Y_1}\right)\exp\left[-\left(\frac{X_1+Y_1}{2}+k_2\right)t\right] \\ & - 3N_2\left(1-\frac{Z_2}{Y_2}\right)\exp\left[-\left(\frac{X_2-Y_2}{2}+k_2\right)t\right] \\ & - 3N_2\left(1+\frac{Z_2}{Y_2}\right)\exp\left[-\left(\frac{X_2+Y_2}{2}+k_2\right)t\right] \end{aligned} \quad (43)$$

where

$$\begin{aligned} & X_1 = \alpha_A + k'_{-1} - k'_1 - k_2 \\ & (X_1^2 - Y_1^2)/4 = k'_{-1}(\alpha_A - k_2) \\ & Z_1 = X_1 - 2k'_{-1} \\ & X_2 = 9\alpha_A + k'_{-1} - k'_1 - k_2 \\ & (X_2^2 - Y_2^2)/4 = k'_{-1}(9\alpha_A - k_2) \\ & Z_2 = X_2 - 2k'_{-1} \end{aligned} \quad (44)$$

k'_1 and k'_{-1} being given by the relationships

$$k'_1 = \frac{4k_1}{2+R^2k_1/D_A} \quad \text{and}$$

$$k'_{-1} = \frac{2k_{-1}}{2+R^2k_1/D_A} \quad (45)$$

It must be pointed out that Eq. 43 reduces to Eq. 33 when $k'_{-1} = k'_1 = k_2 = 0$. Also, Eq. 43 has been derived with initial condition Eq. 29, whereas Eq. 30, i.e., with the analyte injected as a gaseous volume large enough to fill the entire denuder tube initially, leads to a slightly different form of Eq. 43, namely N_2 is replaced by N_3 (cf., Eq. 35) throughout, and the factor -3 in the last two terms becomes $+1$. Therefore, the way of introducing the analyte into the denuder tube may change the appearance of the diffusion bands, because of the change in the prefix sign of some terms, but the theoretical equations remain substantially the same, and the details described for the calculations [9] are exactly the same in both cases.

Equation 43 shows that the diffusion band consists of four exponential functions of time. By using a non-linear regression analysis computer program, the exponential coefficients, termed $B1$, $B2$, $B3$ and $B4$, and the respective pre-exponential factors, denoted $A1$, $A2$, $A3$ and $A4$, can be calculated from the experimental bands. Such a program has been written in GW-BASIC and is given in Appendix A. It can be run on a simple PC by entering in the DATA lines the values H, T in pairs, where H is the height (in arbitrary units, say cm) of the sample peaks and T the respective times, when reversal of the carrier gas-flow was made. The total number of pairs N, the response factor of the detector M (say 1 for a flame ionization detector), and any factor $H1$ to divide H (say 10^3) are entered in the 150, 170 and 180 INPUT lines, respectively. Running the program in Appendix A gives the logarithms $\ln(A1)$, $\ln(A2)$, $\ln(A3)$ and $\ln(A4)$ of the four pre-exponential factors $A1 = N_2(1 - Z_1/Y_1)$, $A2 = N_2(1 + Z_1/Y_1)$, $A3 = 3N_2(1 - Z_2/Y_2)$ and $A4 = 3N_2(1 + Z_2/Y_2)$ of Eq. 43 and the respective exponential coefficients $B1 = -[(X_1 - Y_1)/2 + k_2]$, $B2 = -[(X_1 + Y_1)/2 + k_2]$, $B3 = -[(X_2 - Y_2)/2 + k_2]$ and $B4 = -[(X_2 + Y_2)/2 + k_2]$, together with their standard errors and the prefixes S, P and X ($+1$ or -1).

A similar PC program for the sum of two exponential functions has been published elsewhere [33] and gives $\ln A1$(empty) and $\ln A2$(empty), together with the respective exponential coefficients $B1$(empty) and $B2$(empty), which are equal to $-\alpha_A$ and $-9\alpha_A$,

respectively, of Eqs. 33 and 34. From the above data, the rate constants k_1, k_{-1} and k_2 can be calculated, either from the exponential coefficients of time $B1$, $B2$, $B3$, $B4$, $-\alpha_A$ and $-9\alpha_A$ or from any two exponential coefficients of Eq. 43, the respective pre-exponential factors, and the $-\alpha_A$ and $-9\alpha_A$ coefficients. The details of these calculations are given elsewhere [9] with an Appendix containing a PC program for conducting the calculations based on both methods simultaneously, with all possible combinations of pairs of exponential coefficients and pre-exponential factors.

From the rate constants k_1, k_{-1} and k_2 so determined, the calculation of deposition velocities V_d and reaction probabilities γ becomes very simple. Recalling Eqs. 38–40 and 42, one finds

$$-D_A\left(\frac{\partial c_g}{\partial r}\right)_{r=R} = \frac{Rk_1}{K}(Kc_R - c_s) \tag{46}$$

$$\frac{\partial c_s}{\partial t} = k_{-1}(Kc_R - c_s) - k_2 c_s \tag{47}$$

At the beginning $c_s = 0$, the right-hand side of Eq. 46 becomes $Rk_1 c_R$, and hence, at $t = 0$, the deposition velocity is given by

$$V_d = Rk_1 \tag{48}$$

At a long time, a steady-state assumption for the adsorbed concentration c_s gives, from Eq. 47,

$$c_s = \frac{k_{-1}Kc_R}{k_2 + k_{-1}}$$

This, substituted for c_s in Eq. 46, gives

$$-D_A\left(\frac{\partial c_g}{\partial r}\right)_{r=R} = Rk_1\left(\frac{k_2}{k_2 + k_{-1}}\right)c_R \tag{49}$$

It is seen from this expression that the deposition velocity now becomes

$$V_d = Rk_1\left(\frac{k_2}{k_2 + k_{-1}}\right) \tag{50}$$

i.e., the initial deposition velocity is multiplied by the combination $k_2/(k_2 + k_{-1})$ of the rate constants for surface reaction k_2 and desorption k_{-1}. Having found the values of all rate constants k_1, k_{-1} and k_2, as described above, and the known value of denuder radius R, we can easily calculate V_d by means of Eq. 50.

In Section 2, it was said that the first solution describing the analyte concentration leaving a denuder tube compared with that entering the tube is the GK equation (Eq. 7) based on a boundary condition of zero concentration at the tube wall. In the improved solution of Cooney et al. [13] (CKD solution), a new boundary condition was employed, similar to Eq. 49, but expressed in molecular terms (cf., Eq. 9). Equating the right-hand sides of Eqs. 9 and 49, one can easily calculate γ by the relationship

$$\frac{1}{\gamma} = \left(\frac{R_g T}{2\pi M}\right)^{1/2} \cdot \frac{k_2 + k_{-1}}{Rk_1 k_2} + \frac{1}{2} \tag{51}$$

The calculations based on Eqs. 50 and 51 to find V_d and γ are included in the PC program in the Appendix of Ref. [9], which prints the values of all physico-chemical parameters Rk_1, k_{-1}, k_2, V_d and γ, calculated with both methods mentioned above, from all possible combinations, together with their mean values and their standard error of determination. Tables 1, 2 and 3 in Ref. [9] list the values of the physico-chemical parameters described in this section for the action of propene on a silica gel tube at 310.2 K, an aluminium oxide tube at 373.2 K and a marble powder tube at 310.2 K; also, the action of hydrogen sulfide on a pure silver foil tube at 298.2 K is reported.

A comparison of deposition velocities and reaction probabilities determined as described in this section with those determined by means of the GK and CKD equations (Eqs. 7 and 11, respectively) is given below:

(1) It is clear from the definition of V_d by Eqs. 48 and 50, and the relation of γ to it (Eq. 51), that both parameters are independent of molecular diffusion, being related only to the rate constants k_1 (adsorption), k_{-1} (desorption) and k_2 (surface reaction). The necessity for correcting reaction probabilities by means of such rate constants was pointed out by Judeikis and Stewart [19] almost 20 years ago but, to the best of our knowledge, this has never been done.

(2) Deposition velocities of SO_2 on marble,

measured by parallel plate denuders [6], under various conditions, change continuously with time and this is expected to happen with the other denuder types through which air flows continuously. This is not the case here, however, the initial Rk_1 value (Eq. 48) and the final value (Eq. 50) being just two different physical quantities, or different approximations of V_d.

(3) As seen from Eqs. 12–14 and pointed out in Sections 2 and 5, to measure γ accurately it is necessary to avoid diffusion-limited deposition velocities, or find estimates of it, as long as there are order of magnitude differences between them and the measured deposition velocities. Only when surface resistance becomes the dominant limiting process in transport to the wall are V_d and γ independent of diffusion rates. In the present section methodology gaseous diffusion has become the only carrier of the phenomena, but it does not enter into the calculations of V_d and γ, except as a small correction in the calculation of k_1 and k_{-1} from k_1' and k_{-1}' computed initially (cf., Eqs. 45). To see how small this correction is, one can cast the first of Eq. 45 into a form similar to that of Eq. 14:

$$\frac{2}{V_d'} = \frac{1}{V_d} + \frac{R}{2D_A}$$

where, according to Eq. 48, $V_d' = Rk_1'$ and $V_d = Rk_1$ are the directly measured deposition velocity and the corrected value, respectively. The radius of the tube R here takes the place of δ_c, the thickness of the stationary layer on the solid. It is as if the whole gaseous volume inside the denuder tube has become the stationary layer.

(4) In the previous sections, irreversible surface reactions of the pollutants with the solid were assumed. In contrast, the return flux of accommodated molecules back to the gas phase is not considered negligible in the present section, i.e., reversible reactions are taken into account. This is clearly shown by Eqs. 38 and 39.

With all these differences between the present method and those based on GK and CKD equations, it is not surprising that V_d and γ appear to have one or two orders of magnitude smaller values than before.

6.3. Axial diffusion in the presence of a wall partly coated and no homogeneous reaction

If one tries to apply the method in Section 6.2, namely Eq. 43 and the following calculations, to the action of, say, sulfur dioxide on marble powder covering the internal wall of the diffusion denuder, no sample peaks are obtained, unless large amounts of SO_2 are injected. This is obviously due to high deposition velocities of this gas onto marble, and Eq. 43 cannot be applied, since it predicts zero or negative peak heights H. A further development of the method was therefore required to embrace this case of relatively high deposition velocities. It was accomplished [34] by using a denuder having a wall coating with the solid only in a small part L_2 of its total length $L_1 + L_2$, as shown in Fig. 5.

Adopting as initial condition

$$c_y(0, y) = c_i \quad \text{and} \quad c_z(0, z) = 0$$

which can be fulfilled by injecting into the denuder a volume of analyte gas small enough to fill only section L_2 (approximately), we can apply the mathematical analysis of Topalova et al. [9] only to this part of the denuder tube, whereas for the remaining part L_1 equations applicable in the absence of a wall coating (cf. Section 6.1) are used. Linking the solutions in parts L_2 and L_1 by continuity conditions of concentrations and fluxes, and using certain approximations given in detail elsewhere [34], one finds for the height of the sample peaks, instead of Eq. 43, the equation

$$H^{1/M} = N_4\left(1 - \frac{Z}{Y}\right)\exp\left(-\frac{X - Y}{2}\cdot t\right) + N_4\left(1 + \frac{Z}{Y}\right)\exp\left(-\frac{X + Y}{2}\cdot t\right) \qquad (52)$$

where

$$N_4 = c_i L_2^3 D_A / 3vS_1 \qquad (53)$$

$$X = (S_2 - \lambda_1^2 S_3) D_A / S_1 \qquad (54)$$

$$(X^2 - Y^2)/4 = (2A - \lambda_1^2 S_4 + \lambda_1^4 S_5) D_A^2 / S_1 \qquad (55)$$

$$Z = X - 2D_A\left(\frac{6}{L_2^2} - \lambda_1^2\right) \qquad (56)$$

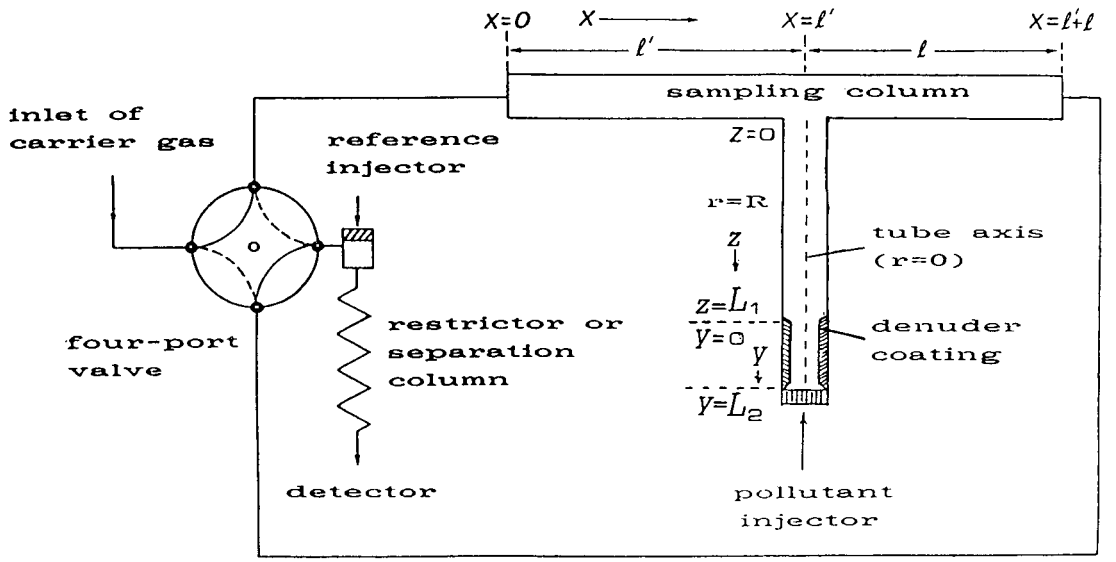

Fig. 5. Schematic representation of columns and gas connections for measuring high deposition velocities and reaction probabilities by a partly coated denuder tube, either near the closed end as shown, or near the junction at $z = 0$. From Ref. [34] with permission.

$$\lambda_1^2 = \frac{4k_1k_2}{2D_A(k_{-1} + k_2) + R^2k_1k_2} \tag{57}$$

S_1, S_2, S_3, S_4 and S_5 being geometrical characteristics of the denuder tube, described by the relationships

$$\begin{aligned} S_1 &= [A(L_1^4 + L_2^4 + 6L_1^2L_2^2) \\ &\quad + 4L_1L_2(L_1^2 + L_2^2)]/12 \\ S_2 &= AL_1^2 + AL_2^2 + 2L_1L_2 \\ S_3 &= (4L_1^3L_2 + 6AL_1^2L_2^2 + 8L_1L_2^3 \\ &\quad + 2AL_2^4)/12 \\ S_4 &= AL_2^2 + 2L_1L_2 \\ S_5 &= (AL_2^4 + 4L_1L_2^3)/12 \end{aligned} \tag{58}$$

with A representing the ratio of sectional areas a_z/a_y of parts L_1 and L_2.

Note that λ_1^2 as given by Eq. 57 is obtained from λ_0^2 in Eq. 41 by setting $p = 0$. This corresponds to a steady-state assumption, but only for the adsorbed analyte concentration c_s.

Calculations using Eqs. 53–58 are carried out with the diffusion bands obtained with the arrangement of Fig. 5. The pre-exponential factors

$$A1 = N_4(1 - Z/Y) \quad \text{and} \quad A2 = N_4(1 + Z/Y)$$

and the exponential coefficients

$$B1 = -(X - Y)/2 \quad \text{and} \quad B2 = -(X + Y)/2$$

can be calculated by using the PC program for the sum of two exponential functions by Niotis and Katsanos [33].

Addition of $B1$ and $B2$ gives the value of the auxiliary parameter $-X$, subtraction yields the value of $-Y$, whilst multiplication of them gives $(X^2 - Y^2)/4$. Then, from the ratio of the two pre-exponential factors $\rho = (1 - Z/Y)/(1 + Z/Y)$, we find

$$Z = \frac{1 - \rho}{1 + \rho} \cdot Y \tag{59}$$

Using these values in Eqs. 52–56, together with the definitions in Eq. 58, one can easily calculate, from the data for a single experiment, both the diffusion coefficient D_A of the analyte gas in the air and the value of the radial diffusion parameter λ_1^2. From these two values, the deposition velocity V_d and the wall reaction probabili-

ty γ are found using again Eqs. 50 and 51, combined into the relationship

$$\frac{1}{\gamma} = \left(\frac{R_g T}{2\pi M}\right)^{1/2} \Big/ V_d + \frac{1}{2} \tag{60}$$

From Eq. 50 and the definition in Eq. 57 of λ_1^2, we obtain

$$V_d = \frac{2RD_A\lambda_1^2}{4 - R^2\lambda_1^2} \tag{61}$$

All these calculations are carried out with the PC program given in Appendix B.

If the lengths L_1 (bare) and L_2 (coated) of the denuder tube (cf., Fig. 5) are interchanged and the initial condition is an instantaneous pulse at $y = L_2$, the resulting equations come out slightly different [34], the central relationship being analogous to Eq. 52:

$$H^{1/M} = \frac{N_5}{Y}\exp\left(-\frac{X-Y}{2}\cdot t\right) - \frac{N_5}{Y} \times \exp\left(-\frac{X+Y}{2}\cdot t\right) \tag{62}$$

where

$$N_5 = \frac{4mD_A^2}{\dot{V}S_1} \tag{63}$$

$$X = (S_2 - \lambda_1^2 S_6)D_A/S_1 \tag{64}$$

$$(X^2 - Y^2)/4 = (2A - \lambda_1^2 S_7 + \lambda_1^4 S_8)D_A^2/S_1 \tag{65}$$

S_1 and S_2 are given by the first two of Eqs. 58 and S_6, S_7 and S_8 are defined as follows:

$$S_6 = (6AL_1^2L_2^2 + 4L_1^3L_2 + 2AL_1^4)/12 \tag{66}$$

$$S_7 = AL_1^2 \quad \text{and} \quad S_8 = AL_1^4/12 \tag{67}$$

Only the exponential coefficients of Eq. 62:

$$B1 = -(X - Y)/2 \quad \text{and} \quad B2 = -(X + Y)/2$$

are usable here, being calculated by means of the PC program for the sum of two exponential functions [33]. As before, addition of $B1$ and $B2$ gives the value of $-X$ and multiplication of them yields the value of $(X^2 - Y^2)/4$. Using these values in Eqs. 64–67, together with the first two of Eq. 58, one can calculate, from the data for a single experiment, both the diffusion coefficient D_A of the analyte and the parameter λ_1^2. From these, the deposition velocity V_d and the wall reaction probability γ are easily found using again Eqs. 61 and 60, respectively. Appendix C lists the necessary PC program.

Experimental details for the application of both methods in the present section are given elsewhere [34]. Examples were sulfur dioxide and acetylene depositing on marble powder at various temperatures. Both arrangements were used (cf., Fig. 5), i.e., L_1 bare and L_2 coated, and vice versa. The results are collected in Table 1 in Ref. [34]. The repeatability of the results is shown by the mean values of D_A, V_d and γ and their standard error, as calculated from experiments under the same conditions. The length of the denuder tube covered with marble on its wall had some effect on V_d and γ, but only a small effect on D_A. Similar results are obtained with L_1 bare and L_2 coated, or vice versa, in most cases.

As expected, deposition velocities and reaction probabilities are greater for SO_2 than for C_2H_2, at the same temperature. The effect of increasing temperature with the same lengths L_1 and L_2 shows a general trend for both V_d and γ, which increase slowly with temperature. This can be easily explained by considering Eqs. 50 and 60 and assuming certain values and behaviour for k_1, k_2 and k_{-1}. A noticeable fact is the accuracy (%) of D_{found}, as can be judged from the ratio $100|D_{found} - D_{calc}|/D_{found}$.

Comparing the V_d and γ values found by this method [34] with those found for propene on marble powder [9], one sees that the values for SO_2 and C_2H_2 are 1–2 orders of magnitude larger. The general conclusion is that high deposition velocities and reaction probabilities of gaseous pollutants on solid surfaces, together with their diffusion coefficient into air, can conveniently be measured in a single experiment lasting a few hours, and using very simple gas chromatographic instrumentation.

6.4. Axial diffusion in the absence of wall coating with an homogeneous reaction

Integration method

Second-order kinetics in gas-phase reactions rarely lead to second-order rate constants, owing to both experimental and calculation difficulties. These are usually circumvented by adopting pseudo-first-order rate constants, based on the presence of an excess amount of one reactant compared with that of the other. Naturally, this approximation cannot be applied to second-order reactions involving only one reactant, e.g., a dimerization.

Bimolecular reactions are important in measuring interaction rates between gaseous pollutants in the atmospheric environment, e.g., between SO_2 and NO_2. These rates may result in synergistic effects, accelerating, delaying or even inhibiting dangerous chemical processes involving the pollutants and buildings, historic monuments and cultural heritage, such as works of art inside a museum. It is understood that such reactions occur not in a closed system, but combined with convection currents and gaseous diffusion in the open atmosphere as shown in Fig. 1. The simulation of such a system is very difficult, if not impossible, but the technique of RF-GC offers an experimental set-up very close to the natural situation in air. This is similar to Fig. 2, but without a wall coating (Fig. 6).

Suppose that air as carrier gas flows through the sampling column with a constant linear velocity v, and small amounts m_A and m_B mol of two gaseous analytes A and B are introduced into the diffusion column through the solute injector; on reversing the flow direction of the carrier gas repeatedly for small time intervals of 10–60 s, a series of narrow sample peaks is recorded again in the chromatogram (cf., Fig. 3). The height H of these peaks measures again concentrations of the reactants being injected, $c_A(l', t)$ and $c_B(l', t)$, or of gaseous products being formed, all at junction $x = l'$ at the time t of the flow reversal, according to Eq. 27. The value of M gives the response factor of the gas chromatographic detector for each substance. Separation of the peaks due to different substances is effected by the additional separation column (cf., Fig. 6).

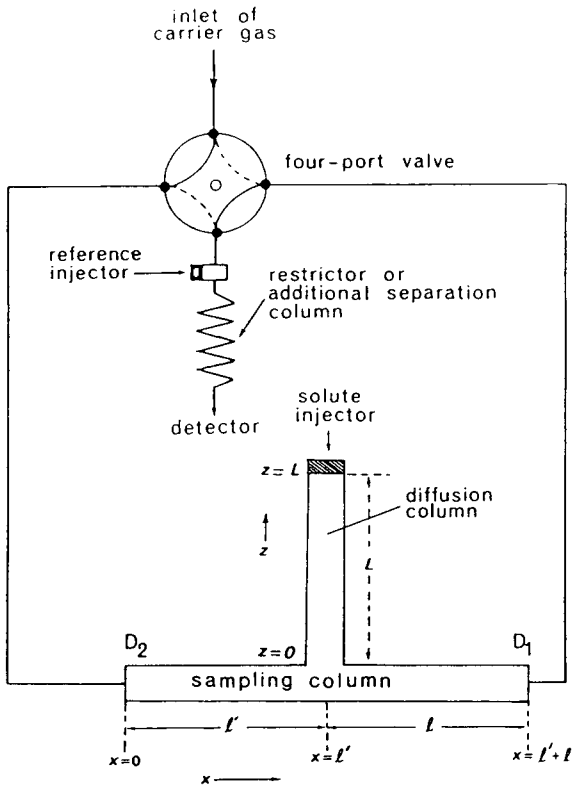

Fig. 6. Schematic representation of the experimental set-up for studying second-order kinetics by the RF-GC technique. From Ref. [36] with permission.

The plot of $H^{1/M}$ or $(1/M)$ ln H against t is again a diffusion band (cf., Fig. 4). Now it is described by the sum or difference of three exponential functions of time:

$$H^{1/M}/2 = c_A(l', t) = A_1 \exp(B_1 t) + A_2 \exp(B_2 t) + A_3 \exp(B_3 t) \quad (68)$$

It is through the pre-exponential factors A_1, A_2 and A_3, and the respective exponential coefficients B_1, B_2 and B_3, that the various physico-chemical parameters pertaining to A and B are determined. If A and B do not interact at the temperature of the diffusion column, only their gaseous diffusion coefficients D_A and D_B into air are extracted from As and Bs (cf., Eqs.

33 and 34). If, however, they interact according to a second-order law, their mass balance equations are given by Eq. 5, without the convection term $v(\partial c_g/\partial z)$ and the radial diffusion term, the reaction rate r_A written as kc_Ac_B:

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial z^2} - kc_Ac_B$$
$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial z^2} - kc_Ac_B \quad (69)$$

where k is the second-order rate constant of the reaction.

To study non-linear systems, such as a second-order reaction, by conventional gas chromatography would be very difficult and very few cases have been reported. A recent publication [35] is worth mentioning. The authors assumed the validity of the model of the extended ideal chromatographic reactor and derived equations for the evaluation of rate constants of irreversible non-first-order reactions from experimental data obtained by means of the reaction gas chromatographic pulse overlay method. The suitability of the method was demonstrated numerically, using experimental data from the esterification of ethanol with acetic anhydride. The basic difference from the present method is that a carrier gas flows through the chromatographic reactor, whereas here the bulk transport term $v(\partial c_g/\partial z)$ is physically separated from the reaction space, making the phenomena simpler to study.

To solve Eqs. 69, one can express concentrations c_A and c_B as series in powers of k:

$$c_A(t, z) = f_0(t, z) + f_1(t, z)k + f_2(t, z)k^2 + \cdots \quad (70)$$

$$c_B(t, z) = g_0(t, z) + g_1(t, z)k + g_2(t, z)k^2 + \cdots \quad (71)$$

where the coefficients f_0, f_1, f_2, ... and g_0, g_1, g_2, ... are functions of the same variables t and z, as those of c_A and c_B, to be determined.

Multiplication of the right-hand side of Eqs. 70 and 71 and substitution of the product for c_Ac_B in the first of Eqs. 69, together with Eq. 70 for c_A, gives a differential equation which can be separated into the following partial equations, by simply collecting terms of the same power of k:

Terms of k^0:

$$\left(\frac{\partial}{\partial t} - D_A \frac{\partial^2}{\partial z^2}\right) f_0 = 0 \quad (72)$$

Terms of k^1:

$$\left(\frac{\partial}{\partial t} - D_A \frac{\partial^2}{\partial z^2}\right) f_1 + f_0 g_0 = 0 \quad (73)$$

Terms of k^2:

$$\left(\frac{\partial}{\partial t} - D_A \frac{\partial^2}{\partial z^2}\right) f_2 + (f_0 g_1 + f_1 g_0) = 0 \quad (74)$$

etc. Analogous equations hold true for c_B, obtained from the second of Eqs. 69 and having D_B and g_0, g_1, g_2, ... instead of D_A and f_0, f_1, f_2, ..., respectively, in the first term of Eqs. 72, 73 and 74.

Solution of Eq. 72 as before [27, 28] gives $f_0(t, z)$ as a function of t and z, whereas the equivalent of Eq. 72 for c_B yields $g_0(t, z)$. From these, f_0g_0 is calculated and used to solve Eq. 73 so that $f_1(t, z)$ is found. To proceed for $f_2(t, z)$, $g_1(t, z)$ is found and then Eq. 74 is solved. At present, it has not gone as far as that with the non-linear system.

Returning to Eqs. 70 and 71 and substituting the results found for f_0, f_1 and g_0, g_1 at $z = 0$ (cf., Fig. 6), using also Eq. 27, one has the height H of the sample peaks as a function of time. For solute A this reads

$$H_A^{1/M} = 2(N_0 - kR_3)\exp(-\alpha_A t) - 2kR_2\exp(-4\alpha_A t) + 2kR_1\exp[-(\alpha_A + \alpha_B)t] \quad (75)$$

where N_0, R_1, R_2 and R_3 are known explicit functions of the amounts m_A and m_B injected, the diffusion coefficients D_A and D_B into air, the velocity of the carrier gas, the gaseous volume V_g and the length L of the diffusion column, the parameters α_A and α_B being given by $\alpha_A = \pi^2 D_A/4L^2$ and $\alpha_B = \pi^2 D_B/4L^2$ according to Eq. 36. A similar expression gives $H_B^{1/M}$, and also $H_A^{1/M}$ for a second-order reaction with one reactant A, the difference in these three cases being

the slightly different definitions of R_1, R_2 and R_3.

A comparison of Eqs. 68 and 75 shows the physical meaning of A_1, A_2 and A_3 and B_1, B_2 and B_3. By means of a relatively simple PC program given in Appendix D, the values of the As and Bs are computed from the pairs H, t of the experimental diffusion band. Then, from the ratio A_1/A_2 or A_1/A_3, the program calculates the second-order rate constant k.

Three examples of application of the method are given elsewhere [37] and repeated in Table 1.

With reactions involving one reactant, fractional orders and the respective rate constants can be determined by performing experiments with varying amounts m_A of reactant. Assuming k to be an apparent second-order rate constant in the rate law $r_A = kc_A^2$, and being related to the true rate constant k' by $k = k'c_A^n = k'(m_A/V_g)^n$, one can find both k' and n by plotting ln k vs. ln m_A according to the equation

$$\ln k = \ln k' - n \ln V_g + n \ln m_A \quad (76)$$

This plot should be linear with a slope n and intercept ln $k' - n$ ln V_g. An example is the reaction of propanal in pure nitrogen at 353.2 K [37]. Six different amounts of propanal ($1.39 \cdot 10^{-5}$–$1.94 \cdot 10^{-4}$ mol) were used, giving $n = -1.18$ and $k' = 4.11 \cdot 10^{-5}$ mol$^{0.18}$ dm$^{-0.54}$ s^{-1}, with a correlation coefficient 0.978. The order of the reaction is therefore $2 + n = 0.82$.

Differential method

In order to interpret synergistic effects on the basis of interaction of pollutants in the gas phase, reference to the detailed mechanism of the interaction is necessary. This mechanism cannot be inferred only from assumed second-order rate constants, determined as described in detail above. A valuable physico-chemical parameter in this respect is the experimental kinetic order of the reaction, and the rate constant pertaining to that order. Thus, the integration method developed above can be complemented by a differential method, which in chemical kinetics is considered the most appropriate kind to determine reaction orders, very often coming out as fractional numbers. There are two kinds of differential orders, the true one, denoted n_c, and the order with respect to time, denoted n_t. The latter is the most informative about the mechanism covering an extended period of the relevant reaction, rather than referring to the initial rates, as n_c does.

Table 1
Second-order rate constants (k) for three reaction systems in air, measured by RF-GC

System	T (K)	k (dm^3 mol^{-1} s^{-1})	
		From A_1/A_2	From A_1/A_3
$SO_2 + NO_2$	323.2	$4.10 \cdot 10^{-2}$	$6.30 \cdot 10^{-2}$
$SO_2 + Br_2$	323.2	10.9	11.2
$SO_2 + Br_2$	373.2	18.7	16.9

One can start from Eq. 28 which the gaseous pollutant A would obey moving along the diffusion column of Fig. 6. As before, RF-GC creates extra chromatographic peaks, and the diffusion band constructed from them is mathematically and theoretically described by Eq. 68. In the absence of a homogeneous chemical reaction, this takes the form (cf., Eq. 34)

$$H^{1/M}/2 = c_A(l', t) = A_1(e^{-\alpha_A t} + e^{-9\alpha_A t} + e^{-25\alpha_A t} + \cdots) \quad (77)$$

where $\alpha_A = \pi^2 D_A/4L^2$ (cf., Eq. 36) is the diffusion parameter depending on the diffusion coefficient D_A and the tube length L. In a short time interval the terms $\exp(-9\alpha_A t) + \exp(-25\alpha_A t) + \cdots$ become negligible compared with $\exp(-\alpha_A t)$, and Eq. 77 is simplified to

$$c_A = A_1 e^{-\alpha_A t} \quad (78)$$

If the rate of change of A, $\partial c_A/\partial t$, is due not only to its longitudinal diffusion along z (cf., Fig. 6), but also to a homogeneous chemical reaction of any order n with respect to A, Eq. 28 becomes

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial z^2} - r_A \quad (79)$$

which is again Eq. 69 with r_A denoting as before the rate of a reaction with respect to A (mol m^{-3} s^{-1}).

It is difficult to solve Eq. 79, because it is a non-linear equation, since r_A in the gas phase generally has the form

$$r_A = kc_A^n c_B^m \tag{80}$$

where B is a second reactant, with the orders n and m being integral or fractional numbers. This problem with $n = m = 1$ (overall a second-order reaction) has been handled in the integration method of the present section by the approximation of expressing c_A and c_B as series of powers in k. Now, a different philosophy is adopted by considering r_A just as an unknown function of z and t, $r_A(z, t)$, and using the rate law Eq. 80 after the solution of Eq. 79 is completed. This can be achieved by taking the double Laplace transforms of its terms with respect to t and z, with initial condition $c_A(z, 0) = c_i$, i.e., with A injected into the diffusion column in a large enough volume (under atmospheric conditions) so that it fills uniformly tube L throughout at $t = 0$, and boundary conditions analogous to those expressed by Eqs. 31 and 32.

After various simple mathematical manipulations and application of the boundary conditions, adopting some approximations already used in the past [27], one takes the double inverse Laplace transforms of the resulting expression and finds [38]

$$c_A(l', t) = \frac{2D_A c_i}{vL} e^{-\alpha_A t} - \frac{\pi D_A}{vL} \times \int_0^t \langle r_A(z, \tau) \rangle e^{-\alpha_A (t-\tau)} d\tau \tag{81}$$

where

$c_A(l', t)$ = concentration of pollutant at the junction $x = l'$ of Fig. 6, at time t;

$\langle r_A(z, \tau) \rangle$ = mean reaction rate with respect to z along the whole diffusion column from 0 to L;

$\alpha_A = \pi^2 D_A / 4L^2$ (Eq. 36);

τ = a dummy variable for time.

The integral on the right-hand side results from the inverse Laplace transformation of the product of two functions of time (convolution). As in Eq. 78, only the first exponential function of time, $\exp(-\alpha_A t)$, was retained from Eq. 77, the rest, $\exp(-9\alpha_A t)$, $\exp(-25\alpha_A t)$, ..., being considered negligible after a short time interval from the start.

Comparing Eq. 81 with Eq. 78, one sees the effect of the chemical reaction on the concentration of A at the exit of the diffusion column. It is a diminishing effect described by the integral over the time period 0–t. If the rate Eq. 80 is unknown, the integral cannot be calculated from the measured $c_A(l', t)$ by the height H of the sample peaks. Unless a reaction order n is assumed and used to calculate the integral, a procedure similar to the integration method of classical chemical kinetics. However, the main problem remaining again is how to check experimentally the validity of the choice of n. This is where the differential method enters into play, to solve the problem of the integral calculation fairly easily: differentiating Eq. 81 with respect to time, one has

$$\begin{aligned} \frac{dc_A}{dt} &= \frac{D_A}{vL}\left[-2\alpha_A c_i e^{-\alpha_A t} - \pi \frac{d}{dt} \times \int_0^t \langle r_A(z, \tau) \rangle e^{-\alpha_A (t-\tau)} d\tau\right] \\ &= \frac{D_A}{vL}\left[-2\alpha_A c_i e^{-\alpha_A t} - \pi \langle r_A(z, t) \rangle + \pi\alpha_A \times \int_0^t \langle r_A(z, \tau) \rangle e^{-\alpha_A (t-\tau)} d\tau\right] \end{aligned} \tag{82}$$

the last expression on the right-hand side resulting from the application of the Leibniz rule [39]. Multiplying Eq. 81 by α_A throughout and adding to Eq. 82 yields

$$\alpha_A c_A + \frac{dc_A}{dt} = -\frac{\pi D_A}{vL} \langle r_A(z, t) \rangle$$

or, substituting Eq. 80 for r_A,

$$-\left(\alpha_A c_A + \frac{dc_A}{dt}\right) = \frac{\pi D_A}{vL} \cdot k c_B^m c_A^n \tag{83}$$

Taking logarithms of both sides, we obtain the linear equation

$$\ln\left(-\alpha_A c_A - \frac{dc_A}{dt}\right) = \ln\left(\frac{\pi D_A}{vL} \cdot k_{app}\right) + n \ln c_A \quad (84)$$

where

$$k_{app} = k c_B^m \quad (85)$$

Using this, k_{app} and n are easily and accurately calculated as follows. One can consider time as a dummy independent variable and calculate from Eq. 68 for chosen arbitrary values of time both c_A and dc_A/dt:

$$\frac{dc_A}{dt} = A_1 B_1 \exp(B_1 t) + A_2 B_2 \exp(B_2 t) + A_3 B_3 \exp(B_3 t) \quad (86)$$

Then, using the calculated c_A and dc_A/dt values, we can plot the left-hand side of Eq. 84 as a function of $\ln c_A$. This linear plot gives k_{app} from the intercept and n from the slope. This value of n corresponds to n_t mentioned above, since it is based on c_A and dc_A/dt values over an extended time period, as long as we like.

If $m = 0$, i.e., the reaction depends only on c_A, the apparent rate constant, k_{app}, corresponds to the true value, k. If $m \neq 0$, its value can be found, together with the true k, by performing experiments with the same initial $c_A(c_i)$, but with varying c_B values, much greater than c_i. Then, according to Eq. 85,

$$\ln k_{app} = \ln k + m \ln c_B \quad (87)$$

In Appendix F a PC program is given for calculating reaction orders and rate constants based on Eqs. 77–86. The necessary values of A_1, A_2, A_3, B_1, B_2 and B_3 are obtained from the diffusion band using the PC program in Appendix E. These, together with the value of α_A and the final time chosen for the calculations, are entered in the DATA line 620 of Appendix F. The program chooses the optimum number of time points, within the limits set, that correspond to the highest correlation coefficient. The dimensionless parameter $\pi D_A/vL$ of Eq. 84 is entered in INPUT line 180 to permit the calculation of k_{app} from the intercept of the plot of this equation.

An example for the reaction of 1 cm^3 C_2H_2 with NO_2 (1.733 mol m^{-3}) at 60°C gave the following results [38]: apparent rate constant = $3.557513 \pm 6.387705 \cdot 10^{-3}$; slope and reaction order = $0.9911004 \pm 3.457481 \cdot 10^{-4}$; square of correlation coefficient = 0.9999143; and optimum number of points = 24.

6.5. Axial diffusion in the presence of a wall coating with a homogeneous reaction

This is the most general case of the RF-GC technique with cylindrical denuders, with a mass balance equation

$$\frac{\partial c_g}{\partial t} = D_A \frac{\partial^2 c_g}{\partial z^2} - D_A\left(\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right) - r_A \quad (88)$$

i.e., Eq. 37 corrected for the rate of a chemical reaction of the pollutant A in the gas phase, r_A, or the general Eq. 5 from which only the convective term $v(\partial c_g/\partial z)$ was omitted. Here the rate of change of A is due to three out of the four causes mentioned there, namely, longitudinal diffusion, radial diffusion and homogeneous chemical reaction.

An easy solution of Eq. 88 can be found by repeating the procedure used for Eq. 37 [9], adopting now a steady state for the adsorbed concentration c_s, i.e., $\partial c_s/\partial t = 0$, and then combining the result with the differential method of determining reaction orders and rate constants of the previous subsection [38]. More specifically, we take the double Laplace transforms of each term of Eq. 88 with respect to time t and length coordinate z, resulting in a second-order differential equation of the radial coordinate r. This is easily solved by using the Frobenius method as before [9], and approximating the solution by its first two terms. Then, the flux boundary condition at the gas–solid interface (Eq. 38), the rate of change of the adsorbed analyte (Eq. 39) by setting $\partial c_s/\partial t = 0$, and the linear isotherm (Eq. 40) are combined with the Frobenius solution of Eq. 88 to give

$$\bar{C}_0 = \frac{sC_g(0) + C'_g(0) - \dfrac{m}{a_z D_A}\exp(-Ls) + \bar{R}_A/D_A}{s^2 - (q^2 - \lambda_1^2)} \tag{89}$$

where
$\bar{C}_0$ = double Laplace transform with respect to t and z of c_g at $r = 0$;
$C_g(0) = t$ transform of c_g at $z = 0$;
$C'_g(0) = dC_g/dz$ at $z = 0$;
$\bar{R}_A$ = double transform with respect to t and z of the reaction rate r_A;
s = transform parameter for z

$$q^2 = p/D_A \tag{90}$$

and λ_1^2 is given by Eq. 57. Eq. 89 has exactly the same form as Eq. 24 in Ref. [9], valid without a homogeneous reaction.

Taking the s inverse transform of Eq. 89 and then setting $(dC_0/dz)_{z=L} = 0$, because there is no flux across the boundary $z = L$ (cf., Fig. 2), one obtains

$$C_A(l', p) = \frac{m}{\dot{V}}\operatorname{sech} fL - \langle R_A(z)\rangle \frac{L}{v}\operatorname{sech} fL \tag{91}$$

where

$$f^2 = q^2 - \lambda_1^2 = \frac{1}{D_A}(p - \lambda_1^2 D_A) \tag{92}$$

and $\langle R_A(z)\rangle$ is the t transformed mean reaction rate along the coordinate z. Comparing Eq. 91 with Eq. 30 in Ref. [9], one sees that the latter is corrected for the presence of the reaction by the appearance of the second term on the right-hand side.

Now, the p inverse transforms of Eq. 91 give

$$c_A(l', t) = \frac{\pi m D_A}{\dot{V}L^2}\, e^{-(\alpha_A - \lambda_1^2 D_A)t} - \frac{\pi D_A}{vL}\int_0^t \langle r_A(z,\tau)\rangle\, e^{-(\alpha_A - \lambda_1^2 D_A)(t-\tau)}\, d\tau \tag{93}$$

which is similar to Eq. 81, with only a small difference in the first pre-exponential factor due to the different initial condition, which here is Eq. 30, rather than Eq. 31.

Adopting the differential method of the previous subsection, Eq. 93 gives on differentiation

$$\frac{dc_A}{dt} = \frac{\pi D_A}{vL}\left[-(\alpha_A - \lambda_1^2 D_A)\frac{m}{a_z L}\, e^{-(\alpha_A - \lambda_1^2 D_A)t} - \langle r_A(z,t)\rangle + (\alpha_A - \lambda_1^2 D_A) \times \int_0^t \langle r_A(z,\tau)\rangle\, e^{-(\alpha_A - \lambda_1^2 D_A)(t-\tau)}\, d\tau\right] \tag{94}$$

As before, multiplication of Eq. 93 by $(\alpha_A - \lambda_1^2 D_A)$ throughout and addition to Eq. 94 gives, replacing also $\langle r_A(z,t)\rangle$ by Eq. 80,

$$(\alpha_A - \lambda_1^2 D_A)c_A + \frac{dc_A}{dt} = -\frac{\pi D_A}{vL}\cdot k c_B^m c_A^n \tag{95}$$

which has exactly the same form as Eq. 83. It becomes identical with that when $\lambda_1^2 = 0$, which holds true in the absence of a wall coating in the denuder tube.

By first conducting an experiment with the denuder devoid of solid coating, and using Eqs. 84 and 86, with the help of the PC program in Appendix F one finds n and $k_{app} = kc_B^m$ of Eq. 95, as already described. Then, performing the same experiment in the presence of a solid wall coating, and rewriting Eq. 95 as

$$\ln\left(-\frac{\pi D_A}{vL}\cdot k_{app} c_A^n - \frac{dc_A}{dt}\right) = \ln(\alpha_A - \lambda_1^2 D_A) + \ln c_A \tag{96}$$

we can find $\alpha_A - \lambda_1^2 D_A$ from the intercept of the plot of the left-hand side of Eq. 96 vs. $\ln c_A$. Eqs. 68 and 86 are used again to calculate c_A and dc_A/dt, considering time as a dummy variable. Absolute values of the expression in parentheses may be used if necessary.

Now, since α_A is known (cf., Eq. 36), $\lambda_1^2 D_A$ is found, and then the deposition velocity V_d from the inverse of Eq. 61:

$$\frac{1}{V_d} = \frac{2}{R}\cdot\frac{1}{\lambda_1^2 D_A} - \frac{R}{2D_A} \tag{97}$$

where R is the radius of the tube void space.

Finally, using Eq. 60, the reaction probability γ is calculated. Both these values, V_d and γ,

pertain here to a homogeneous chemical reaction in the gas phase above the solid, and therefore take into account synergistic effects of air pollutants.

This concludes the description of gas chromatographic instrumentation in conjunction with the RF-GC technique to measure rate coefficients in some air pollution phenomena.

7. Determination of experimental isotherms

The effects of air pollutants on buildings, monuments, artefacts, etc., depend not only on the mechanism of the various rate processes, but also on another important physico-chemical parameter, namely the equilibrium isotherms for the distribution of the pollutants between the solids and the surrounding gaseous phase. So far these isotherms were assumed to be linear, like that described by Eq. 40. However, as pointed out recently [9], this linear isotherm is only an approximation of a Langmuir-type isotherm. Could denuder tubes, assisted by gas chromatographic instrumentation, possibly offer an easy method for the experimental determination of isotherms? The answer to this question is in the affirmative and the RF-GC method combined with a cylindrical denuder can be used again.

The older chromatographic methods for the determination of equilibrium isotherms are based on the study of the propagation of concentration signals and its variation with concentration. They have been reviewed by Huber and Gerritse [40] and they mainly use frontal analysis with step injection, or the elution method with pulse injection. A later development, the so-called step-and-pulse method [41], combines these two techniques and extends the determination of isotherms to large concentrations, taking into account the sorption effect, the isotherm effect and the pressure gradient. However, this method neglects the effects of longitudinal diffusion along the chromatographic column and the kinetics of mass transfer across the gas–solid or gas–liquid boundaries. Moreover, the theoretical equation relating the isotherm to the experimental data is an integral equation with its unknown k' appearing under an integral. A series of complex calculations are necessary to derive the optimum values of the parameters of a selected isotherm equation. Thus, the method does not give directly an independent experimental isotherm, but needs a correct choice of an equation for the adsorption isotherm. This choice sometimes seems difficult, e.g., for benzene and cyclohexane adsorption on graphitized carbon black [42] various isotherm equations gave similar results.

Most, if not all, of the above difficulties arise from the presence of a carrier gas flowing through the chromatographic column. If the role of a "gaseous carrier" of substances is assigned only to axial gaseous diffusion along the column, holding the solid adsorbent or the liquid phase, isotherm determination becomes much simpler with the following additional advantages compared with the older methods: the diffusion and resistance to mass transfer are not neglected, the sorption effect is non-existent, the pressure gradient is negligible along the bed, the method can lead directly to an independent experimental isotherm over a wide range of concentrations, without specifying a priori an isotherm equation, and the isotherm can be determined in the presence of a surface reaction of the adsorbed analyte.

All the above can be achieved by using exactly the same experimental arrangement and procedure as described at the beginning of Section 6 (Figs. 2–4), but treating the experimental results differently, as described elsewhere [43]. The mathematical analysis, by means of which experimental isotherms are determined from the diffusion bands, follows the same lines of derivation as that in Ref. [9]. In that work the diffusion denuder tube was used to measure deposition velocities and reaction probabilities of gaseous analytes on the denuder wall coating, assuming a linear isotherm relationship (cf., Eq. 40) between the equilibrium concentration c_s^* (mol g^{-1}) of the adsorbed analyte and the gaseous concentration at the coating surface, $(c_g)_{r=R} = c_R$ (mol cm^{-3}), with K (cm^3 g^{-1}) designating the equilibrium distribution constant. Here this assumption is abandoned and replaced by

$$c_s^* = F + k\int_0^t c_R(\tau)\,d\tau \quad (98)$$

where c_s^* is the equilibrium adsorbed concentration at time t, F is the initial adsorbed concentration, which is a function of the initial gaseous concentration at $r = R$, i.e., of $(c_R)_{t=0}$, and k ($cm^3\ g^{-1}\ s^{-1}$) the equilibrium factor transforming into c_s^* the area under the curve c_R vs. time at any later time t. It is understood that if this relationship is applied to the descending branch of the diffusion band, i.e., after the maximum, k should have a negative value. In what follows only the necessary minimum mathematical analysis is given, the steps that are the same as those in Ref. [9] being mentioned.

The analysis starts with the mass balance equation of the adsorbate A in the denuder, i.e., Eq. 37, the solution of which is again based on taking the double Laplace transforms of each term with respect to time t and length z along the axis, resulting in a second-order differential equation of the independent variable r along the tube radius. This is easily solved with respect to r, giving a series solution, approximated by the first two terms of a modified Bessel function of order zero. The flux boundary condition of Eq. 38 at the gas–solid (or gas–liquid) interface is combined with the rate of change of the adsorbed analyte concentration c_s (mol g^{-1}), under a non-steady-state condition (Eq. 39), taking into account the isotherm Eq. 98, and the result is used with the Bessel function mentioned above. A time parameter analogous to λ_0^2 of Eq. 41 appears in the calculations, which, after taking the inverse Laplace transform with respect to z, applying the boundary conditions of Eqs. 31 and 32 and finally taking the inverse transform with respect to time, gives the height H of the sample peaks [43] as

$$H^{1/M} = gc_R(0) = A_1\exp(B_1t) + A_2\exp(B_2t) + A_3\exp(B_3t) \quad (99)$$

where M is the response factor of the detector, g the proportionality constant and $c_R(0)$ the concentration at $r = R$ and $z = 0$.

The exponential coefficients of time B_1, B_2 and B_3 satisfy Eqs. 100, 101 and 102, while the pre-exponential factors A_1, A_2 and A_3 are given by relationships not needed here:

$$X = \alpha_A + k_2 + k_{-1} + R^2k_3/2D_A = -(B_1 + B_2 + B_3) \quad (100)$$

$$Y = \alpha_Ak_2 + \alpha_Ak_{-1} + \left(\frac{R^2\alpha_A}{2D_A} - 2\right)k_3 + \frac{R^2k_3k_2}{2D_A} = B_1B_2 + B_1B_3 + B_2B_3 \quad (101)$$

$$Z = \frac{R^2k_3k_2\alpha_A}{2D_A} - 2k_3k_2 = -B_1B_2B_3 \quad (102)$$

where $\alpha_A = \pi^2D_A/4L^2$, k_{-1} (s^{-1}) is the rate constant of desorption of the analyte from the surface, k_2 (s^{-1}) is the rate constant of a possible first-order or pseudo-first-order surface reaction and k_3 (s^{-2}) is given by

$$k_3 = kk_{-1}/RS_a \quad (103)$$

Determining the values of B_1, B_2, B_3 and α_A experimentally, one can easily find the values of all physico-chemical quantities k_3, k_{-1}, k_2 and k and the isotherms, as described in detail below.

By using the non-linear regression analysis computer program in Appendix E, the exponential coefficients B_1, B_2 and B_3 and the respective pre-exponential factors A_1, A_2 and A_3 of Eq. 99 can be calculated from the experimental bands. This program is similar to that listed in Appendix A and used for Eq. 43, but it differs in that it deals with the sum of three, instead of four, exponential functions of time. As before, the DATA lines contain the values H, T in pairs, where H is the height of the sample peaks and T the respective times. Also, the total number of pairs N, the response factor of the detector, M, and any factor $H1$ to divide H are entered in INPUT lines 140, 160 and 170, respectively. Running the program in Appendix E gives the logarithms $\ln(A_1)$, $\ln(A_2)$ and $\ln(A_3)$ of the three pre-exponential factors, and B_1, B_2 and B_3, together with their standard errors and the prefixes S and P (+1 or −1).

From the values of B_1, B_2 and B_3, found as described above, one calculates the auxiliary

parameters X, Y and Z by means of Eqs. 100–102. Solving this system of equations for k_3, k_2 and k_{-1}, we find

$$k_3 = \left[\alpha_A X - \alpha_A^2 - Y + \frac{Z}{\alpha_A(1 - 16L^2/\pi^2R^2)}\right]\Big/2 \quad (104)$$

$$k_2 = \frac{Z}{(\pi^2R^2/8L^2 - 2)k_3} \quad (105)$$

$$k_{-1} = X - \alpha_A - k_2 - \pi^2R^2k_3/8L^2\alpha_A \quad (106)$$

It is seen that, except for X, Y and Z calculated from B_1, B_2 and B_3, the internal radius R and the length L of the denuder tube are required, and also the diffusion parameter α_A, calculated by Eq. 36 from the diffusion coefficient D_A. The latter can be determined experimentally as described elsewhere [27].

Coming now to the calculation of isotherms, the equilibrium differential isotherm $\partial c_s^*/\partial c_R$ is easily found, since on differentiating Eq. 98 with respect to time we obtain

$$\frac{\partial c_s^*}{\partial t} = k\frac{\partial}{\partial t}\int_0^t c_R(\tau)\,d\tau = kc_R(t) \quad (107)$$

while

$$\frac{\partial c_s^*}{\partial t} = \frac{\partial c_s^*}{\partial c_R}\cdot\frac{\partial c_R}{\partial t} \quad (108)$$

Comparing these two expressions, one finds

$$\frac{\partial c_s^*}{\partial c_R} = \frac{kc_R}{\partial c_R/\partial t} \quad (109)$$

The value of k is found from k_3 by means of the definition in Eq. 103 and c_R and $\partial c_R/\partial t$ are obtained from Eq. 99, corresponding to $z = 0$. This is based to the fact that $H^{1/M}$ is proportional to the sampling concentration $c(l', t)$, which is identical with $(c_g)_{r=0}$, $(c_g)_{r=R}$ or $\langle c_g\rangle$, as can be easily proved. Thus, using Eq. 99,

$$\partial c_s^*/\partial c_R = k \times \frac{A_1\exp(B_1t) + A_2\exp(B_2t) + A_3\exp(B_3t)}{A_1B_1\exp(B_1t) + A_2B_2\exp(B_2t) + A_3B_3\exp(B_3t)} \quad (110)$$

The integrated isotherm is simply found by performing the indicated integration in Eq. 98, using again Eq. 99 for $c_R(\tau)$. After having found the value of F on the condition that at $t = \infty$, $c_R = 0$ and also $c_s^* = 0$, the result for the isotherm comes out as

$$c_s^* = (k/g)[A_1\exp(B_1t)/B_1 + A_2\exp(B_2t)/B_2 + A_3\exp(B_3t)/B_3] \quad (111)$$

From Eq. 99, one can write

$$c_R = (1/g)[A_1\exp(B_1t) + A_2\exp(B_2t) + A_3\exp(B_3t)] \quad (112)$$

From the above, it is obvious that both the isotherms in Eqs. 110 and 111 do not give $\partial c_s^*/\partial c_R$ or c_s^* as proper functions of c_R, as expected, but as analytical functions of time t. However, this is most desirable since one can consider time as a dummy independent variable and calculate, for chosen arbitrary values of it, both $\partial c_s^*/\partial c_R$ by Eq. 110 and c_s^* by Eq. 111, together with the corresponding values of c_R by Eq. 112. Plotting $\partial c_s^*/\partial c_R$ or c_s^* against c_R for each chosen time, independent experimental isotherms are then obtained, without having chosen a priori a physical model equation.

The value of the proportionality constant g between peak height H and concentration can be determined for a particular adsorbate by repeating the experiment under exactly the same conditions, in the absence of the adsorbent coating, i.e., with an empty diffusion tube (cf., Fig. 2). If m is the amount (mol) of adsorbate introduced, then

$$gm = g\int_0^m dm = g\int_0^\infty c_R\,dV = g\dot{V}\int_0^\infty c_R\,dt = \dot{V}\int_0^\infty H^{1/M}\,dt$$

If the pre-exponential factors and the exponential coefficients of Eq. 99 determined in this case are denoted A_1', A_2', A_3' and B_1', B_2', B_3', respectively, the last integral is easily calculated as

$$\int_0^\infty H^{1/M}\,dt = -(A_1'/B_1' + A_2'/B_2' + A_3'/B_3')$$

and thus

$$g = -\frac{\dot{V}}{m}\left(\frac{A_1'}{B_1'} + \frac{A_2'}{B_2'} + \frac{A_3'}{B_3'}\right) \quad \text{in cm mol}^{-1}\ \text{cm}^3 \tag{113}$$

with $\dot{V}$ in $cm^3\ s^{-1}$, A_i' in cm and B_i' in s^{-1} ($i = 1, 2, 3$).

If one compares this value of g with that calculated by using in Eq. 113, the A_i and B_i values found in the presence of the adsorbent coating, say g', the fraction of irreversibly adsorbed analyte can be calculated from the ratio g'/g. Since the isotherms usually pertain to reversible processes, it is better to use the g' value in the calculations based on Eqs. 111 and 112, rather than the value of g.

All calculations of the rate constants k_3, k_2, k_{-1} and k, and also of the isotherms, can be made by the PC program in GW-BASIC given in Appendix G. The first-order rate constants k_2 pertain obviously to irreversible adsorption, the rate constant k_{-1} pertains to mass transfer resistance across the gas–solid boundary, as seen from Eq. 38, whereas the distribution constant determining the isotherm is k, having a negative value as expected from Eq. 98. This kinetic distribution constant replaces the equilibrium distribution constant K of the linear isotherm in Eq. 40.

The effects of gaseous diffusion, both longitudinal and radial, on the isotherms are taken into account quantitatively, a fact which has always been neglected in the chromatographic determination of isotherms.

The most important point in this work [43], however, is that one can compute experimental isotherms directly without an a priori specification of an isotherm theoretical or empirical equation. The use of time as an auxiliary dummy variable does not mean that one deals with kinetic adsorption isotherms, and this variable can simply be omitted. Even if one considers the isotherms obtained as kinetic ones, they differ from traditional kinetic isotherms, which are derived with the assumption that the adsorption rate is much greater than the desorption rate.

The above theoretical analysis has been applied to benzene and cyclohexane adsorbed on graphitized carbon black, to ethene, ethyne, propene and sulfur dioxide on marble powder and to propene on silica gel [43].

Acknowledgements

The authors thank the DG-XII of the European Communities for financial support under contract STEP-CT90-0108. They also acknowledge the help of Mrs. Margaret Barkoula and Miss Anna Malliori in preparing the typescript.

Appendix A

```
10 REM Non-Linear Regression Analysis of Function:
20 REM H^(1/M)=A1*EXP(B1*T)+S*A2*EXP(B2*T)+P*A3*EXP(B3*T)+X*A4*EXP(B4*T)
30 REM VARIABLES
40 REM     N2     = Minimum number of points of first exponential function
50 REM     MAX    = Square of maximum correlation coefficient
60 REM     OPT    = Final optional choice of variables when OPT=1
70 REM     J      = Number of points of first exponential function
80 REM     G      = Number of points of second exponential function
90 REM     F      = Number of points of third exponential function
100 REM    K,L    = First and last point of linear regression in subroutine
110 REM    SA,SB  = Standard errors of A and B in each linear regression
120 REM    Y(I)   = Ordinate for each linear regression in the subroutine
130 REM    U(I)   = Variable remaining by  removal of the previous one, two or
                    three exponential functions
140 REM    D(I)   = Function for calculating the correlation coefficient
150 INPUT "Total number of pairs H,T=";N
160 DIM H(N),T(N),Y(N),U(N),D(N)
170 INPUT "Response factor=";M
180 INPUT "Factor to divide H(I)=";H1
```

```
190 FOR I=1 TO N
200    READ H(I),T(I)
210    H(I)=H(I)/H1
220 NEXT I
230 N2=INT(N/7+.5)
240 MAX=0:OPT=0
250 REM Calculation of A1 and B1 with H,T pairs ranging from N2 to N-2*N2-3
260 FOR J=N2 TO N-2*N2-3
270    K=N-J+1
280    L=N
290    FOR I=K TO L
300       Y(I)=(1/M)*LOG(H(I))
310    NEXT I
320    GOSUB 2040       :REM Subroutine for linear regression analysis
330    A1=EXP(A)
340    B1=B
350    SA1=SA
360    SB1=SB
370    IF OPT=1 THEN  410
380 REM Calculation of A2 and B2 with H,T pairs ranging from N2 to N-J-N2-3

       ,and both prefixes -1 or +1
390    FOR S=-1 TO +1 STEP 2
400       FOR G=N2 TO N-J-N2-3
410          K=N-J-G+1
420           L=N-J
430          FOR I=K TO L
440             U(I)=S*H(I)^(1/M)-S*A1*EXP(B1*T(I))
450             Y(I)=LOG(ABS(U(I)))
460          NEXT I
470          GOSUB 2040     :REM Subroutine for linear regression analysis
480          A2=EXP(A)
490          B2=B
500          SA2=SA
510          SB2=SB
520          IF OPT=1 THEN 560
530 REM Calculation of A3 and B3 with H,T pairs ranging from N2 to N-J-G-3

       and both prefixes -1 or +1
540          FOR P=-1 TO +1 STEP 2
550             FOR F=N2 TO N-J-G-3
560                K=N-J-G-F+1
570                 L=N-J-G
580                FOR I=K TO L
590                   U(I)=P*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I)))
600                   Y(I)=LOG(ABS(U(I)))
610                NEXT I
620                GOSUB 2040:REM Subroutine for linear regression analysis
630                A3=EX?(A)
640                B3=B
650                SA3=SA
660                SB3=SB
670                IF OPT=1 THEN 700
680 REM Calculation of A4 and B4 with H,T pairs ranging from 1 to N-J-G-F,and

       both prefixes -1 or +1
690                FOR X=-1 TO +1 STEP 2
700                   K=1
710                   L=N-J-G-F
720                   FOR I=K TO L
730                      U(I)=X*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))

                              -P*A3*EXP(B3*T(I)))
740                      Y(I)=LOG(ABS(U(I)))
750                   NEXT I
760                   GOSUB 2040:REM Subroutine for linear regression
770                   A4=EXP(A)
780                   B4=B
790                   SA4=SA
800                   SB4=SB
810                   IF OPT=1 THEN 1030
820                   C1=0
830                   C2=0
```

```
840                   C3=0
850                   FOR I=1 TO N
860                      D(I)=H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))-P*
A3*
                              EXP(B3*T(I))-X*A4*EXP(B4*T(I))
870                      C1=C1+D(I)^2
880                      C2=C2+H(I)^(2/M)
890                      C3=C3+H(I)^(1/M)
900                   NEXT I
910                   R=1-C1/(C2-C3^2/N)
920                   IF R>MAX THEN MAX=R:SMAX=S:PMAX=P:XMAX=X:JMAX=J:GMAX=G:

                        FMAX=F
930                   PRINT MAX
940 REM When satisfied with the MAX value reached,Ctrl Break and GOTO 1010
950                NEXT X
960             NEXT F
970          NEXT P
980       NEXT G
990    NEXT S
1000 NEXT J
1010 S=SMAX:P=PMAX:X=XMAX:J=JMAX:G=GMAX:F=FMAX:OPT=1
1020 GOTO 270
1030 PRINT
1040 PRINT "Intercept Ln(A1) and its Standard error =";LOG(A1*H1) "+-"SA1
1050 PRINT "Slope B1 and its Standard error=";B1 "+-"SB1
1060 PRINT
1070 PRINT "Intercept Ln(A2) and its Standard error=";LOG(A2*H1) "+-"SA2
1080 PRINT "Slope B2 and its Standard error=";B2 "+-"SB2
1090 PRINT
1100 PRINT "Intercept Ln(A3) and its Standard error=";LOG(A3*H1) "+-"SA3
1110 PRINT "Slope B3 and its Standard error=";B3 "+-"SB3
1120 PRINT
1130 PRINT "Intercept Ln(A4) and its Standard error=";LOG(A4*H1) "+-"SA4
1140 PRINT "Slope B4 and its Standard error=";B4 "+-"SB4
1150 PRINT
1160 PRINT "Square of maximum correlation coefficient r^2=";MAX
1170 PRINT
1180 PRINT "Optimum values of points for 1st, 2nd , 3rd and 4th exponential

       functions, respectively=";JMAX","GMAX","FMAX"and"N-JMAX-GMAX-FMAX
1190 PRINT
1200 PRINT "Values of S,P and X,respectively ="; SMAX","PMAX"and"XMAX
1210 REM Enter in DATA the pairs of peak height H and the respective time T
2000 DATA
2010 DATA
2020 DATA
2030 END
2040 REM Linear regression of Y(I) = A + B T(I)
2050 S1=0
2060 S2=0
2070 S3=0
2080 S4=0
2090 S5=0
2100 FOR I=K TO L
2110    S1=S1+T(I)
2120    S2=S2+T(I)^2
2130    S3=S3+Y(I)
2140    S4=S4+Y(I)^2
2150    S5=S5+T(I)*Y(I)
2160 NEXT I
2170 Z=L-K+1      :REM Number of points  for the linear regression analysis
2180 M1=S5-S1*S3/Z
2190 M2=S2-S1^2/Z
2200 M3=S4-S3^2/Z
2210 A=(S3-S1*M1/M2)/Z
2220 B=M1/M2
2230 SYT=SQR(ABS(S4-A*S3-B*S5)/(Z-2))
2240 SA=SYT*SQR(S2/Z/M2)
2250 SB=SYT/SQR(M2)
2260 RETURN
```

Appendix B

```
10 REM Calculation of Deposition Velocities, Reaction Probabilities and
       Diffusion Coefficients from a Single Experiment with a Denuder
       partly Coated at its Closed End and No Homogeneous Reaction
20 INPUT "Expt,Analyte gas,Solid coating,Temperature in K";NO,GAS$,SOLID$,T
30 PRINT
40  REM CONSTANTS
50  REM     L1      = Bare length of the denuder tube
60  REM     L2      = Coated length of the denuder tube
70  REM LNA1,LNA2 = Logarithms of pre-exponential factors A1 and A2 of a two-
                    term exponential function of time, expressed by Eq.52
80  REM    B1,B2    = Exponential coefficients of time of a two-term
                    exponential function of time, expressed by Eq.52
90  REM      R      = Denuder internal radius
100 REM      M      = Molar mass of analyte
110 REM      A      = Ratio of cross sectional area of L1 to that of L2
120 READ L1,L2,LNA1,LNA2,B1,B2,R,M,A
130 PRINT "L1,L2 in cm =";L1 ","L2
140 PRINT "LNA1,LNA2=";LNA1 "," LNA2
150 PRINT "B1,B2 in 1/min=";B1","B2
160 PRINT "R in cm=";R;",M in kg/mol=";M;",A=";A
170 PRINT
180 REM   VARIABLES
190 REM S1,S2,S3,S4,S5 = Geometrical factors defined by Eq.58 in text
200 REM      X, Y, Z    = Auxiliary parameters of Eq.52
210 REM        R2       = Variable ( of Eq.59
220 S1=(A*(L1^4+L2^4+6*L1^2*L2^2)+4*L1*L2*(L1^2+L2^2))/12
230 S2=A*L1^2+A*L2^2+2*L1*L2
240 S3=(4*L1^3*L2+6*A*L1^2*L2^2+8*L1*L2^3+2*A*L2^4)/12
250 S4=A*L2^2+2*L1*L2
260 S5=(A*L2^4+4*L1*L2^3)/12
270 X=(B1+B2)/60
280 Y=(B2-B1)/60
290 R2=EXP(LNA1)/EXP(LNA2)
300 Z=Y*(1-R2)/(1+R2)
310 P=B1*B2/3600                          :REM P=(X^2-Y^2)/4
320 V=SQR(8.314*T/(2*3.1416*M))           :REM V=the square root in Eq.60
330 R1=S1*X^2/P
340 REM Squaring Eq.54,multiplying by S1 and division by Eq.55 gives a
       quadratic equation in λ^2 = L of the form W1*L^2 + W2*L + W3 = 0,
       where W1,W2 and W3  are given by
350 W1=S5*R1-S3^2
360 W2=2*S2*S3-R1*S4
370 W3=2*A*R1-S2^2
380 REM The solution of the quadratic equation is given in the following loop
390 FOR S=-1 TO +1 STEP 2
400    L=(-W2+S*SQR(W2^2-4*W1*W3))/2/W1
410    IF (L<0) THEN 600
420    D=SQR(P*S1/(2*A-L*S4+L^2*S5))
430    IF D<0 GOTO 600
440    VD1=(2*R*L*D/(4-R^2*L))/100        :REM According to Eq.61
450    G1=1/((V/VD1)+(1/2))               :REM According to Eq.60
460    PRINT "D (cm^2/s) from slopes of filled tube=";D
470    PRINT "Vd (m/s) from slopes=";VD1
480    PRINT "G from slopes=";G1
490    PRINT
500    LI=(Z-X)/2/D+6/(L2^2)               :REM LI is "^2 from Eq.56
510    VD2=(2*R*LI*D/(4-R^2*LI))/100       :REM According to Eq.61
520    G2=1/((V/VD2)+.5)                   :REM According to Eq.60
530    PRINT "Vd(m/s) from intercepts=";VD2
540    PRINT  "G from intercepts=";G2
550    VD12=(VD1+VD2)/2
560    G12=(G1+G2)/2
570    PRINT
580    PRINT "Mean value Vd(m/s) from slopes and intercepts=";VD12
590    PRINT "Mean value G from slopes and intercepts=";G12
600 NEXT S
```

```
610 PRINT
620 REM  In DATA Enter values of L1,L2 in cm,LNA1,LNA2,B1,B2 (positive)
         in l/min,R in cm,M in kg/mol,A
630 DATA
640 END
```

Appendix C

```
10 REM Calculation of Deposition Velocities,Reaction Probabilities and
       Diffusion Coefficients from a Single Experiment with a Denuder
       partly Coated near the Junction with the Sampling Column
20 INPUT "Expt,Analyte gas,Solid coating,Temperature in K";NO,GAS$,SOLID$,T
30 PRINT
40  REM  CONSTANTS
50  REM      L1      = Coated length of the denuder tube
60  REM      L2      = Bare length of the denuder tube
70  REM     B1,B2    = Exponential coefficients of time of a two-term
                       exponential function of time, expressed by Eq.62
80  REM       R      = Denuder internal radius
90  REM       M      = Molar mass of analyte
100 REM       A      = Ratio of cross sectional area of L1 to that of L2
110 READ L1,L2,B1,B2,R,M,A
120 PRINT "L1,L2 in cm =";L1 ","L2
130 PRINT "B1,B2 in 1/min=";B1","B2
140 PRINT "R in cm=";R;",M in kg/mol=";M;",A=";A
150 PRINT
160 REM   VARIABLES
170 REM S1,S2,S6,S7,S8 = Geometrical factors defined by Eqs.58,66 and 67
                         in text
180 REM       X,Y       = Auxiliary parameters of Eq.62
190 S1=(A*(L1^4+L2^4+6*L1^2*L2^2)+4*L1*L2*(L1^2+L2^2))/12
200 S2=A*L1^2+A*L2^2+2*L1*L2
210 S6=(4*L1^3*L2+6*A*L1^2*L2^2+2*A*L1^4)/12
220 S7=A*L1^2
230 S8=A*L1^4/12
240 X=(B1+B2)/60
250 P=B1*B2/3600                              : REM P=(X^2-Y^2)/4
260 V=SQR(8.314*T/(2*3.1416*M))               : REM V=the squre root in Eq.60
270 R1=S1*X^2/P
280 REM Squaring Eq.64,multiplying by S1 and division by Eq.65 gives a
       quadratic equation in λ^2 = L of the form W1*L^2 + W2*L + W3 = 0,
       where W1,W2 and W3 are given by
290 W1=S8*R1-S6^2
300 W2=2*S2*S6-R1*S7
310 W3=2*A*R1-S2^2
320 REM The solution of the quadratic equation is given in the following loop
330 FOR S=-1 TO +1 STEP 2
340    L=(-W2+S*SQR(W2^2-4*W1*W3))/2/W1
350    IF (L<0) THEN 430
360    D=SQR(P*S1/(2*A-L*S7+L^2*S8))
370    VD1=(2*R*L*D/(4-R^2*L))/100            : REM According to Eq.61
380    G1=1/((V/VD1)+(1/2))                   : REM According to Eq.60
390    PRINT "D (cm^2/s) from slopes of filled tube=";D
400    PRINT "Vd (m/s) from slopes=";VD1
410    PRINT "G from slopes=";G1
420    PRINT
430 NEXT S
440 REM  In DATA Enter values of L1,L2 in cm,B1,B2 (positive) in 1/min,
       R in cm,M in kg/mol,A
450 DATA
460 END
```

Appendix D

```
10 REM Non-Linear Regression Analysis of Function:
20 REM H^(1/M)=A1*EXP(B1*T)+S*A2*EXP(B2*T)+P*A3*EXP(B3*T)
30 REM And Calculation of the Second-Order Rate Constant
40 REM VARIABLES
50 REM     N2     = Minimum number of points of first exponential function
60 REM     MAX    = Square of maximum correlation coefficient
70 REM     OPT    = Final optional choice of variables when OPT=1
80 REM     J      = Number of points of first exponential function
90 REM     G      = Number of points of second exponential function
100 REM    K,L    = First and last point for linear regression analysis in the

                    subroutine
110 REM    SA,SB  = Standard errors of A and B in each linear regression
120 REM    Y(I)   = Ordinate for each linear regression in the subroutine
130 REM    U(I)   = Variable remaining by removal of the previous one or two

                    exponential functions
140 REM    D(I)   = Function for calculating the correlation coefficient
150 INPUT "Total number of pairs H,T=";N
160 DIM H(N),T(N),Y(N),U(N),D(N)
170 INPUT "Response factor=";M
180 INPUT "Factor to divide H(I)=";H1
190 INPUT "Quantity of second reactant in mol=";MB
200 INPUT "Gaseous volume of diffusion column in cm^3=";VG
210 FOR I=1 TO N
220    READ H(I),T(I)
230    H(I)=H(I)/H1
240 NEXT I
250 N2=INT(N/6+.5)
260 MAX=0:OPT=0
270 REM Calculation of A1 and B1 with H,T pairs ranging from N2 to N-N2-3
280 FOR J=N2 TO N-N2-3
290    K=N-J+1
300    L=N
310    FOR I=K TO L
320       Y(I)=(1/M)*LOG(H(I))
330    NEXT I
340    GOSUB 2040          : REM Subroutine for linear regression analysis
350    A1=EXP(A)
360    B1=B
370    SA1=SA
380    SB1=SB
390    IF OPT=1 THEN  430
400 REM Calculation of A2 and B2 with H,T pairs ranging from N2 to N-J-3 and

       both prefixes -1 and +1
410    FOR S=-1 TO +1  STEP 2
420       FOR G=N2 TO N-J-3
430          K=N-J-G+1
440          L=N-J
450          FOR I=K TO L
460             U(I)=S*H(I)^(1/M)-S*A1*EXP(B1*T(I))
470             Y(I)=LOG(ABS(U(I)))
480          NEXT I
490          GOSUB 2040      : REM Subroutine for linear regression analysis
500          A2=EXP(A)
510          B2=B
520          SA2=SA
530          SB2=SB
540          IF OPT=1 THEN 570
550 REM Calculation of A3 and B3 with H,T pairs ranging from 1 to N-J-G, with

      both prefixes -1 and +1
560          FOR P=-1 TO +1 STEP 2
570             K=1
580             L=N-J-G
590             FOR I=K TO L
600                U(I)=P*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I)))
610                Y(I)=LOG(ABS(U(I)))
620             NEXT I
630             GOSUB 2040     : REM Subroutine for linear regression analysis
640             A3=EXP(A)
```

```
650             B3=B
660             SA3=SA
670             SB3=SB
680             IF OPT=1 THEN  880
690             C1=0
700             C2=0
710             C3=0
720             FOR I=1 TO N
730                D(I)=H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))

                        -P*A3*EXP(B3*T(I))
740                C1=C1+D(I)^2
750                C2=C2+H(I)^(2/M)
760                C3=C3+H(I)^(1/M)
770             NEXT I
780             R=1-C1/(C2-C3^2/N)
790             IF R>MAX THEN MAX=R:SMAX=S:PMAX=P:JMAX=J:GMAX=G
800             PRINT MAX
810 REM When satisfied with the MAX value reached,Ctrl Break and GOTO 860
820          NEXT P
830       NEXT G
840    NEXT S
850 NEXT J
860 S=SMAX:P=PMAX:J=JMAX:G=GMAX:OPT=1
870 GOTO 290
880 PRINT
890 PRINT "Intercept Ln(A1) and its Standard error=";LOG(A1*H1) "+-"SA1
900 PRINT "Slope B1 and its Standard error=";B1 "+-"SB1
910 PRINT
920 PRINT "Intercept Ln(A2) and its Standard error=";LOG(A2*H1) "+-"SA2
930 PRINT "Slope B2 and its Standard error=";B2 "+-"SB2
940 PRINT
950 PRINT "Intercept Ln(A3) and its Standard error=";LOG(A3*H1) "+-"SA3
960 PRINT "Slope B3 and its Standard error=";B3 "+-"SB3
970 PRINT
980 PRINT "Square of maximum correlation coefficient r^2=";MAX
990 PRINT
1000 PRINT "Optimum values of points for 1st, 2nd and 3rd exponential

          functions, respectively=";JMAX","GMAX"and"N-JMAX-GMAX
1010 PRINT
1020 PRINT "Values of S and P, respectively =";SMAX"and"PMAX
1030 REM Calculation of the second-order rate constant from B1,B2,B3, the

        ratio  A1/A2 or A1/A3, the quantity MB of the second reactant,

        and the gaseous volume of diffusion column VG, according to Eq.75
1040 REM  CONSTANTS
1050 REM    16/3π  =1.69765
1060 REM    16/π   =5.09296
1070 B1=ABS(B1)    :B2=ABS(B2)    :B3=ABS(B3)
1080 K12=(1.69765*MB/VG)*(1/(B3-B1)-A1/A2/(B3-B2))     : REM From A1/A2
1090 K13=(5.09296*MB/VG)*(B1)/(B3-B1)*(1/(B2-B1)-A1/A3/(B3-B2)) :

     REM From A1/A3
1100 K1=1/K12/60/1000
1110 K2=1/K13/60/1000
1120 KM=(K1+K2)/2
1130 PRINT
1140 PRINT "Second order rate constant from A1 and A2, k (dm^3/mol s)=";K1
1150 PRINT "Second order rate constant from A1 and A3, k (dm^3/mol s)=";K2
1160 PRINT "Mean value of the two above, <k> (dm^3/mol s)=";KM
1170 REM Enter in DATA the pairs of peak height H and the respective time T
2000 DATA
2010 DATA
2020 DATA
2030 END
2040 REM Linear regression of Y(I) = A + B T(I)
2050 S1=0
2060 S2=0
2070 S3=0
2080 S4=0
2090 S5=0
2100    FOR I=K TO L
2110    S1=S1+T(I)
```

```
2120    S2=S2+T(I)^2
2130    S3=S3+Y(I)
2140    S4=S4+Y(I)^2
2150    S5=S5+T(I)*Y(I)
2160 NEXT I
2170 Z=L-K+1  :REM Number of points for the linear regression analysis
2180 M1=S5-S1*S3/Z
2190 M2=S2-S1^2/Z
2200 M3=S4-S3^2/Z
2210 A=(S3-S1*M1/M2)/Z
2220 B=M1/M2
2230 SYT=SQR(ABS(S4-A*S3-B*S5)/(Z-2))
2240 SA=SYT*SQR(S2/Z/M2)
2250 SB=SYT/SQR(M2)
2260 RETURN
```

Appendix E

```
10 REM Non-Linear Regression Analysis of Function:
20 REM H^(1/M)=A1*EXP(B1*T)+S*A2*EXP(B2*T)+P*A3*EXP(B3*T)
30 REM VARIABLES
40 REM     N2     = Minimum number of points of first exponential function
50 REM     MAX    = Square of maximum correlation coefficient
60 REM     OPT    = Final optional choice of variables when OPT=1
70 REM     J      = Number of points of first exponential function
80 REM     G      = Number of points of second exponential function
90 REM    K,L    = First and last point for linear regression analysis in the

                    subroutine
100 REM    SA,SB = Standard errors of A and B in each linear regression
110 REM    Y(I)  = Ordinate for each linear regression in the subroutine
120 REM    U(I)  = Variable remaining by removal of the previous one or two

                    exponential functions
130 REM    D(I)  = Function for calculating the correlation coefficient
140 INPUT "Total number of pairs H,T=";N
150 DIM H(N),T(N),Y(N),U(N),D(N)
160 INPUT "Response factor=";M
170 INPUT "Factor to divide H(I)=";H1
180 FOR I=1 TO N
190    READ H(I),T(I)
200    H(I)=H(I)/H1
210 NEXT I
220 N2=INT(N/6+.5)
230 MAX=0:OPT=0
240 REM Calculation of A1 and B1 with H,T pairs ranging from N2 to N-N2-3
250 FOR J=N2 TO N-N2-3
260    K=N-J+1
270    L=N
280    FOR I=K TO L
290       Y(I)=(1/M)*LOG(H(I))
300    NEXT I
310    GOSUB 2040          : REM Subroutine for linear regression analysis
320    A1=EXP(A)
330    B1=B
340    SA1=SA
350    SB1=SB
360    IF OPT=1 THEN  400
370 REM Calculation of A2 and B2 with H,T pairs ranging from N2 to N-J-3 and

        both prefixes -1 and +1
380    FOR S=-1 TO +1  STEP 2
390       FOR G=N2 TO N-J-3
400          K=N-J-G+1
410          L=N-J
420          FOR I=K TO L
430             U(I)=S*H(I)^(1/M)-S*A1*EXP(B1*T(I))
440             Y(I)=LOG(ABS(U(I)))
450          NEXT I
460          GOSUB 2040      : REM Subroutine for linear regression analysis
470          A2=EXP(A)
480          B2=B
490          SA2=SA
```

```
500          SB2=SB
510          IF OPT=1 THEN 540
520 REM Calculation of A3 and B3 with H,T pairs ranging from 1 to N-J-G, with

       both prefixes -1 and +1
530          FOR P=-1 TO +1 STEP 2
540             K=1
550             L=N-J-G
560             FOR I=K TO L
570                U(I)=P*(H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I)))
580                Y(I)=LOG(ABS(U(I)))
590             NEXT I
600             GOSUB 2040    : REM Subroutine for linear regression analysis
610             A3=EXP(A)
620             B3=B
630             SA3=SA
640             SB3=SB
650             IF OPT=1 THEN  850
660             C1=0
670             C2=0
680             C3=0
690             FOR I=1 TO N
700                D(I)=H(I)^(1/M)-A1*EXP(B1*T(I))-S*A2*EXP(B2*T(I))

                        -P*A3*EXP(B3*T(I))
710                C1=C1+D(I)^2
720                C2=C2+H(I)^(2/M)
730                C3=C3+H(I)^(1/M)
740             NEXT I
750             R=1-C1/(C2-C3^2/N)
760             IF R>MAX THEN MAX=R:SMAX=S:PMAX=P:JMAX=J:GMAX=G
770             PRINT  MAX
780 REM When satisfied with the MAX value reached,Ctrl Break and GOTO 830
790          NEXT P
800       NEXT G
810    NEXT S
820 NEXT J
830 S=SMAX:P=PMAX:J=JMAX:G=GMAX:OPT=1
840 GOTO 260
850 PRINT
860 PRINT "Intercept Ln(A1) and its Standard error=";LOG(A1*H1) "+-"SA1
870 PRINT "Slope B1 and its Standard error=";B1 "+-"SB1
880 PRINT
890 PRINT "Intercept Ln(A2) and its Standard error=";LOG(A2*H1) "+-"SA2
900 PRINT "Slope B2 and its Standard error=";B2 "+-"SB2
910 PRINT
920 PRINT "Intercept Ln(A3) and its Standard error=";LOG(A3*H1) "+-"SA3
930 PRINT "Slope B3 and its Standard error=";B3 "+-"SB3
940 PRINT
950 PRINT "Square of maximum correlation coefficient r^2=";MAX
960 PRINT
970 PRINT "Optimum values of points for 1st, 2nd and 3rd exponential

          functions, respectively=";JMAX","GMAX"and"N-JMAX-GMAX
980 PRINT
990 PRINT "Values of S and P, respectively =";SMAX"and"PMAX
1000 REM Enter in DATA the pairs of peak height H and the respective time T
2000 DATA
2010 DATA
2020 DATA
2030 END
2040 REM Linear regression of Y(I) = A + B T(I)
2050 S1=0
2060 S2=0
2070 S3=0
2080 S4=0
2090 S5=0
2100    FOR I=K TO L
2110    S1=S1+T(I)
2120    S2=S2+T(I)^2
2130    S3=S3+Y(I)
2140    S4=S4+Y(I)^2
2150    S5=S5+T(I)*Y(I)
2160 NEXT I
2170 Z=L-K+1  :REM Number of points for the linear regression analysis
```

```
2180 M1=S5-S1*S3/Z
2190 M2=S2-S1^2/Z
2200 M3=S4-S3^2/Z
2210 A=(S3-S1*M1/M2)/Z
2220 B=M1/M2
2230 SYT=SQR(ABS(S4-A*S3-B*S5)/(Z-2))
2240 SA=SYT*SQR(S2/Z/M2)
2250 SB=SYT/SQR(M2)
2260 RETURN
```

Appendix F

```
10 REM Differential Method for Calculating Reaction Orders and Rate Constants

       in the absence of solid
20 REM  CONSTANTS
30 REM  LNA1,LNA2,LNA3 = Logarithms of pre-exponential factors of Eq.68 in

                         text ,as calculated with the program of Appendix E
40 REM  B1,B2,B3       = Exponential coefficients of time of Eq.68 in text,

                         as calculated with the program of Appendix E
50 REM     A4          = Diffusion parameter as defined by Eq. 36 in text
60 REM    TEND         = Last experimental time, used as first trial "final

                         time" for the differential plot
70 REM     S,P         = Prefixes of the 2nd and 3rd term of Eq.68,as

                         calculated by the program of Appendix E
80 REM     D           = Diffusion coefficient of reactant in carrier gas

                        (cm^2/s)
90 REM     v           = Linear velocity of carrier gas (cm/s)
100 REM    L           = Length of diffusion column (cm)
110 REM  VARIABLES
120 REM     Y(I)        = Ordinate for linear regression in subroutine
130 REM     X(I)        = Abscissa for linear regression in subroutine
140 REM     C(I)        = Gaseous concentration , calculated by Eq.68, as

                          a function of time
150 REM     DC(I)       = Derivative dc/dt, as calculated by Eq.86 in text
160 READ LNA1,B1,LNA2,B2,LNA3,B3,A4,TEND,S,P
170 DIM Y(200),X(200),C(200),DC(200)
180 INPUT "Dimensionless Parameter 3.1416D/vL=";DVL
190 A1=EXP(LNA1)   :A2=S*EXP(LNA2)   :A3=P*EXP(LNA3)
200 LPRINT "Time/min","Ln(C)", "Ln(Abs(-A4C-dC/dt))"
210 MAX=0:OPT=0
220 FOR T1=TEND TO 3*TEND STEP 5
230    I=0
240    FOR T=T1 TO 0 STEP -2
250       I=I+1
260       C(I)=A1*EXP(B1*T)+A2*EXP(B2*T)+A3*EXP(B3*T)
270       X(I)=LOG(C(I))
280       DC(I)=A1*B1*EXP(B1*T)+A2*B2*EXP(B2*T)+A3*B3*EXP(B3*T)
290       Y(I)=LOG(ABS(-A4*C(I)-DC(I)))
300       IF OPT=1 THEN LPRINT T, X(I), Y(I)
310    NEXT T
320    N=INT(T1/2+1) :REM Number of values of the dummy variable T
330    FOR J=15 TO N  :REM J is the chosen starting number of values of T
340       FOR I=1 TO J
350       NEXT I
360       GOSUB 650          :REM Linear regression analysis
370       A=EXP(A)
380       K=A/DVL       :REM The division by DVL leads to the calculation

                             of the apparent k, according to Eq.84
390       B4=B
400       SK=SA*A/DVL   :REM Standard error of apparent k
410       SB1=SB        :REM Standard error of slope B, calculated in the

                             subroutine
420       IF OPT=1 THEN 490
430       R1=R
```

```
440       IF R1>MAX THEN MAX=R1:JMAX=J:T1MAX=T1
450    NEXT J
460 NEXT T1
470 J=JMAX:T1=T1MAX:OPT=1
480 GOTO 230
490 PRINT
500 PRINT "Date, Experiment,Gaseous analyte,Temperature";
510 PRINT "_____    _______    _________________    _____"
520 PRINT
530 PRINT "Diffusion parameter A4=";A4
540 PRINT "3.1416D/vL=";DVL
550 PRINT "DATA=";LNA1;","B1;","LNA2;","B2;","LNA3;","B3;","A4;","TEND;","S;"
,"P
560 PRINT "(3.1416D/vL)kapp=";A
570 PRINT "Apparent Rate Constant=";K"+-"SK
580 PRINT "Slope and reaction order=";B4"+-" SB1
590 PRINT "Square of Correlation coefficient=";R1
600 PRINT "Optimum number of points=";JMAX
610 PRINT "Optimum final time of differential plot=";T1MAX
620 DATA
630 END
640 REM Linear regression of Y(I) = A + B*X(I)
650 S1=0
660 S2=0
670 S3=0
680 S4=0
690 S5=0
700 S5=0
710 FOR I=1 TO J
720    S1=S1+X(I)
730    S2=S2+X(I)^2
740    S3=S3+Y(I)
750    S4=S4+Y(I)^2
760    S5=S5+X(I)*Y(I)
770 NEXT I
780 Z=J                :REM Number of points for the linear regression
790 M1=S5-S1*S3/Z
800 M2=S2-S1^2/Z
810 M3=S4-S3^2/Z
820 A=(S3-S1*M1/M2)/Z
830 B=M1/M2
840 SYT=SQR(ABS(S4-A*S3-B*S5)/(Z-2))
850 SA=SYT*SQR(S2/Z/M2)
860 SB=SYT/SQR(M2)
870 R=M1^2/(M2*M3)
880 RETURN
```

Appendix G

```
10 REM Calculation of Rate Constants and Isotherms
20 REM  CONSTANTS
30 REM  LNA1,LNA2,LNA3 = Logarithms of pre-exponential factors of Eq.99
                         in text, as calculated by the program of Appendix E
40 REM  B1,B2,B3       = Exponential Coefficients of time of Eq.99 in text,
                         as calculated by the program of Appendix E
50 REM     A4          = Diffusion parameter  as defined by Eq.36 in text
60 REM     R           = Denuder internal radius
70 REM     SA          = Surface area per unit mass of solid (cm^2/g)
80 REM     L           = Length of denuder tube (cm)
90 REM     V           = Volumetric flow-rate of carrier gas (cm^3/s)
100 REM    M           = Amount of adsorbate injected (mol)
110 REM    T1,T2       = Initial and Final time, respectively (min)
120 REM    S,P         = Prefixes of the second and third term of Eq.99,
                         as calculated by the program of Appendix E
130 REM    G           = Calibration factor of the detector g or g'
140 REM    π^2         = 9.8696
150 REM  VARIABLES
160 REM    X,Y,Z       = Auxiliary parameters defined by Eqs.100,101 and 102
170 REM      K         = Isotherm equilibrium factor k, defined by Eq.98
180 REM    K1,K2       = Rate constants k_1 and k2, respectively, as defined
```

```
                        in text after Eq.102
190 REM       K3          = Auxiliary variable defined by Eq.103
200 REM       DCS          = Differential isotherm dcs*/dcR,according to Eq.110
210 REM       CS           = Integrated isotherm cs*, according to Eq.111
220 REM       CR           = Gaseous concentration cR above the solid, Eq.112
230 INPUT "Analyte Gas,Solid Denuder Coating,Temp.in K";GAS$,SOLID$,T
240 INPUT "Factor 1 or 60 if B1,B2,B3 and A4 are entered in DATA in 1/s

          or 1/min, respectively ="; H1
250 READ LNA1,B1,LNA2,B2,LNA3,B3,A4,R,SA,L,V,M,T1,T2,S,P
260 B1=B1/H1    :B2=B2/H1    :B3=B3/H1    :A4=A4/H1
270 X=-(B1+B2+B3)
280 Y= B1*B2+B1*B3+B2*B3
290 Z=-B1*B2*B3
300 K3=(A4*X-A4^2-Y+Z/A4/(1-16*L^2/9.8696/R^2))/2
310 K2=Z/(9.8696*R^2/8/L^2-2)/K3
320 K1=X-A4-K2-9.8696*R^2*K3/8/L^2/A4
330 PRINT "k3 in 1/s^2=";K3
340 PRINT "k2 in 1/s=";K2
350 PRINT "k_1 in 1/s=";K1
360 A1=EXP(LNA1)    :A2=S*EXP(LNA2)    :A3=P*EXP(LNA3)
370 K=K3*R*SA/K1
380 PRINT "k in cm^3/g/s=";K
390 A=A1/B1+A2/B2+A3/B3
400 G=-V*A/M              : REM According to Eq.113
410 PRINT "Calibration Factor of Detector g'in cm per mol/cm^3=";G
420 PRINT
430 PRINT TAB(1);"Time(min)";TAB(17);"dCS/dCR";TAB(35);"CS";TAB(50);"CR"
440 T1=T1*60    :T2=T2*60
450 FOR T=T1 TO T2 STEP 300
460   DCS=K*(A1*EXP(B1*T)+A2*EXP(B2*T)+A3*EXP(B3*T))/(A1*B1*EXP(B1*T)

          +A2*B2*EXP(B2*T)+A3*B3*EXP(B3*T))
470   CS=K*(A1*EXP(B1*T)/B1+A2*EXP(B2*T)/B2+A3*EXP(B3*T)/B3)/G
480   CR=(A1*EXP(B1*T)+A2*EXP(B2*T)+A3*EXP(B3*T))/G
490   PRINT TAB(1);T/60;TAB(15);DCS;TAB(30);CS;TAB(45);CR
500 NEXT T
510 REM Enter DATA in the order LnA1,B1,LnA2,B2,LnA3,B3,A4,R in cm,Surface

        area in cm^2/g,Denuder length in cm,Flow-rate in cm^3/s,Amount
        injected  in mol,Initial time in min, Final time in min,Prefixes S,P
520 DATA
530 END
```

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Journal of Chromatography A, 710 (1995) 229–235

JOURNAL OF CHROMATOGRAPHY A

Development of gas standards from solid 1,4-dichlorobenzene

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Abstract

For over fifteen years the National Institute of Standards and Technology (NIST) has been preparing gas standards containing volatile organic compounds at sub μmol/mol (ppm) concentrations. These standards have been prepared using organic compounds that are either gases or liquids at room temperature. A micrograviметric technique was developed previously to prepare standards containing these compounds in treated aluminum gas cylinders using a one step dilution. Requests were received to prepare gas standards containing the compound 1,4-dichlorobenzene. These requests posed a major problem in that 1,4-dichlorobenzene is a solid at room temperature. Research was undertaken, using the micrograviметric procedure, to determine if it was feasible to prepare gas standards from solid phase compounds. In the first stage of research the liquid phase compound 1,2-dichlorobenzene, previously studied at NIST in gas mixtures, was used as an internal standard. Results from analyses of a prepared gas standard showed that the response factor on a gas chromatograph flame-ionization detector for 1,3-dichlorobenzene was 3% less than that for 1,2-dichlorobenzene. Additional analyses using liquid solution standards also showed a lower response factor for 1,3-dichlorobenzene of 2.9% on average. It was assumed that 1,4-dichlorobenzene would have a similar response and that the 1,2-dichlorobenzene response could be used to determine the concentration of 1,4-dichlorobenzene. Analyses of a liquid solution standard confirmed that the response factor for 1,4-dichlorobenzene was on average 3.2% less than that of 1,2-dichlorobenzene. A gas standard was prepared containing 1,2- and 1,4-dichlorobenzene at nominal concentrations of 250 nmol/mol (ppb). Analytical results showed that the concentration of 1,4-dichlorobenzene determined from 1,2-dichlorobenzene was within 3% of the gravimetric value. Further research using two standards containing 1,4-dichlorobenzene revealed that they agreed exactly with the gravimetric concentrations. These results verified the ability to prepare accurate gas standards of 1,4-dichlorobenzene in gas cylinders.

1. Introduction

The compound 1,4-dichlorobenzene is of interest to such agencies as the United States Environmental Protection Agency (US-EPA) and the California Air Resources Board (CARB) in their toxic organic air monitoring programs. The US-EPA has listed 1,4-dichlorobenzene as a priority pollutant. It is of interest due to its human health effects. Prolonged and repeated exposure to 1,4-dichlorobenzene may result in permanent damage to the liver, lungs, and kidneys. The compound is a suspected carcinogen and is also thought to cause leukemia. This compound is used commercially as an insecticide for control of ants and fruit borers, especially in peach trees. It may be applied to tobacco seed beds for blue mold control and to leather and fabrics to control mildew and mold. In domestic use it is a combatant against clothes moths. Sometimes 1,4-dichlorobenzene is used as a fumigant for garbage and restrooms. It is used as

SSDI 0021-9673(94)01211-3

a chemical intermediate for the production of engineering plastics used for surface coatings and model resins [3].

In order to determine the amount of 1,4-dichlorobenzene in ambient air, gas standards are needed to calibrate the analytical instruments used to make those determinations. 1,4-Dichlorobenzene is a solid in the form of crystals at room temperature, with a melting point of 53°C. Therefore it was thought to be extremely difficult, if not impossible, to quantitatively transfer a solid organic compound into an aluminum gas cylinder and have it remain completely in the gas phase. A micrograviметric technique previously developed to prepare gas standards from liquid organic compound was considered as a possible method [1,2]. Research was undertaken to determine if this micrograviметric technique could be employed to accurately prepare gas standards containing 1,4-dichlorobenzene in nitrogen.

2. Experimental

2.1. Chemicals

The reagents 1,2-dichlorobenzene and 1,4-dichlorobenzene were purchased from commercial suppliers. These compounds were analyzed for impurities by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID) at NIST. High purity nitrogen (99.9995%) diluent gas was obtained from a commercial gas supplier. The nitrogen was analyzed by NIST and was found to be free of the compounds of interest.

2.2. Gas cylinders

New 30 liter volume aluminum gas cylinders with CGA-350 brass valves were used to prepare the gravimetric standards. The cylinders were cleaned by the manufacturer using a caustic etch process followed by an acid wash. These cylinders were then treated by Scott Specialty Gases using a proprietary chemical vapor deposition process, ACULIFE®[1], to passivate the interior wall surface.

2.3. Weighing apparatus

The solid and liquid organics were sealed into glass capillary tubes and weighed before and after filling on a microbalance. The balance used has a mechanical tare capacity of up to 2.99 g, an electrical weighing range of 15 mg, and a readability of 0.1 μg. The 30 liter aluminum gas cylinders were weighed on a floor balance with a capacity of 54 kg and a readability of 1 g.

2.4. Gravimetric procedure for preparing gas standards

A micrograviметric procedure was used to prepare the gas standards containing 1,2-dichlorobenzene and the solid 1,4-dichlorobenzene. A thin-walled glass capillary tube of 1.6 mm O.D. by approximately 2.0 cm long was prepared from a 10 cm tube by heating a section in a flame and pulling it into a fine point. The tube was broken in the thin drawn area, leaving a very small opening. The other end of the tube was drawn out to a fine point and then sealed. Several tubes were prepared in this manner and then weighed several times against a control tube sealed at both ends. This control tube was weighed first and last, being used to correct for balance drift. A small amount of 1,4-dichlorobenzene crystals was placed in a glass vial. This vial was heated using a heat gun until the crystals melted. The open end of a capillary tube was placed into the liquid 1,4-dichlorobenzene in the vial. A plastic syringe was adapted onto the vial. While still heating the vial with the now liquid 1,4-dichlorobenzene, the syringe plunger

[1] *Disclaimer.* Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards an Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

was pulled out, drawing air from the vial and enclosed capillary tube. When the syringe plunger was subsequently released, liquid 1,4-dichlorobenzene moved into the capillary tube. The capillary tube was removed and centrifuged such that the liquid was forced to the sealed end. Some of the 1,4-dichlorobenzene crystallized on the capillary walls before it was forced to the sealed end of the tube. The open capillary end was then flame sealed. The 1,4-dichlorobenzene quickly recrystallized in the capillary tube. Acetone, in which 1,4-dichlorobenzene is very soluble, was used to carefully wipe the capillary tube to remove any 1,4-dichlorobenzene which may have crystallized on the outside surface. The capillary tube was reweighed three times to determine the amount of organic compound. A capillary tube containing 1,2-dichlorobenzene was prepared in the same manner, except that heating the vial was not necessary since the compound is already a liquid at room temperature.

An evacuated, preweighed cylinder was fitted with the appropriate CGA-350 fitting to which a piece of tubing, made from fluorinated ethylene-propylene copolymer, was attached. The capillary tube containing the 1,4-dichlorobenzene was inserted into the tubing. The diameter of the tubing was such that the capillary fit tightly and created a seal. Since 1,4-dichlorobenzene boils at 174°C, the potential for recrystallization of the compound in the valve fitting before it actually reached the interior of the cylinder was a major concern. The stainless steel fitting on the cylinder valve was therefore heated (the temperature inside the fitting was measured at 200°C) during transfer. After opening the cylinder valve, the capillary tube was broken at the end closest to the valve. Heating the capillary tube with a heat gun first liquified the crystalline 1,4-dichlorobenzene and eventually vaporized the compound, at which point it was pulled into the cylinder by the vacuum. After it appeared that all the 1,4-dichlorobenzene had been vaporized, the other end of the capillary tube was broken. The area was purged with pure nitrogen, with continued heating, to flush residual 1,4-dichlorobenzene into the cylinder. The 1,2-dichlorobenzene was then added into the cylinder in the same manner except that only some heat was needed. High-purity nitrogen was then added to a pressure of 12.4 MPa and the cylinder weighed to determine the amount added. The concentrations of the two organic compounds were calculated on a nmol/mol basis using the weight data.

Caution. Since the compounds employed are toxic, all procedures involving the use of the pure reagents were performed in a exhaust hood. Before the cylinders were pressurized with high-purity nitrogen, all manifold fittings were checked for leaks. Safety glasses were worn at all times. Extreme care must also be taken not to overheat the cylinder valve to prevent melting of the material in the safety relief valve.

2.5. Analytical conditions

Analysis of the gas standards was conducted using a gas chromatograph equipped with a flame-ionization detector (GC–FID) operated at 250°C. A 60 m × 0.75 mm I.D. open tubular capillary column coated with a 1 μm thick film of polyethylene glycol was use. The initial temperature was held at 50°C for 4 min then temperature programmed to 240°C at 10°C/min. The column carrier flow-rate was 10 ml/min of nitrogen with a detector make-up flow of 30 ml/min. Each sample was cryogenically trapped at −100°C for 5 min at a sample flow-rate of 50 ml/min. Flow was controlled by a mass flow controller. After the trapping sequence was finished, the sample valve was actuated to the inject position. The sample trap was electrically heated to 200°C to desorb the analytes into the GC column.

3. Results and discussion

It is ideal to prepare a standard containing organic species using the simplest technique possible so as to reduce errors and sources for compound loss. Since 1,4-dichlorobenzene is a solid at room temperature there was a major

concern as to whether it could be quantitatively transferred to a gas cylinder without losing some, if not all, by crystallization on the surface of the transfer area. One possible method would be to place some 1,4-dichlorobenzene in a small stainless steel container fitted with a valve, warm it slightly, and transfer that headspace into an evacuated cylinder. However, this method would be limited to preparing high concentration mixtures. Successive dilutions of this high concentration standard would be required to reach a low nmol/mol concentration mixture, due to weighing limitations. This method would greatly increase the possibility of losing 1,4-dichlorobenzene in the transfer process. The amount of 1,4-dichlorobenzene needed to prepare a 250 nmol/mol gas standard in one step using a 30 l aluminum gas cylinder is approximately 6.5 mg. Use of the headspace method to prepare the standard would result in weighing errors of approximately 10%; therefore, a microgravimetric technique previously used to prepared organic gas standards for liquids [1,2] was modified for use with low melting point solids. The cylinder valve fitting in which the transfer of the 1,4-dichlorobenzene to the cylinder would take place would be heated to 200°C.

Instead of preparing, at a minimum, two gas standards containing 1,4-dichlorobenzene to determine the ability to prepare a mixture, one was prepared which also contained 1,2-dichlorobenzene as an internal standard. Previous work at NIST with the compound 1,2-dichlorobenzene has shown that gas standards containing this compound are both accurate and stable. The standards were compared to each other by GC–FID using the previously described analytical conditions. Regression analysis was used to plot gravimetric concentration versus GC peak area response. The resulting line was then used to determine the concentration of the standards using the peak area response. The average absolute residual was 0.02% indicating good agreement between standards. The expanded relative uncertainty in the gravimetric concentration is 1.0%. This uncertainty is determined from the equation $U = ku_c$. The coverage factor k equals 2 (a confidence interval of approximately 95%) and u_c is the root sum of squares of the uncertainties arising from weighing the 1,2-dichlorobenzene and nitrogen and their purities. These results demonstrate the ability to prepare accurate 1,4-dichlorobenzene standards.

Theoretically, 1,2-dichlorobenzene and 1,4-dichlorobenzene should have the same molar response to the FID. The compounds have the same number of carbon atoms, and differ only by the placement of the chlorine atoms. Consequently, the 1,2-dichlorobenzene could potentially be used as an internal standard and the 1,4-dichlorobenzene concentration could be determined by comparison. Previous work at NIST involving the comparison of 1,3-dichlorobenzene to 1,2-dichlorobenzene, both liquids at room temperature, has shown that these two compounds have the same FID response factor to within 3%. Table 1 shows data for three gas standards, each containing 1,3- and 1,2-di-

Table 1
Response ratios for 1,2-dichlorobenzene and 1,3-dichlorobenzene in several gas standards

Standard	1,2-Dichlorobenzene			1,3-Dichlorobenzene			Percent diff.
	Avg. peak response	Grav. conc.[a]	Response factor	Avg. peak response	Grav. conc.[a]	Response factor	
009020	46980	460.2	102.1	48793	491.7	99.2	2.9
033788	13066	127.7	102.3	25317	251.7	100.6	1.7
033820	6619	64.4	102.7	10612	106.3	99.8	2.8
							average = 2.5

[a] Gravimetric concentration is in nanomole/mole, with a preparation uncertainty of ±1% at the 95% confidence level.

chlorobenzene. The peak response given is an average of three injections made for each cylinder, which resulted in a maximum standard deviation of 0.4% for the same mixture. A response factor was determined for each compound by dividing the average GC peak area response by the appropriate gravimetric concentration. The response factor for 1,3-dichlorobenzene was 2.5% less than that for 1,2-dichlorobenzene. A solution standard of 1,2- and 1,3-dichlorobenzene in acetone was prepared. Five injections of 0.1 μl of the standard resulted in an average response factor for 1,3-dichlorobenzene that was 2.9% less than that of 1,2-dichlorobenzene, confirming the gas standards results. An assumption was therefore made that a difference in response factors for 1,2- and 1,4-dichlorobenzene of the same magnitude might occur under the same analytical conditions. A solution standard of 1,2- and 1,4-dichlorobenzene at nominal 5000 μmol/mol each in acetone was prepared. Five injections of 0.1 μl were made, resulting in an average response factor for 1,4-dichlorobenzene that was 3.2% less than that for 1,2-dichlorobenzene. This difference was considered acceptable and it was concluded that 1,2-dichlorobenzene could be used as an internal standard to determine the 1,4-dichlorobenzene concentration. It should be noted that this difference in response factors may change or be nonexistent using a different type of column material and GC conditions; therefore, when using such a method, the analytical conditions must be well qualified for the compounds being studied.

The gravimetric standard prepared was analyzed using the conditions described earlier. A ratio was calculated for each analysis by dividing the 1,4-dichlorobenzene GC peak area response by that for the 1,2-dichlorobenzene. This ratio was then multiplied by the gravimetric concentration of the 1,2-dichlorobenzene. Table 2 shows the results of several analyses of the standard. The average concentration determined for 1,4-dichlorobenzene was 288.9 ± 9.2 nmol/mol (the uncertainty of 9.2 representing the

Table 2
Results of October 1993 and February 1994 analysis of standard ALM-033823

October 1993		February 1994	
Ratio of 1,4-dichlorobenzene[a] to 1,2-dichlorobenzene[b]	Concentration[c] of 1,4-dichlorobenzene from 1,2-dichlorobenzene	Ratio of 1,4-dichlorobenzene to 1,2-dichlorobenzene	Concentration[a] of 1,4-dichlorobenzene from 1,2-dichlorobenzene
1.190	290.9	1.163	284.2
1.168	285.4	1.164	284.4
1.191	291.0	1.164	284.4
1.187	290.0	1.166	284.9
1.178	287.8	1.167	285.2
1.197	292.4	1.167	285.2
1.166	284.9	1.167	285.2
		1.168	285.5
		1.169	285.7
		1.169	285.7
Avg. = 1.182	288.9	1.166	285.0
S.D. = 0.012	2.9	0.002	0.5
R.S.D. = 1.0%	1.0%	0.2%	0.2%

[a] Gravimetric concentration is 290.4 nmol/mol.
[b] Gravimetric concentration is 238.6 nmol/mol.
[c] Concentration is in nmol/mol.

variance in response factors). The standard deviation of the average concentration was 3 nmol/mol, which is 1.0% relative. This value is in excellent agreement with the calculated gravimetric concentration of 290.2 nmol/mol.

After this gas standard was shelved for four months, it was again analyzed. Table 2 shows the data for this analysis. The average concentration of the 1,4-dichlorobenzene determined by ratioing to the 1,2-dichlorobenzene was 285.0 ± 9.1 nmol/mol with a standard deviation of 1 nmol/mol, or 0.4% relative. The analytical precision was much better for this analysis; however, the average concentration determined for this analysis was 3.9 nmol/mol less (1.4%) than that for the first analysis. It might appear from this data that the 1,4-dichlorobenzene concentration is decreasing in the cylinder. Taking into account the uncertainty in the concentrations, the determinations of 1,4-dichlorobenzene are within the error bars; therefore, it can be stated that the compound is not degrading in the cylinder. Long term stability of 1,4-dichlorobenzene in a gas mixture is unknown beyond four months. Data from as many as eight gas standards containing 1,2- and 1,3-dichlorobenzene show that these two compounds are stable in a gas mixture for at least 2.5 years at concentrations as low as 5 nmol/mol. Table 3 shows stability data for one of those mixtures. It is highly likely that 1,4-dichlorobenzene would behave in a similar manner and be stable over years.

From the data in Table 2 it appeared that it was feasible to prepare a gas standard for a solid organic compound at room temperature. Because one standard is not conclusive, a second standard was prepared containing both compounds. The standard was analyzed using the exact same conditions. Table 4 shows the results of that analysis. The concentration of the 1,4-dichlorobenzene was calculated from the ratio to 1,2-dichlorobenzene. The value for 1,4-dichlorobenzene of 284.5 nmol/mol calculated from this ratio is low by 5.9 nmol/mol (2.0%) when compared to the gravimetric concentration of 290.4 ± 2.9 nmol/mol. This value still lies within the ±3.2% range of 281–290 nmol/mol.

The data in Table 4 supplied further evidence that the preparation procedure was feasible for this particular solid organic compound. Comparison of the 1,4-dichlorobenzene concentrations in each cylinder could have a greater impact on the accuracy of the procedure. The

Table 4
Results of analysis of second standard ALM-040272

Ratio of 1,4-dichlorobenzene[a] to 1,2-dichlorobenzene[b]	Concentration[c] of 1,4-dichlorobenzene from 1,2-dichlorobenzene
1.198	285.8
1.191	284.2
1.192	284.4
1.190	283.9
1.192	284.4
1.191	284.2
1.192	284.4
1.194	284.9
Avg. = 1.192	284.5
S.D. = 0.003	0.6
R.S.D. = 0.2%	0.2%

[a] Gravimetric concentration is 290.4 nmol/mol.
[b] Gravimetric concentration is 238.6 nmol/mol.
[c] Concentration is in nmol/mol.

Table 3
Stability of 1,2- and 1,3-dichlorobenzene gas standards (ALM-008399)

Compound	Gravimetric concentration[a]	Concentration, nmol/mol February 1990	July 1992
1,2-Dichlorobenzene	5.01 ± 0.05	5.2 ± 0.3	5.0 ± 0.3
1,3-Dichlorobenzene	4.99 ± 0.05	5.2 ± 0.3	5.0 ± 0.3

[a] Concentration is in nmol/mol (ppb). The uncertainty is derived from the equation $U = ku_c$ where u_c represents the preparation errors and the coverage factor k equals 2.

Table 5
Comparison of two 1,4-dichlorobenzene standards

Standard	Average GC response	Gravimetric concentration[a]	Concentration[a] vs. ALM-040272
ALM-033823	148954	290.2 ± 2.9	290.2
ALM-040272	149072	290.4 ± 2.9	–

[a] Concentration in nmol/mol. The uncertainty is at the 95% confidence level determined from the equation $U = ku_c$.

two standards were analyzed together using the exact same conditions. Table 5 shows the data for this comparison. The GC peak area response for 1,4-dichlorobenzene in the first standard (ALM-033823) was divided by the peak area for the second standard (ALM-040272). This ratio was then multiplied by the gravimetric concentration for 1,4-dichlorobenzene in the first standard. The resulting concentration of 290.2 nmol/mol was exactly the same as the calculated gravimetric concentration of 290.2 nmol/mol. These results add more support to the ability to accurately prepare gas standards from solid 1,4-dichlorobenzene at low concentration levels.

4. Conclusions

Results of this research exhibit strong support that gas standards containing 1,4-dichlorobenzene can be prepared without losses. The possibility exists, but is not likely, that the same amount of 1,4-dichlorobenzene is lost each time a gas standard is prepared. It is more likely to have random losses from mixture to mixture, which the data do not support. The data provide strong evidence that accurate gas standards can be prepared from crystalline 1,4-dichlorobenzene when care is taken using this procedure. It is likely that other organic compounds that are solids at room temperature can be quantitatively transferred into a gas cylinder, resulting in the preparation of accurate gas standards. It is ideal to include a compound of similar structure in the mixture as an internal standard. The compound should be a liquid at room temperature, be well characterized in a gas mixture, and theoretically have the same FID response. This research has shown the ability to quantitatively and accurately prepare gas standards with a relative uncertainty of 1.0% at the 95% confidence level using a compound that is crystralline at room temperature.

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Journal of Chromatography A, 710 (1995) 237–241

JOURNAL OF CHROMATOGRAPHY A

Sampling and analysis of 1,3-butadiene in air by gas chromatography on a porous-layer open-tubular fused-silica column

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Abstract

The preparation of standards for 1,3-butadiene analysis is complicated, because butadiene is a gas at room temperature. The method to prepare stock solutions developed in this study is reliably, as confirmed by a standard plot from these independent stock solutions. The qualitative and quantitative analysis was carried out using high-resolution gas chromatography with flame ionization detection (FID) and a fused-silica porous-layer open-tubular (PLOT) column. The use of acetonitrile as a desorption solvent gave a good recovery from charcoal and no interfering impurities were present. Active and passive sampling were tested in the laboratory and in petrochemical plants. These two methods had a very good correlation when tested in the field.

1. Introduction

1,3-Butadiene (BD) is a colourless flammable gas used mainly in the production of synthetic rubbers and it is one of the top 50 chemicals manufactured in the USA [1]. The National Institute for Occupational Safety and Health (NIOSH) estimated that 9500 workers in the USA are potentially exposed to BD, and the worldwide exposure to this chemical has been estimated to involve ca. 50 000 workers [2].

Also the US Environmental Protection Agency (EPA) expressed concern that this compound may be potentially carcinogenic, and more recently the California Air Resources Board has estimated that BD is the second important toxic compound, after benzene, in the emission from motor vehicles [3].

The conventional methods of sampling gaseous impurities require the use of pumps to draw a known volume of air through tubes packed with adsorbent. In recent years an alternative sampling system has been developed in the form of the "passive" or more correctly "diffusive" sampler. These devices sample, by gaseous diffusion of the analyte, onto a collecting medium. Their advantages are lower costs and greater user acceptability, as they do not require bulky, expensive pumps that are subject to regular checking and an inherent error in flow-rate.

For the analysis, a chromatographic method capable of resolving BD from other light hydrocarbons present in petroleum refineries is desired. Such separations reported in the literature used high-resolution gas chromatography mainly with KCl-deactivated aluminium oxide porous-

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0021-9673/95/$09.50
SSDI 0021-9673(95)00073-9

layer open-tubular (PLOT) columns, or with a methyl silicone fused-silica column with a thick film using subambient temperature [3–6].

The detection has been carried out mainly with flame ionization detection (FID) which gives a satisfactory detection limit, but which may not be sufficiently selective [4–6]. It has also been shown that photoionization detection (PID) offers a high selectivity and sensitivity for unsaturated hydrocarbons [7].

2. Materials and methods

Butadiene used in this study was a kind gift from a Finnish petrochemical company. Before use the purity was tested in our laboratory using gas chromatography (GC), and it was observed to be higher than 99%. Pentadiene, hexadiene, heptadiene, octadiene, nonadiene, dodecadiene, dodecan and undecan were all from Aldrich (Germany). Acetonitrile was HPLC grade from Rathburn (Walkerburn, UK).

Charcoal tubes, type 226-01, having front and rear sections of 100 and 50 mg, respectively, were from SKC (Wimborne, UK), and type 3520 passive monitors, also having a backup section, were from 3M (St. Paul, MN, USA). The flow-rate in active sampling was set at 50 ml/min, which was confirmed before and after sample collection. A diffusion rate of 42.8 ml/min was used in calculations and the amounts of BD were lower than 0.4 mg in all analyses.

Standard atmospheres with varying concentrations of BD were generated in a stainless-steel dynamic 1 m^3 exposure chamber. The desired air concentration was kept constant by an automatically controlled feedback mechanism. The valve which controlled the gas flow of BD was regulated by a power integrated derivative controller (Eurotherm 70, Eurotherm, Sussex, UK) based on the feedback circuit signal from an infrared analyser (Miran 1A, Wilks Scientific Corp., USA), which was used for continuous monitoring of BD concentrations in the chamber air. The chamber air exchange rate was 6 times/h, and short-term deviations from nominal concentrations were less than 5%.

The standards were made in 10-ml bottles (in each batch five separate stock solutions were made), which were weighted and cooled in dry ice (10 min). Butadiene was liquefied into the bottle (ca. 100–200 μl) and 5 ml of acetonitrile was added. The bottles were allowed to warm to room temperature and weighted, the amount of butadiene in the bottle calculated, after which they were filled to the reference point (10 ml). The concentrations of BD in these stock solutions were determined and one of the bottles which lay in the calibration line of stock solutions was selected as stock solution to prepare a calibration curve suitable for actual air samples.

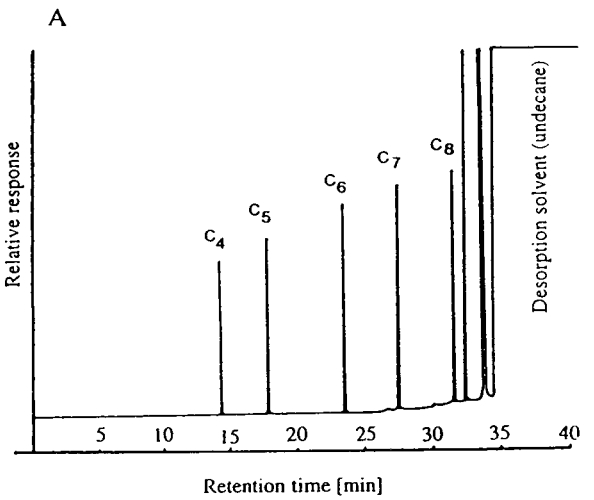
The desorption efficiencies were tested in autosampler vials at + 6°C in 1 ml of desorption solvent. Before the solvent was slowly added, the vials were cooled in an ice bath (ca. 0°C).

The samples were analysed with a gas chromatograph equipped with a FID detector (HP 5890, Hewlett-Packard, CA, USA). The detector and injector temperatures were 280°C and 200°C, respectively. Air and hydrogen flow-rates were set at 280 ml/min and 30 ml/min, respectively. The helium make-up gas flow-rate was 30 ml/min. The samples (1 μl) were introduced using splittless injection (splittless time 0.5 min) and both autosampler and manual injections were used.

A PLOT AL_2O_3/KCl (50 m × 0.32 mm I.D.) fused-silica column was used (Chrompack, Netherlands). The carrier gas flow-rate was set at 1 ml/min and the following temperature program was used. The injection temperature of 40°C was kept for 1 min after which the temperature was raised to 190°C with 5°C/min. The final temperature was maintained for 12 min.

3. Results and discussion

The gas chromatographic profiles of the five terminal dienes from 1,3-butadiene to 1,7-octadiene using linear temperature programming are shown in Fig. 1. The carrier gas did not have a great influence on the retention behaviour and, as expected, helium (Fig. 1A) gave longer retention times than hydrogen (Fig. 1B). When



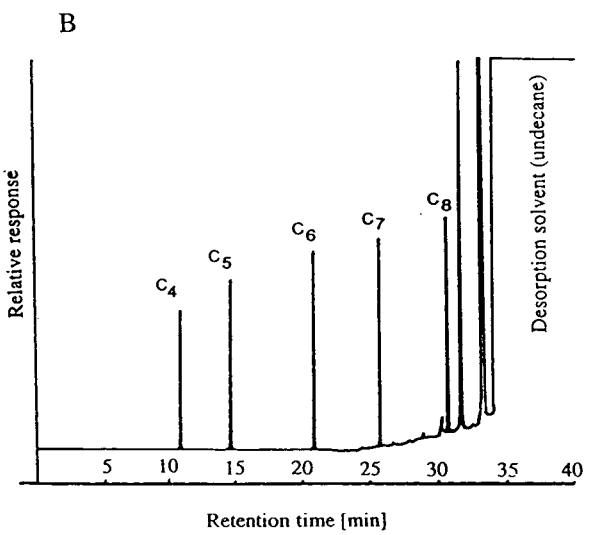


Fig. 1. Gas chromatographic profiles containing a homologous series of terminal dienes (from 1,3-butadiene to the 1,7-octadiene). Helium (A) and hydrogen (B) were used as carrier gases. C_4, C_5, C_6, C_7 and C_8 refer to the number of carbons in the dienes.

retention times are plotted as a function of the carbon number, it can be seen that the total retention times t_R or the retention temperatures are not linearly proportional to the number of carbon atoms of the homologues when using linear temperature programming. A non-linear increment in retention time was observed between C_5 and C_6 dienes. The type of carrier gas had no effect on these nonlinear increments in retention time. Dienes in a PLOT-type column also behave differently when the half height of the peaks is compared to the half height of the peaks traditionally obtained with capillary columns. BD has the highest half height in this series and the other dienes have a half height of approximately the same size. This phenomenon is shown in Fig. 2 where the half height of the dienes is plotted as a function of carbon number. The results of the studies on the chromatographic behavior indicate that the use of the diene homologue series may not be applicable to the

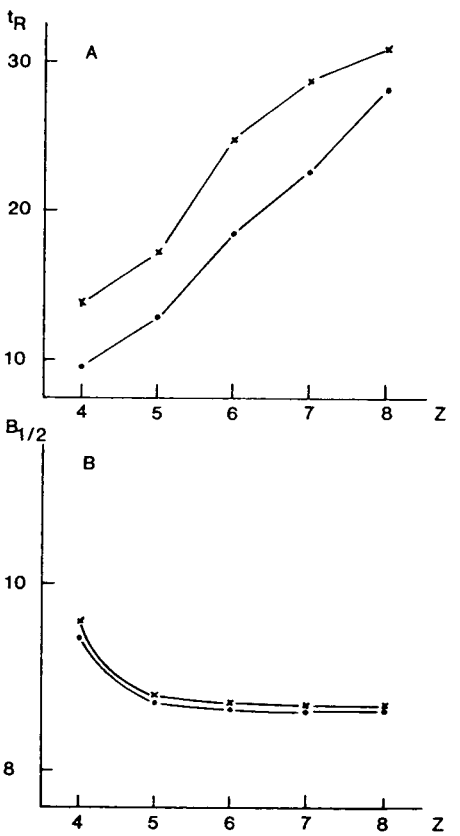


Fig. 2. The total retentions t_R (A) and the peak widths at half height (B) as a function of the number of carbons in the dienes; (×) helium, (●) hydrogen.

determination of the BD concentration in samples.

In the quantitative analysis of BD one of the most critical steps is the preparation of stock solutions. To overcome this problem various techniques have been described in the literature, but none of them worked satisfactorily in our hands [4,5,8]. Therefore we had to develop our own method for the preparation of standards. The method we are currently using is a user-friendly method which reveals possible problems at an early stage in the analysis. The reliability of the stock solutions is confirmed by performing a standard plot of stock solutions ($n = 5$, $r = 0.9999$). These stock solutions cannot be stored for more than 12 h in a refrigerator due to the high concentration of BD in the solution. The loss of BD from stock solutions is mainly caused by dimerization of BD to vinylcyclohexene and a loss of BD through evaporation. However, once the stock solutions have been diluted, the standards can be stored for up to 2 weeks in a refrigerator without any loss of BD (data not shown).

Dichloromethane, carbon disulphide, dodecan, undecan and acetonitrile were tested as possible desorption solvents for butadiene. Several gas chromatographic conditions were tested, but BD could not be separated from dichloromethane or carbon disulphide. Therefore, the solvents which were further tested were dodecan, undecan and acetonitrile and the desorption efficiency for the selected dienes is presented in Table 1. Because the desorption efficiency of BD was low when hydrocarbons were used, acetonitrile was selected.

The standard deviation of injection was tested for 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene using autosampler and manual injections and acetonitrile as a solvent. The concentration of dienes in the samples was 11 μg/ml and 12 injections were made. The standard deviations for injections made with the autosampler were 6.2, 6.7 and 6.4% for each diene. Better results were obtained when manual injections were performed with the "hot needle technique" [9]. The standard deviations for manual injection were 2.6, 2.8 and 1.9% for each diene.

Table 1
Desorption efficiencies of butadiene into dodecane, undecane and acetonitrile ($n = 3$)

Concentration (μg/ml)	Desorption efficiency (%)	S.D. (%)
Dodecane		
13	13.2	12.1
27	15.8	11.1
Undecane		
13	11.3	13.1
27	21.5	10.1
Acetonitrile		
2.5	53.9	4.4
5.4	58.2	3.3
8.8	60.0	3.2
12.9	64.2	3.5
26.3	64.1	3.0

The detection limit of the passive sampling method was 400 ng/ml, which corresponds to 0.01 ppm for an 8-h sample using a diffusion rate of 42.8 ml/min. About the same sensitivity was achieved using SKC charcoal tubes with a flow-rate of 50 ml/min. A typical chromatogram of a sample collected from a petrochemical plant is shown in Fig. 3.

In order to compare the two different sampling methods, they were first tested in the

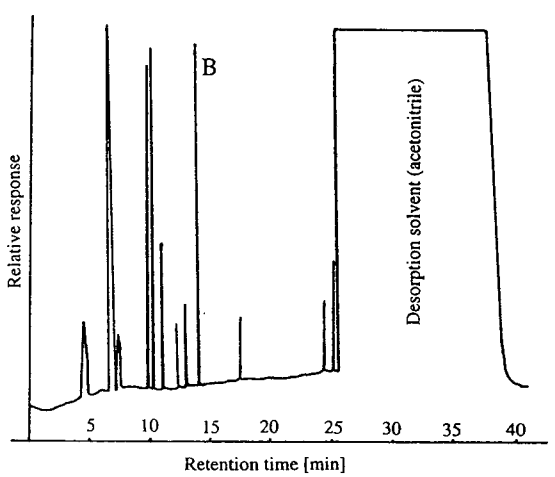


Fig. 3. A typical chromatogram of an air sample collected from a petrochemical plant worker (B = butadiene).

laboratory in a dynamic exposure chamber. The relative humidity was monitored (R.H. 82%) but not altered during the measurements. The sampling efficiency and possible breakthrough were tested for two different BD concentrations. The first experiment was carried out at 8.8 ppm and the sampling time was 3 h. Nine active and passive samples were taken, each of them having a backup section to detect possible breakthrough. No breakthrough could be observed in either sampling method. The samples based on passive diffusion showed values somewhat lower than the set value. The mean value of the dosimeters was 8.6 ppm, S.D. ± 0.5 ppm, S.E.M. ± 0.1 ppm, and the range was from 7.9 to 9.4 ppm. The samples taken with active air sampling showed values somewhat higher than the set value. The mean value of the charcoal tubes was 9.8 ppm, S.D. ± 0.5 ppm, S.E.M. ± 0.3 ppm, and the range was from 9.2 to 10.6 ppm. With a higher concentration of BD (16 ppm), also no breakthrough could be detected. The mean value of the passive dosimeter was 13.7 ppm, S.D. ± 1.1 ppm, S.E.M. ± 0.3 ppm, and the range was from 12.2 to 15.3 ppm. For the charcoal tubes the mean value was 18.7 ppm, S.D. ± 1.0 ppm, S.E.M. ± 0.4 ppm, and the range was from 17.5 to 20.3 ppm.

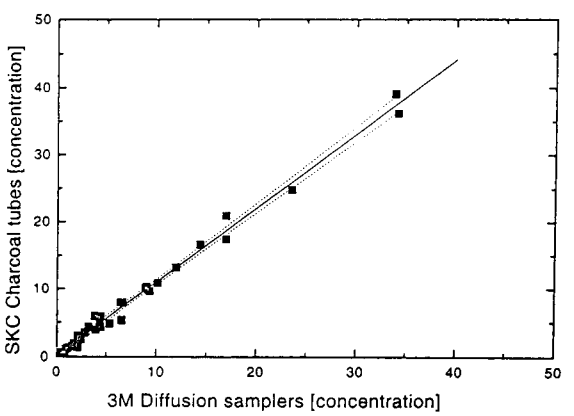


Fig. 4. The correlation of active and passive sampling. The samples were collected from three different petrochemical plants during winter, summer and autumn ($n = 35$, $r = 0.9956$).

The methods were also tested in a field study in three different petrochemical plants, where the work is mainly performed outdoors. All samples were personal samples, the sampling device being placed on the right shoulder of a worker during the full shift (6–8 h). The samples were collected during the winter when the temperature range was from −4 to −13°C, during summer with a temperature range from 15 to 25°C, and during autumn with a temperature range from 3 to 10°C. The two methods showed a good correlation ($r = 0.9956$) when field-tested (Fig. 4).

Acknowledgements

The authors would like to acknowledge Mr. Yrjö Peltonen for his professional technical assistance. Financial support for the study was obtained from the STEP project CT 91-0152 of the DG XII of the Commission of European Communities, coordinated by Dr. M. Sorsa. Neste OY is thanked for donating the 1,3-butadiene.

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Journal of Chromatography A, 710 (1995) 243–250

JOURNAL OF CHROMATOGRAPHY A

Monitoring of pesticides in air by gas chromatography–mass spectrometry and the use of quartz-fibre wool and activated carbon for sampling

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Abstract

A simple monitoring method has been developed to determine the mean concentrations of pesticides in air over a period of one week. The pesticides investigated were buprofezin, edifenphos, ethofenprox, fenitrothion, fenobucarb, fenthion, flutolanil, fthalide, malathion, pencycuron, phentoate, pyridaphenthion, tetrachlorvinphos and tricyclazole. The pesticides were collected using quartz-fibre wool and activated carbon and eluted with acetone and toluene–ethanol (4:1, v/v). The eluate was reduced to a small volume and an acetone solution of the internal standards 1,4-diiodobenzene and 9-bromoanthracene was added for gas chromatography–mass spectrometry (GC–MS). Recoveries of the pesticides, indicating the overall performance of this method, ranged from 82.4 to 94.6%. The minimum detectable concentrations ranged from 0.1 ng/m^3 to 1 ng/m^3. This method has been successfully applied to the monitoring of pesticides in air over a rural area near paddy fields.

1. Introduction

In recent years the effect on human health of pesticide residues in the atmosphere has become of major concern. Although annual variations of atmospheric pesticide concentrations have to be considered when evaluating the impact of pesticides on human health by inhalation, only very few reports have been presented on long-term variations [1,2]. A number of studies have described attempts to collect pesticides in air for gas chromatographic (GC) or gas chromatographic–mass spectrometric (GC–MS) determination using Carbowax 20M [3], Chromosorb 102 [4–6], Porapak C_{18} [3], polyurethane foam [1,7], Tenax GC [8], XAD-4 [9], glass-fibre filters [10], quartz-fibre filters and activated-carbon-fibre filters [11–14], etc. However, only a few papers have described simple methods for long-term monitoring of pesticides in air. We have previously reported a simple GC method for this purpose [15] using activated carbon for collection, and have investigated annual variations of two insecticides, fenitrothion (O,O-dimethyl-O-4-nitro-*m*-tolyl phosphorothioate) and fenobucarb (O-*sec*.-butylphenyl methylcarbamate), in the atmosphere over some rural and suburban areas near paddy fields [16]. This method, however, has the disadvantage of being limited in multicomponent monitoring, because we adopted GC determination: GC equipped with a flame photometric detector for fenitrothion and a flame thermionic detector for fenobucarb.

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0021-9673/95/$09.50
SSDI 0021-9673(95)00138-7

This report presents the results of GC–MS analysis for 14 common pesticides (9 insecticides and 5 fungicides) using quartz-fibre wool and an activated-carbon granule for sampling. The pesticides investigated were buprofezin (2-*tert.*-butylimino - 3 - isopropyl - 5 - phenyl - 1,3,5 - thiadiazinan-4-one), edifenphos (O-ethyl-S,S-diphenyl phosphorodithionate), ethofenprox [2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl ether], fenitrothion, fenobucarb, fenthion (O,O-dimethyl-O-3-methyl-4-methylthio-*m*-tolyl phosphorothionate), flutolanil (α,α,α-trifluoro-3′-isopropoxy-*o*-toluanilide), fthalide (4,5,6,7-tetrachlorophthalide), malathion [S-1,2,-bis-(ethoxycarbonyl)ethyl-O,O-dimethyl phosphorodithioate], pencycuron [1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea], phenthoate [S-(α-(ethoxycarbonyl)-benzyl)dimethyl phosphorothiolothionate], pyridaphenthion [O,O-diethyl-O-(3-oxo-2-phenyl-2H-pyridaxin-6-yl)phosphorothionate], tetrachlorvinphos [2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate] and tricyclazole (5-methyl-1,2,4-triazolo[3,4-*b*]-benzothoazole).

2. Materials and methods

2.1. Apparatus and materials

An air pump NS-S2 (Nissei, Tokyo, Japan) and a gas meter DC-2A (Shinagawa, Tokyo, Japan) were used for sample collection. A tube pump TMP-6L (Toyo, Tokyo, Japan) was used for sample elution. A mass spectrometer SX-102A (JEOL, Tokyo, Japan) equipped with a gas chromatograph, HP-5890 II (Hewlett-Packard), was used for quantitative analysis. A fused-silica column HP-5 (0.25 μm film thickness, 30 m × 0.32 mm I.D.) was purchased from Hewlett-Packard.

Activated carbon BPL-1 (Calgon) was ground to 0.25–0.42 mm in diameter and was washed with carbon disulfide, methanol, acetone and toluene in a Soxhlet apparatus for 8 h for each solvent. Quartz-fibre wool (fine grade) was purchased from Iuchi (Osaka, Japan). The collection tube used was made of glass (115 × 18 mm I.D. with 3 mm I.D. at both ends) and packed with 0.5 g quartz-fibre wool and 5 g of the cleaned activated carbon supported by a small plug of quartz-fibre wool. The tube was preconditioned with nitrogen at 150°C for 48 h at a flow-rate of 50 ml/min. The tube was sealed with silicon plugs at both ends, and stored in a glass desiccator with the cleaned activated carbon.

Tricyclazole was purchased from Hayashi (Osaka, Japan). A solution of a mixture of C_{11}–C_{30} normal alkanes (except for C_{29}), used to measure the programmed temperature retention index (PTRI) [17,18] of each pesticide and as an internal standard, was purchased from Hewlett-Packard. Other pesticides and reagents were purchased from Wako (Osaka, Japan). An acetone solution containing 100 μg/ml of 1,4-diiodobenzene and 9-bromoanthracene was prepared as an internal standard solution.

2.2. Sample collection and analysis

Air was sampled for 7 days with a collection tube set at a flow-rate of 0.1–0.2 l/min (Fig. 1). The pesticides collected were eluted from the collection tube first with 100 ml of acetone and then with 100 ml of toluene–ethanol (4:1, v/v) at a flow-rate of 0.5 ml/min (Fig. 2). The combined eluates were concentrated first to 5 ml in a Kuderna-Danish apparatus and then to 1 ml under a purified nitrogen gas stream. A volume of 10 μl of the internal standard solution was

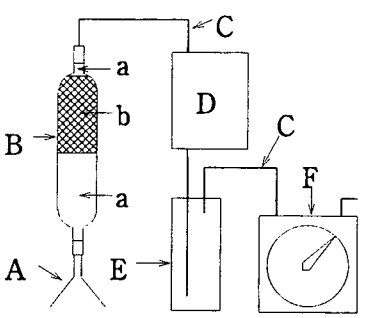

Fig. 1. Apparatus for sampling pesticides in air. A = glass funnel; B = collection tube; C = silicone tube; D = air pump; E = bottle; F = gas meter; a = quartz-fibre wool; b = activated carbon.

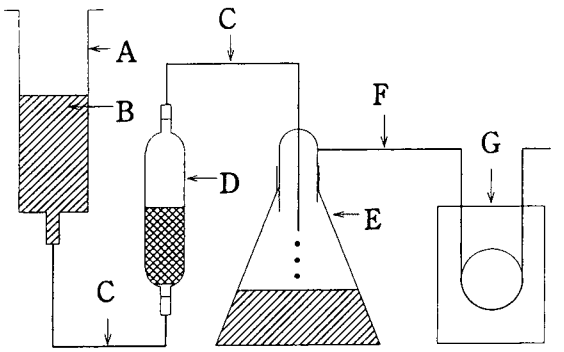

Fig. 2. Apparatus for the elution of pesticides from the collection tube. A = glass syringe; B = elution solvent; C = glass tube; D = collection tube; E = Erlenmeyer flask; F = silicone tube; G = tube pump.

added to the concentrated eluate solution and the resulting mixture was analysed by GC–MS in the selected-ion monitoring mode (SIM). GC–MS conditions were as follows: column temperature programmed from 50°C (held for 1 min) to 280°C (held for 5 min) at a rate of 20°C/min; injector temperature 200°C; injection mode, splitless; carrier gas pressure from 2 psi to 15 psi (held for 1 min) at a rate of 99 psi/min, then back to 2 psi at the same rate; ionization current 300 μA; electron energy 70 eV. The ions selected for SIM quantification of the pesticides are listed in Table 1, together with pesticide types and molecular masses [19,20]. PTRIs for the pesticides and the internal standards are also shown in Table 1. PTRIs were calculated using the following equation:

$$\mathrm{PTRI_A} = 100N + 100(\log t_\mathrm{A} - \log t_\mathrm{N})/(\log t_{N+1} - \log t_\mathrm{N})$$

where $\mathrm{PTRI_A}$ is the PTRI of compound A, t_A is the retention time for compound A, and t_N and t_{N+1} are the retention times for the normal alkanes with carbon number N and $N+1$ plus compound A [17,18]. The selected ions were divided into three groups according to PTRI data: SIM group No. 1, PTRI < 1800; SIM group No. 2, 1800 ≤ PTRI < 2300; SIM group No. 3, PTRI ≥ 2300.

Table 1
Selected ions for SIM determination of pesticides

Pesticide		M_r[a]	m/z	PTRI	SIM group No.
Buprofezin	I[b]	305.4	305	2224	2
Edifenphos	F[c]	310.4	310	2367	3
Ethofenprox	I	376.2	376	2840	3
Fenitrothion	I	277.2	277	1965	2
Fenobucarb	I	207.3	150	1620	1
Fenthion	I	278.3	278	2002	2
Flutolanil	F	323.3	323	2190	2
Fthalide	F	271.9	243	2040	2
Malathion	I	330.3	125	2150	2
Pencycuron	F	328.8	180	1702	1
Phenthoate	I	320.4	274	2106	2
Pyridaphenthion	I	340.3	340	2483	3
Tetrachlorvinphos	I	366.0	329	2152	3
Tricyclazole	F	189.2	189	2209	2
1,4-Diiodobenzene	I.S.[d]	329.9	330	1434	1
9-Bromoanthracene	I.S.	257.1	256	2190	2

[a] Cited from Refs. [19,20].
[b] Insecticide.
[c] Fungicide.
[d] Internal standard.

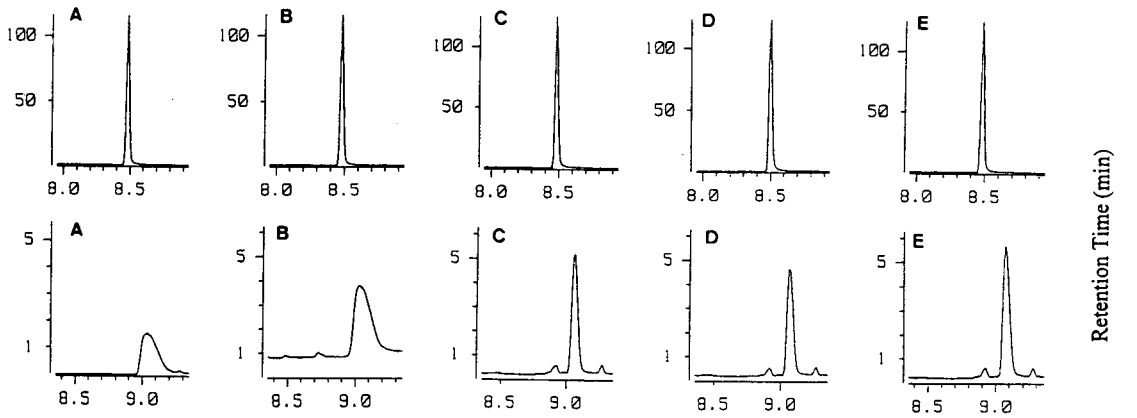

Fig. 3. Effect of polyethylene glycols on peak shapes of pesticides. Concentrations of PEG 200 and 300 are: 0 μg/ml (A); 500 μg/ml (B); 1000 μg/ml (C); 1500 μg/ml (D); and 2000 μg/ml (E); 1st row: fenobucarb; 2nd row: pencycuron.

3. Results and discussion

3.1. GC–MS analytical conditions

Some pesticides, particularly pencycuron and tricyclazole, provide wide tailing peaks in standard solutions. On the other hand, this phenomenon has not been observed for environmental samples. This suggests that compounds present in the environmental samples passivate the active surfaces in GC or MS. Thus, the quantitative evaluation of these pesticides has been difficult. It has been reported that metolcarb (*m*-tolyl methylcarbamate) and XMC (3,5-xylyl methylcarbamate) in the standard solution gave wide tailing peaks, whereas the two pesticides provided sharp, symmetric peaks with poly(ethylene glycol) (PEG) 200 and PEG 300 [21]. This was caused by the PEGs passivating the activated surface. It was further reported that

Table 2
Efficiencies of pesticides desorption[a] (%) from the activated carbon

Pesticide	Solvent				
	Acetone	Hexane	DCM[b]	Toluene	Toluene–EtOH[c]
Buprofezin	23.1	6.6	23.9	43.7	91.4
Edifenphos	14.4	8.4	21.8	76.9	90.3
Ethofenprox	3.1	0.4	49.1	96.8	94.5
Fenitrothion	61.3	7.5	19.8	43.5	90.8
Fenobucarb	65.2	1.5	46.7	58.2	86.2
Fenthion	51.1	8.2	32.0	45.5	91.2
Flutolanil	5.7	2.7	7.1	18.5	90.7
Fthalide	3.2	1.6	0.6	4.3	10.3
Malathion	89.8	5.7	44.7	97.6	98.5
Pencycuron	92.3	53.2	64.1	33.5	69.0
Phenthoate	53.7	17.5	46.7	100	98.7
Pyridaphenthion	41.7	9.1	9.6	8.3	97.4
Tetrachlorvinphos	46.3	9.8	59.9	87.6	92.4
Tricyclazole	9.1	0.4	1.5	10.5	90.5

[a] Mean ($n = 2$).
[b] Dichloromethane.
[c] Toluene–ethanol (4:1, v/v).

the PEGs did not interrupt SIM determinations of most pesticides involving the use of fragment ions of m/z 100 or higher, because they give no fragment ions of in that range [21]. Hence, we elucidated the effect of PEG 200 and PEG 300 on the peak shapes of the 14 standard pesticides.

Fig. 3 shows the chromatograms of fenobucarb and pencycuron. While the peak shape of fenobucarb did not change when the PEGs were added, that of pencycuron sharpened as concentrations increased from 0 to 1000 mg/ml. An improvement in the peak shape of tricyclazole was also achieved in the same manner. The PEGs gave none of the fragment ions selected for SIM determination of the pesticides (Table 1). We therefore used 1000 mg/ml of PEG 200 and 300 (acetone solution) to prepare the pesticide standard solutions for SIM determinations. All 14 pesticides prepared in this way gave sharp peaks.

3.2. Extraction solvent

Extraction efficiencies for the 14 pesticides from the quartz-fibre wool and the activated carbon were determined by adding 100 ng of the pesticide as an acetone solution to the glass tube packed with 0.5 g of the quartz-fibre wool without the activated carbon (quartz-fibre wool tube) and to the glass tube packed with 5 g of the cleaned activated carbon held by small plugs of the quartz-fibre wool (activated-carbon tube). Purified air was passed through the tube at 0.2 l/min for 30 min in order to evaporate the acetone. The pesticides were then eluted from the tube as described above by using five different solvents. All pesticides were eluted quantita-

Table 3
Recoveries of pesticides from the collection column

Pesticide	Run 1[a]				Run 2[b]		Run 3[c]	
	Recovery[d] (%)			R.S.D.[e] (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
	QW[f]	AC[g]	Total					
Buprofezin	88.2	5.4	93.6	4.63	90.7	3.67	87.8	5.95
Edifenphos	85.9	6.2	92.1	2.84	84.9	2.42	83.4	3.78
Ethofenprox	84.5	4.7	89.2	3.62	83.7	3.93	92.9	7.42
Fenitrothion	47.0	42.7	89.7	4.17	89.0	1.23	95.5	1.97
Fenobucarb	23.3	66.2	90.5	5.52	88.4	5.54	90.9	3.55
Fenthion	74.2	18.3	92.5	3.65	91.2	6.19	87.8	4.10
Flutolanil	81.7	8.3	90.0	2.99	87.8	3.13	94.6	2.77
Fthalide	90.1	1.1	91.2	2.67	89.1	1.43	90.7	7.37
Malathion	80.1	10.3	90.4	3.95	88.5	4.12	89.4	9.32
Pencycuron	73.7	20.5	94.2	7.39	97.6	3.68	91.2	5.57
Phenthoate	71.7	15.4	87.1	5.78	84.5	4.04	87.6	7.13
Pyridaphenthion	72.2	17.1	89.3	7.25	87.8	3.02	87.2	8.01
Tetrachlorvinphos	66.9	20.2	87.1	0.87	82.4	6.49	86.1	3.94
Tricyclazole	69.5	21.0	90.5	6.72	93.8	4.80	86.6	7.14

[a] Mean air temperature = 26.7°C (21.6–34.8°C); mean humidity = 76%.
[b] Mean air temperature = 14.9°C (8.1–21.5°C); mean humidity = 68%.
[c] Mean air temperature = 20.8°C (10.2–28.7°C); mean humidity = 71%.
[d] Mean ($n = 3$).
[e] Relative standard deviation.
[f] Quartz-fibre wool.
[g] Activated carbon.

tively (>92%) from the quartz-fibre wool by each solvent. On the other hand, none of the solvents investigated could elute all the pesticides from the activated carbon, as can be seen from Table 2. Twelve pesticides, with the exception of fthalide and pencycuron, were eluted quantitatively by toluene–ethanol (4:1, v/v). While pencycuron was eluted quantitatively by acetone, fthalide could not be eluted by any solvent investigated. However, the low recovery of fthalide does not appear important, because this compound can be collected efficiently by the quartz-fibre wool, as described later. Therefore, acetone and toluene–ethanol (4:1) were chosen as the best solvents for elution. No pesticides were observed in the solvent or in the procedure blanks.

3.3. Retention efficiency on filters by air passing

It is difficult to determine collection tube efficiencies for the different pesticides, since it is

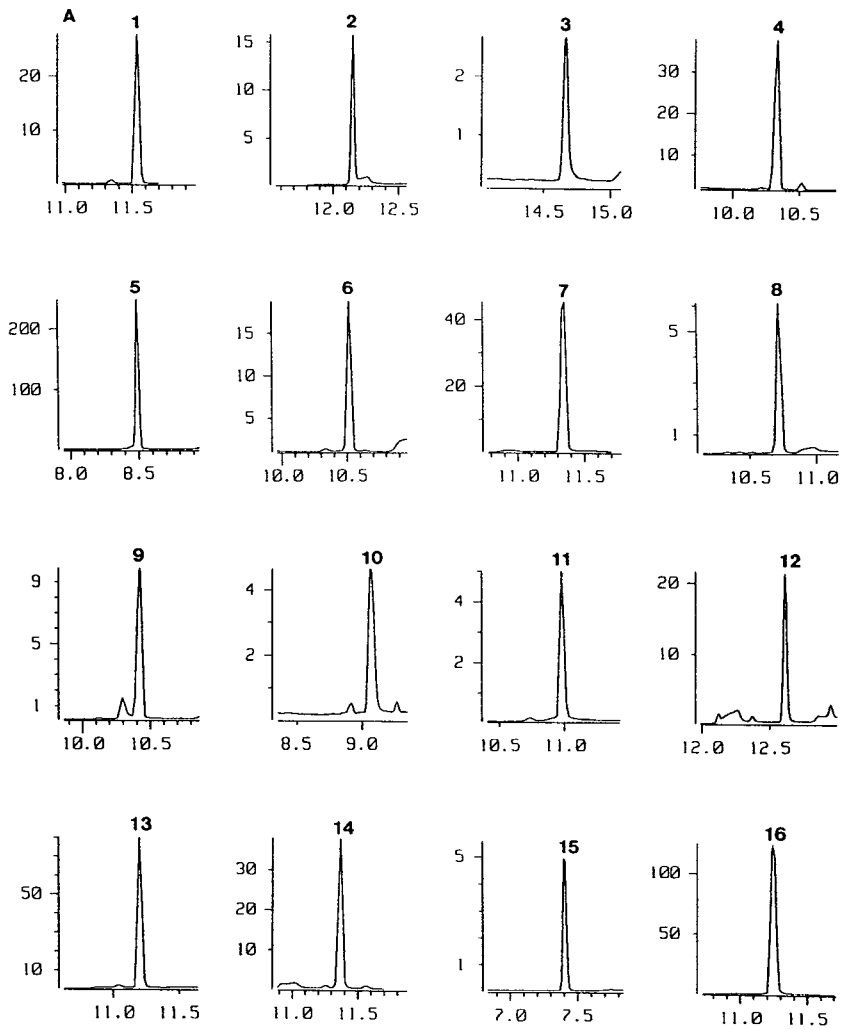

Fig. 4.

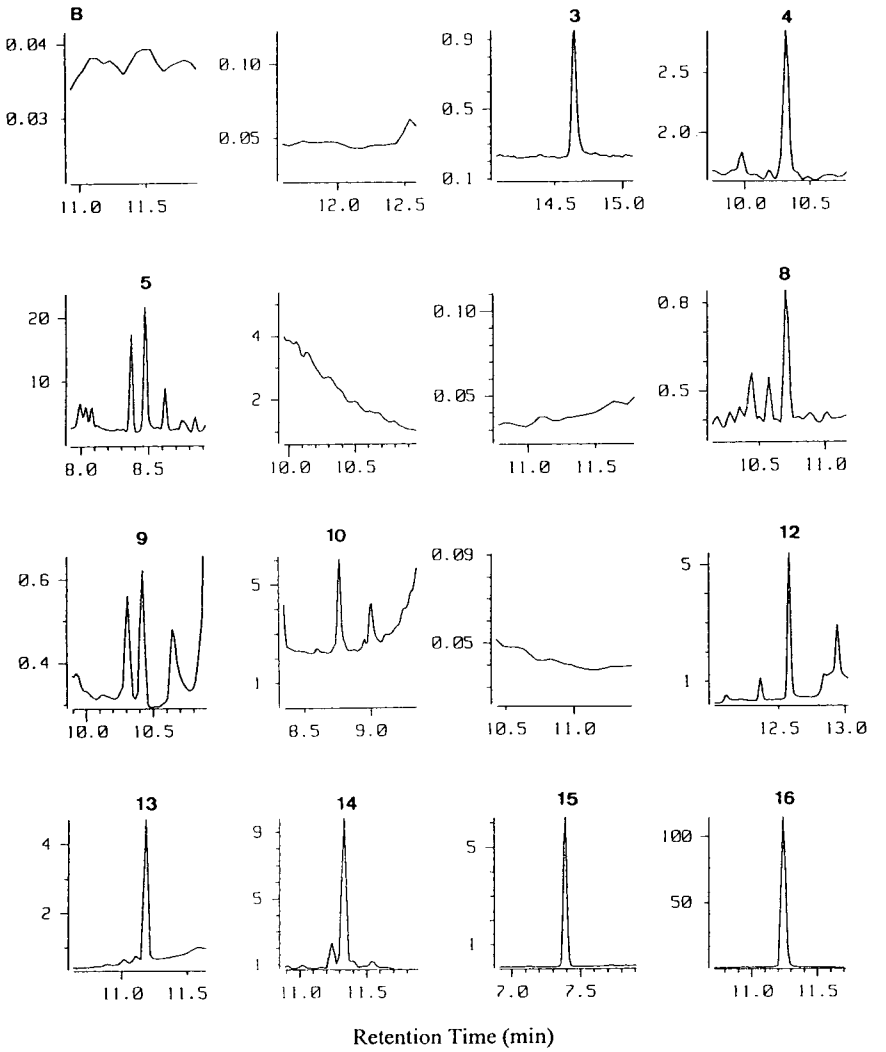

Fig. 4. SIM chromatograms of pesticides. (A) standard; (B) samples. Peaks: 1 = buprofezin; 2 = edifenphos; 3 = ethofenprox; 4 = fenitrothion; 5 = fenobucarb; 6 = fenthion; 7 = flutolanil; 8 = fthalide; 9 = malathion; 10 = pencycuron; 11 = phenthoate; 12 = pyridaphenthion; 13 = tetrachlorvinphos; 14 = tricyclazole; 15 = 1,3-diiodobenzene; 16 = 9-bromoanthracene.

impossible to prepare air samples containing known quantities of specific chemicals. Hence, we elucidated the collection efficiency via the retention efficiency [22,23].

The retention efficiencies of the collection tube with respect to the individual pesticides were determined as follows. A known amount of the pesticide was added to a quartz-fibre wool tube as an acetone solution. Air was passed at 0.2 l/min for 7 days through the tube, connected to two activated-carbon tubes as back-ups. The retention efficiencies of the quartz-fibre wool were very good (>88%) with respect to buprofezin and fthalide, as shown in Table 3, but for the other pesticides a combination with the activated-carbon system would be recommended. No pesticide was detected from the second activated-carbon tube. Therefore, 5 g of

the activated carbon provided sufficient back-up to the quartz-fibre wool. Some experiments for recoveries of spiked pesticides from the collection tube were carried out. The results are shown in Table 3. Recoveries of all pesticides were good (82.4–94.6%).

The minimum detectable concentrations [24] were 0.1 ng/m^3 for fenobucarb, fenthion, flutolanil, fthalide, malathion, tetrachlorvinphos and tricyclazole, 0.2 ng/m^3 for edifenphos, phenthoate and pyridaphenthion, and 1 ng/m^3 for buprofezin, ethofenprox, fenitrothion and pencycuron.

3.4. Application to environmental samples

This method was used to monitor pesticides in the air over a rural area near paddy fields from July 5 to August 30, 1993. In all, nine pesticides were detected. The pesticides and concentrations detected were as follows: ethofenprox, 1–110 ng/m^3; fenitrothion, 1–13 ng/m^3; fenobucarb, 0.1–430 ng/m^3; fthalide, 0.1–13 ng/m^3; malathion, 0.1–60 ng/m^3; pencycuron, 1–69 ng/m^3; pyridaphenthion, 0.2–19 ng/m^3; tetrachlorvinphos, 0.1–2.7 ng/m^3; tricyclazole, 0.1–6.1 ng/m^3. Typical SIM chromatograms of standards and samples are shown in Fig. 4. Every pesticide could be determined well without interferences.

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Journal of Chromatography A, 710 (1995) 251–257

JOURNAL OF CHROMATOGRAPHY A

Field comparison of polyurethane foam plugs and mini-tubes containing Tenax-TA resin as trapping media for the aerodynamic gradient measurement of trifluralin vapour fluxes

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Abstract

The effectiveness of a low-volume (0.3 l min^{-1}) mini-tube (MT) sampler packed with Tenax-TA resin was compared in a field study with that of a polyurethane foam (PUF) sampler (25 l min^{-1}) for measurement of herbicide vapour concentrations in air following fall soil-incorporation of trifluralin at 690 g ha^{-1}. Based on a paired comparison, no significant difference was observed in trifluralin concentrations (ng m^{-3}) determined by gas chromatographic (GC) analysis of air samples collected using the MT and PUF samplers. As a consequence, fluxes determined using the aerodynamic gradient method of measurement for either sampler type were also similar. Because the entire air sample collected by the MT sampler was transferred onto the GC column, greater sensitivity was achieved using the MT sampler.

1. Introduction

Due to its high trapping efficiency [1,2], polyurethane foam (PUF) has been the preferred trapping medium for the determination of pesticide residues in air. As well as being inexpensive, PUF also permits relatively high air sampling flow-rates and is convenient to use both in the field and in the laboratory. One drawback to the use of PUF, however, is the time-consuming step of soxhlet extraction required both for initial cleanup and for extraction of trapped pesticides after sampling. In addition, PUF extracts generally require a concentration step to enhance sensitivity to gas chromatographic (GC) analysis.

Recently, a thermal desorption mini-tube (MT) system, in which both the MT sampler and the thermal desorption unit were automated, was evaluated for air sampling and GC analysis [3]. The MT technology offers some advantages over the use of PUF for air sampling. In addition to considerable time savings due to elimination of the soxhlet extraction and subsequent extract concentration steps, automated MT cleaning and sample desorption for GC analysis are accomplished thermally, thus eliminating the use of organic solvents. As well, the entire air sample is thermally desorbed onto the GC column (compared to the small fraction of the PUF extract

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0021-9673/95/$09.50
SSDI 0021-9673(95)00081-X

injected) which results in increased sensitivity even though the MT air sampling flow-rate is lower (100 to 300 ml min^{-1}). Also, since conditions can be chosen to effect complete thermal desorption of trapped pesticides, no correction for pesticide recovery from the MTs is necessary. Drawbacks to the use of the MT technology are that once an air sample has been thermally desorbed, there is no possibility of re-analysis in the case of equipment malfunction, and there is no recourse when pesticide amounts trapped on the MT make quantitation impossible due to detector saturation or when air contaminants interfere with the quantitation of pesticides being monitored.

The MT system evaluated previously [3] used Tenax-TA resin as a trapping medium. This resin, which was packed into glass MTs, demonstrated trapping efficiencies (>99%) for the herbicides triallate and trifluralin [3] which were equivalent to those determined previously for PUF [1,2]. In addition, thermal desorption of these two herbicides from the resin was quantitative [3]. Recently, an attempt was made to determine whether MTs aspirated at a relatively much lower air sampling flow-rate would be as effective under field conditions in determining herbicide fluxes using the relaxed eddy-accumulation (REA) method of measurement as the PUF samplers [4]. The REA system conditionally samples air at a constant rate according to updrafts or downdrafts via PTFE inlet tubes. Unfortunately, sorption of the herbicides (triallate and trifluralin) to the inner walls of the PTFE inlet tubes of the MT sampler did not permit differentiation of the trapping/sorption effects so that air concentrations determined gas chromatographically for the two sampler types could be compared.

In the present study, the effectiveness of the MT and PUF samplers for determination of herbicide fluxes in air is again compared, this time using the aerodynamic gradient (AG) method of measurement. The AG system offers the advantage that the MT and PUF samplers become source samplers; that is, air is aspirated directly into both sampler types so that the effect of herbicide sorption on the determination of herbicide concentrations in air, as observed with the REA system [4], is circumvented. The soil-incorporated herbicide, trifluralin, was selected for study. This herbicide, applied either in the fall or pre-emergence in the spring, is used on the Canadian prairies to control grassy weeds in a wide variety of crops [5]. Significant vapour loss of this herbicide (vapour pressure = 14.80 mPa [6]) has been observed previously following spring soil-incorporation as a tank mixture with triallate [7].

2. Experimental

2.1. Study site/herbicide application

The experiment was carried out on a 300-m diameter circular plot (7 ha) of fine sandy loam soil (45.3% sand, 16.7% clay, 38.0% silt; 2.36% organic matter, pH = 6.1) located in field 20 on the Greenbelt Farm of Agriculture and Agri-Food Canada, Ottawa, ON, Canada. Wheat was grown on the site in 1993 and following harvest, the field was chisel plowed on September 22 (calendar day 265) and then cultivated on day 288. Trifluralin was then applied to the site at 690 g active ingredient (a.i.) ha^{-1} using a sprayer-equipped discer so that incorporation into the upper 10 cm of soil occurred with the application. Spraying began at 12:20 h Eastern Standard Time on day 292.

2.2. Air sampling

The sampling mast for the PUF and MT samplers was located at the centre of the treated circular plot which ensured the same fetch regardless of wind direction. PUF and MT samplers were positioned in pairs (Fig. 1) on the mast such that the inlets of both samplers were at the following heights from the soil surface: 30, 50, 75, 100, 150 and 200 cm. The samplers were positioned such that the sampler inlet centres were approximately 15 cm apart. Three manifolds, each aspirated by a single pump (GAST Mfg. Corp., Model 4VCF-10-M400X), were

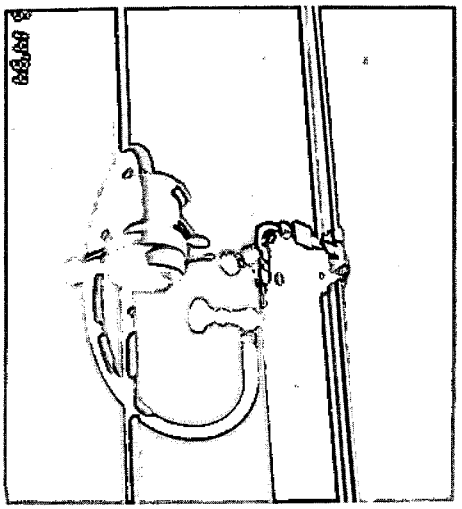

Fig. 1. Photograph showing a MT and a PUF sampler mounted at the 150-cm height on the sampling mast.

mounted on the sampling mast. One manifold, equipped with six inlets, was used for the six MT samplers. Each of the other manifolds had three inlets and was interfaced with three PUF samplers. All manifold inlets were equipped with needle valves to regulate air flow.

Each PUF sampler, which consisted of an aluminum housing and a removable glass liner into which a 45-mm diameter × 50-mm long PUF plug was inserted, was aspirated at approximately 25 l min^{-1}. The MTs (Canadian Centre for Advanced Instrumentation, Saskatoon, SK, Canada) consisted of a 2-mm I.D. × 38-mm borosilicate glass tube packed with 14 mg Tenax-TA resin centred between stainless-steel screens and were aspirated at approximately 300 ml min^{-1}. In order to avoid sampling droplet drift which occurs during application, air sampling was begun at 13:15 h when the first half of the circular plot had been sprayed and the spraying equipment was downwind of the sampling mast. Air was then sampled continuously during daylight hours over the next two days using 1- or 2-h sampling intervals as outlined in Table 1.

At the beginning of each sampling period, the air sampling flow-rate through each MT and PUF sampler was set to approximately 300 ml min^{-1} and 25 l min^{-1}, respectively, by adjustment of the needle valves and use of a flowmeter (mass airflow sensor AWM3300V, Honeywell Canada Ltd., Ottawa, ON, Canada for the MT samplers and Series 2211L mass flow transducer, TSI, St. Paul, MN, USA for the PUF samplers). At the end of each sampling period, the flow-rate through each sampler was measured again using the appropriate flowmeter. The mean of these initial and final flow-rate values for each sampler was corrected for the change in air temperature and pressure over the corresponding sampling period and the corrected flow-rate values were used for calculation of corresponding trifluralin air concentrations and fluxes.

2.3. Mini-tube analysis

The automated thermal desorption unit (ATDU; Canadian Centre for Advanced Instrumentation, Saskatoon, SK, Canada) w as mounted onto a Varian Model 3600 gas chromatograph which was equipped with a thermionic specific detector and controlled by the Varian Star chromatography workstation. The ATDU, directly interfaced to the GC system via a 30-m × 0.530-mm I.D. DB-5 fused-silica column (J and W Scientific; 1.5 μm film thickness), was operated isothermally at 240°C with a desorption cycle of 15 min. The column oven temperature program for the GC system was as follows: 70°C for 16 min, then 15°C min^{-1} to 250°C and finally hold for 2 min at 250°C. The carrier gas (helium UHP) flow-rate was 8 ml min^{-1}. Detector gas flow-rates were 4 ml min^{-1} (hydrogen UHP) and 175 ml min^{-1} (air UZ), whereas that for the detector make-up gas (helium UHP) was 22 ml min^{-1}. The detector bead current was set at 3.14 A and the detector temperature at 300°C. Under the above conditions, the desorption of trifluralin from the MTs was quantitative and the retention time for trifluralin was 25.24 min with the total run time being 30 min. The detector response was linear over the range 0.08 to 50 ng and the calibration curve passed through the origin ($r^2 = 0.99$).

Table 1
Trifluralin air concentrations and amounts analyzed as determined by mini-tube (MT) and polyurethane foam (PUF) samplers at six heights above the soil surface for each sampling period over 2 days

Sampler height (cm)	Day 292					Day 293				
	Time	MT air conc. (ng m^{-3})	Amount desorbed (ng)	PUF air conc. (ng m^{-3})	Amount injected (ng)	Time	MT air conc. (ng m^{-3})	Amount desorbed (ng)	PUF air conc. (ng m^{-3})	Amount injected (ng)
200	13:15	1441	22	1339	1.7	10:00	128	4.0	298	0.71
150	to	1662	26	1352	1.7	to	206	6.6	325	0.77
100	14:15	1920	29	1984	2.5	12:00	261	8.3	384	0.92
75		2229	34	2072	2.5		311	9.9	429	1.0
50		2607	40	2470	3.1		324	10.1	465	1.1
30		2283	36	2517	3.0		303	9.5	513	1.2
200	14:15	675	23	667	1.6	12:00	89[a]	3.3	148	0.35
150	to	846	28	805	2.0	to	104[a]	2.8	169	0.39
100	16:15	1018	35	1030	2.5	14:00	123[a]	3.9	200	0.46
75		1139	39	1140	2.8		142[a]	4.5	199	0.46
50		1308	44	1454	3.5		148[a]	4.7	205	0.47
30		1514	46	1528	3.7		143[a]	4.5	157[b]	0.35
200	16:15	395	13	409	0.95	14:00	83	2.6	93	0.23
150	to	612	19	575	1.4	to	108	3.5	115	0.28
100	18:15	939	29	864	2.1	16:00	131	4.2	138	0.34
75		1114	35	1088	2.7		135	4.3	176	0.43
50		1328	44	1336	3.2		137	4.4	145	0.36
30		1479	48	1459	3.4		149	4.7	154	0.37
200	18:15	–[c]	–	–	–	16:00	88	2.8	88	0.22
150	to	–	–	–	–	to	104	3.3	107	0.28
100	20:15	–	–	–	–	18:00	128	4.1	139	0.34
75		–	–	–	–		147	4.7	133	0.33
50		–	–	–	–		166	5.2	147	0.37
30		–	–	–	–		176	5.6	156	0.39

[a] Circuit breaker for the MT manifold pump tripped and pump did not operate for the complete sampling period.
[b] Hexane extract was inadvertently taken to dryness.
[c] No air samples were collected.

2.4. PUF extraction and analysis

PUF plugs were individually soxhlet extracted for 2 h using 300 ml of hexane [1]. The hexane extract was then concentrated to 2 ml prior to GC analysis.

A Varian Model 3400 gas chromatograph, equipped with a thermionic specific detector and on-column injector, was used with a Model 8200CX autosampler set to inject 2 μl and controlled with the Varian Star chromatography workstation. A 30-m × 0.530-mm I.D. HP-1 fused-silica column (Hewlett-Packard; 0.88 μm film thickness) was used with the following operating conditions: a column oven temperature program consisting of 60°C for 1 min, then 10°C min^{-1} to 270°C and finally hold for 3 min at 270°C; carrier gas (helium UHP) flow-rate, 7 ml min^{-1}; injector 150°C; detector gas flow-rates, 4.5 ml min^{-1} (hydrogen UHP) and 175 ml min^{-1} (air UZ); detector make-up gas (helium UHP) flow-rate, 23 ml min^{-1}; detector bead current, 3.10 A; detector temperature, 300°C. Under the above conditions, the total run time was 25 min and the retention time for trifluralin was 14.74 min. A linear detector response was observed over the range 0.4 to 50 ng, and the calibration curve passed through the origin ($r^2 = 1.00$). Amounts of trifluralin detected were corrected for recovery from the PUF plugs by soxhlet

extraction. Recovery was 83.7 ± 1.1% (mean ± standard error; $n = 12$) from PUF plugs fortified with 1 μg of trifluralin.

2.5. Vertical flux calculations

Herbicide flux was calculated for the PUF and MT samplers for each 1- and 2-h sampling period using the AG method [8]. The flux was determined as a product of the turbulent eddy diffusivity coefficient and the gradient of herbicide concentration over the six sampling heights [8,9]. The eddy diffusivity coefficient was determined from the corresponding profiles of various meteorological parameters obtained using a micrometeorological station which has been described earlier [7,9].

Micrometeorological data were collected continuously over each sampling period at 15-min intervals by a data acquisition system (Campbell Scientific datalogger) interfaced to a Digital 380 minicomputer. The eddy diffusivity coefficient was calculated for each 1- or 2-h data collection period that coincided with the air sampling periods. All profiles were corrected for the effects of atmospheric stability, as described earlier [7].

3. Results and discussion

3.1. Climatic data

Rainfall in amounts of 11.2 and 20.8 mm occurred on days 289 and 290, respectively, prior to the commencement of the study. As a consequence, the trifluralin was incorporated on day 292 into relatively moist soil. Over the air-sampling periods of the 2-day study, air temperatures showed a diurnal trend with maximum temperatures occurring in mid-afternoon (14:00 to 16:00 h; Fig. 2). Somewhat warmer temperatures were recorded on day 293. Soil surface temperatures, obtained by extrapolation of a profile of soil temperatures at 10-, 5- and 2-cm depths, also showed a diurnal trend (Fig. 2). Because of relatively cool air and soil surface temperatures and a light rain on day 293 (0.3 mm; 12:00 to 14:00 h), the soil surface tended to remain moist over the study period. Average wind speed on day 292 was 1.1 m s^{-1} whereas that for day 293 was 3.6 m s^{-1}.

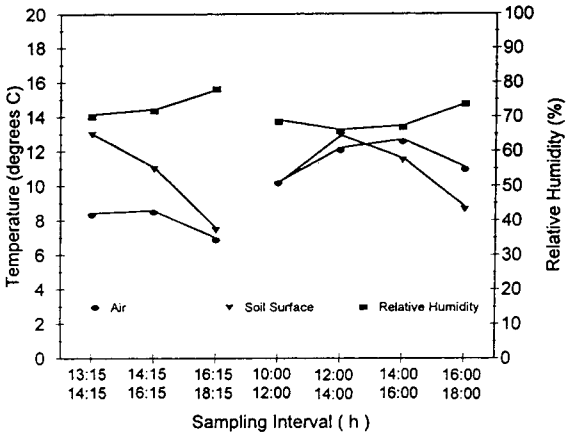

Fig. 2. Mean air temperature at the 100-cm height, mean soil surface temperature, and mean relative humidity at the 200-cm height for each sampling period over the 2-day study.

3.2. Trifluralin concentrations in air

Mean PUF air sampling flow-rates at the six heights over all sampling periods varied from 23.0–25.6 l min^{-1} and the mean volume sampled was 2.878 ± 0.014 m^3 (mean ± standard error; $n = 36$) over 2 h. The corresponding mean flow-rates (not including the 12:00 to 14:00 h sampling period when pump failed) for the MT samplers ranged from 255–286 ml min^{-1} with the mean volume sampled being 0.0321 ± 0.0002 m^3 ($n = 30$) over 2 h. Even though the volume of air aspirated through the PUF samplers was approximately 90 times that aspirated through the MT samplers, the trifluralin concentrations in air detected with the MT samplers were essentially the same as those detected with the PUF samplers (Table 1). A paired comparison of the air concentrations as determined with the MT and PUF samplers ($n = 36$ since data from the 12:00 to 14:00 sampling period on day 293 when the MT pump failed were not included) indicated no significant difference in air concentration between the two samplers. This confirms that the

relatively low air sampling flow-rate used with the MT samplers provided representative air samples for herbicide vapour analysis.

Soil surface and air temperatures (Fig. 2) were relatively cool during the sampling periods of days 292 and 293 and, because of rainfalls just prior to the start of the study, the upper 10 cm of soil and the soil surface remained relatively moist during this time. The enhancing effect of soil and soil surface moisture on volatilization of soil-incorporated pesticides [10,11], including trifluralin [7,12,13], has been well established. Thus, even though air and soil surface temperatures were relatively cool on the day of application, trifluralin concentrations in air across the six sampling heights above the soil surface were of the same magnitude as those reported earlier in studies carried out under warmer conditions [7,13]. Air concentrations at all sampling heights were greatest during the 1-h sampling period immediately after application (Table 1). Trifluralin concentrations were decreased by approximately half over the following 2-h sampling period and showed a continued decrease over the second 2-h sampling period on day 292. Twenty-four hours after spraying (12:00 to 14:00 h on day 293), air concentrations of trifluralin had decreased by a factor of 10. Such a rapid decrease in air concentrations of trifluralin following soil incorporation has been observed previously [7,13].

Amounts of trifluralin injected onto the GC column for quantitation also differed with the samples collected by the MT and PUF samples. The entire air sample was thermally desorbed from the MT onto the GC column and the amounts of trifluralin desorbed from the MTs were generally more than 10-fold greater (Table 1) than the amounts injected in 2 μl of the corresponding PUF extract (concentrated to 2 ml). Thus, for the lowest air concentration (88 ng m^{-3}) aspirated through a PUF sampler, 0.22 ng of trifluralin were injected. With the thermionic specific detector, this was equivalent to only 545 area counts and thus was close to the limit at which reliable quantitation would be obtained using this detector. In contrast, for the same air concentration aspirated through a MT sampler, 2.8 ng of trifluralin were desorbed onto the column. Assuming 0.2 ng of trifluralin to be the minimum amount that could be reliably quantitated, the MT technology would permit quantitation of trifluralin air concentrations of the order of 6 ng m^{-3}. Thus, to obtain the same order of sensitivity using a PUF sampler, the PUF plug extract would have to be concentrated to 200 μl. Alternatively, increased sensitivity using PUF samplers may effectively be achieved by transferring several microlitres of PUF extract onto a MT with subsequent GC analysis. This possibility is currently being investigated in our laboratory.

3.3. Trifluralin fluxes

The trifluralin fluxes calculated for both the MT and PUF samplers for the 7 sampling periods over the 2-day study are shown in Fig. 3. Flux values for each sampler type paralleled the corresponding air concentrations (Table 1). Thus, maximum fluxes were observed for the 1-h sampling period immediately after application and were of the order of 175 ng m^{-2} s^{-1} or 6.3 g ha^{-1} h^{-1}. Fluxes then decreased over subsequent 2-h sampling periods such that, 24 h after spraying, fluxes were less than 10 ng m^{-2} s^{-1} or 360 mg ha^{-1} h^{-1}. Flux values calculated for the MT and PUF samplers for each sampling period were similar reflecting the fact that the corresponding

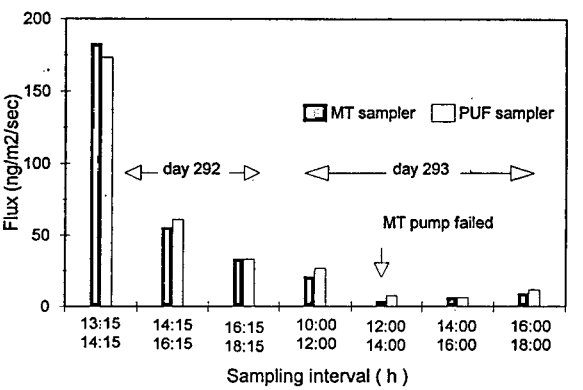

Fig. 3. Trifluralin fluxes for each sampling period over the 2-day study as calculated by the AG method using air concentration data derived from the MT and PUF samplers.

air concentrations used to derive the flux for each sampler type were not significantly different. At least part of the difference in flux between the MT and PUF samplers for the 12:00 to 14:00 h period (day 293) would have been due to failure of the pump aspirating the MT manifold.

In summary, the MT technology used in the present study provided representative air sampling for trifluralin vapour analysis following a fall soil-incorporated application. Use of the MT samplers also resulted in increased sensitivity, with respect to determination of trifluralin concentrations in air, when compared to PUF samplers. Finally, reliable trifluralin concentration gradients were obtained using the MT sampler. Potentially, trifluralin fluxes in the order of 1 ng m^{-2} s^{-1} (36 mg ha^{-1} h^{-1}) or less may be detected using the MT technology. It is concluded that the MT technology would be equally applicable for the determination of fluxes of other pesticides, provided trapping breakthrough volumes and desorption efficiencies have been determined.

Acknowledgements

This study was supported by funding from the Agriculture Canada Great Lakes Water Quality Program. The authors thank the Centre for Food and Animal Research for cultural preparation of the study site and for applying the trifluralin. This is Publication No. 1162 from the Saskatoon Research Centre, and Contribution No. 95-55 from the Centre for Land and Biological Resources Research.

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END OF SPECIAL ISSUE

Carbohydrate Analysis

High Performance Liquid Chromatography and Capillary Electrophoresis

Edited by **Z. El Rassi**

Journal of Chromatography Library, Volume 58

The objective of the present book is to provide a comprehensive review of carbohydrate analysis by HPLC and HPCE by covering analytical and preparative separation techniques for all classes of carbohydrates including mono- and disaccharides; linear and cyclic oligosaccharides; branched heterooligosaccharides (e.g., glycans, plant-derived oligosaccharides); glycoconjugates (e.g., glycolipids, glycoproteins); carbohydrates in food and beverage; compositional carbohydrates of polysaccharides; carbohydrates in biomass degradation; etc.

The book will be of interest to a wide audience, including analytical chemists and biochemists, carbohydrate, glycoprotein and glycolipid chemists, molecular biologists, biotechnologists, etc. It will also be a useful reference work for both the experienced analyst and the newcomer as well as for users of HPLC and HPCE, graduates and postdoctoral students.

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1. Preparation of carbohydrates for analysis by HPLC and HPCE (A.J. Mort, M.L. Pierce).
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2. Reversed-phase and hydrophobic interaction chromatography of carbohydrates and glycoconjugates (Z. El Rassi). 3. High performance hydrophilic interaction chromatography of carbohydrates with polar solvents (S.C. Churms). 4. HPLC of carbohydrates with cation- and anion-exchange silica and resin-based stationary phases (C.G. Huber, G.K. Bonn). 5. Analysis of glycoconjugates using high-pH anion-exchange chromatography (R.R. Townsend). 6. Basic studies on carbohydrate - protein interaction by high performance affinity chromatography and high performance capillary affinity electrophoresis using lectins as protein models (S. Honda). 7. Modern size exclusion chromatography of carbohydrates and glycoconjugates (S.C. Churms). 8. High performance capillary electrophoresis of carbohydrates and glycoconjugates (Z. El Rassi, W. Nashabeh). 9. Preparative HPLC of carbohydrates (K.B. Hicks).
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Trace Element Analysis in Biological Specimens

Edited by **R.F.M. Herber** and **M. Stoeppler**

Techniques and Instrumentation in Analytical Chemistry Volume 15

The major theme of this book is analytical approaches to trace metal and speciation analysis in biological specimens. The emphasis is on the reliable determination of a number of toxicologically and environmentally important metals. It is essentially a handbook based on the practical experience of each individual author. The scope ranges from sampling and sample preparation to the application of various modern and well-documented methods, including quality assessment and control and statistical treatment of data. Practical advice on avoiding sample contamination is included.

In the first part, the reader is offered an introduction into the basic principles and methods, starting with sampling, sample storage and sample treatment, with the emphasis on sample decomposition. This is followed by a description of the potential of atomic absorption spectrometry, atomic emission spectrometry, voltammetry, neutron activation analysis, isotope dilution analysis, and the possibilities for metal speciation in biological specimens. Quality control and all approaches to achieve reliable data are treated in chapters about interlaboratory and intralaboratory surveys and reference methods, reference materials and statistics and data evaluation.

The chapters of the second part provide detailed information on the analysis of thirteen trace metals in the most important biological specimens. The following metals are treated in great detail: Aluminium, arsenic, cadmium, chromium, copper, lead, selenium, manganese, nickel, mercury, thallium, vanadium and zinc.

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Journal of Chromatography B: Biomedical Applications		663–666	667/1 667/2	668/1 668/2	669/1 669/2	670/1 670/2	671/1 + 2	

[a] Vol. 701 (Cumulative Indexes Vols. 652–700) expected in October.

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Quality Assurance for Environmental Analysis

Method Evaluation within the Measurements and Testing Programme (BCR)

Edited by **Ph. Quevauviller**, **E.A. Maier** and **B. Griepink**

Techniques and Instrumentation in Analytical Chemistry, Volume 17

Quality assurance (QA) for environmental analysis is a growing feature of the nineties as is illustrated by the number of QA guidelines and systems which are being implemented nowadays. This book focuses on the technical aspects of quality assurance. The techniques used in different analytical fields are critically reviewed and existing tools for evaluating their performance are described. Particular reference is made to the activities of the Measurements and Testing Programme (BCR) of the European Commission towards the improvement of quality control of environmental analysis.

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