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Determination of airborne formaldehyde by active sampling on 3-methyl-2-benzothiazolinone hydrazone hydrochloride-coated glass fibre filters

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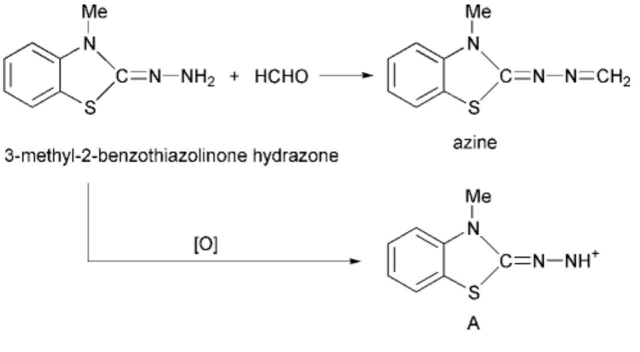
Formaldehyde was sampled with the use of a standard miniature glass fibre filter coated with 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH). The formaldehyde hydrazone formed [*i.e.*, the adduct of formaldehyde (HCHO) and MBTH] was desorbed from the filter with water and then oxidised by an iron(III) chloride–sulfamic acid solution to form a blue cationic dye in acidic medium which was subsequently determined by visible absorption at 628 nm. The recovery of HCHO as the cationic dye from MBTH-coated filters is 87–102% in the range 0.065–2.9 μg of HCHO. This corresponds to 4.3–193.3 μg m^{-3} in a 15 L air sample. The collection efficiency of the MBTH-coated filter is higher than 90%. When the filter sampling system is used in active mode, air can be sampled at a rate of up to 1 L min^{-1}, affording an overall sensitivity of about 3 μg m^{-3}, corresponding to about 2 ppb v/v HCHO at 1 atm and 273 K. The method was successfully applied to the determination of HCHO in samples of indoor and outdoor air with satisfactory results.

Formaldehyde (HCHO) has attracted considerable attention due to its toxicity and possible carcinogenic properties in studies of air pollution, especially in non-occupational indoor environments, where the outgassing of HCHO from a variety of products such as particle-board, plywood, and urea–formaldehyde foam insulation can cause irritation and potential harm to occupants.[1,2] Formaldehyde concentration levels in indoor air change from near ambient levels (1–25 ppb v/v) to as high as 4 ppm in new mobile homes.[3] Some European countries[4] give HCHO concentration guidelines of 100 ppb v/v. At concentrations slightly greater than 100 ppb v/v, HCHO can induce watery eyes, itching skin, burning sensations in the mucous membrane and difficulty in breathing. Acceptable concentrations of HCHO in ambient air are reported to range from 20 to 100 ppb v/v.[5] Thus, chemically active HCHO monitoring methodology, applicable at low ambient levels under a variety of environmental conditions, is necessary.

In general, the numerous sampling and analysis methods for HCHO include spectrophotometry, electrochemical methods including polarography and adsorption voltammetry, and chromatography. Most spectrophotometric methods have been found to be insensitive and rarely sufficient for occupational monitoring purposes.[6,7] High-performance liquid chromatographic (HPLC) methods mainly depend on the selective reaction of airborne carbonyl with the reagents 2,4-dinitrophenylhydrazine or 1,5-dansylhydrazine and subsequent separation and determination of the corresponding hydrazones by UV[8–10] or fluorometric detection.[11] However, HPLC methods require a fairly elaborate analytical procedure and a long measuring time for the sample. A number of attempts have been made to improve sensitivity and to simplify the methods.[12–16] Different types of devices have been applied to the collection of HCHO from air samples.[17] Impinger collection was most frequently used. However, it is not available for monitoring of personal exposure due to its inconvenience. The use of solid adsorbents for HCHO is gaining popularity because it offers several important advantages over the liquid impinger sampling method. First, the apparatus used is simpler and more portable. This makes it especially suitable for field work or personal monitoring. Second, a larger amount of the reagents can be impregnated onto the solid sorbents. This ability gives the sorbents a higher sampling capacity than liquid absorbers. Several chemically impregnated or coated solid absorbents in combination with pumped or diffusive sampling have been reported and to some extent have improved HCHO stability and capacity characteristics. Absorbents such as glass beads,[18] glass fibre filters,[19,20] 2,4-dinitrophenylhydrazine-coated filters,[21,22] silica gel,[23] and poly(dimethylsiloxane)–divinylbenzene solid-phase microextraction fibres have been tried.[24]

We have reported various electroanalytical methods for the determination of HCHO with good sensitivity.[20,25] Considering the extremely low concentration levels of HCHO in an indoor atmosphere, the development of a simple, sensitive and cost-effective method is needed and would be of benefit. In this paper, a simple spectrophotometric method is proposed for the determination of trace amounts of airborne formaldehyde. The method involves the adsorption of HCHO on a 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH)-coated glass fibre filter with subsequent oxidation of the HCHO azine formed from the adduct of the HCHO and MBTH. The final product is a blue cationic dye with visible absorption at 628 nm.[7] The reaction scheme of the proposed method is as follows:



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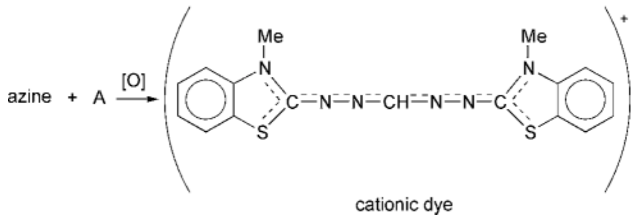

This method provides a simple and reliable way of determining HCHO. The procedure for glass fibre filter pre-treatment, HCHO desorption, and subsequent spectrophotometric analysis is described in detail.

Experimental

Materials

All chemicals used were of analytical-reagent grade unless otherwise stated. A 1 mg cm^{-3} HCHO stock solution was prepared by diluting an appropriate amount of 36% aqueous HCHO solution (Guangzhou Chemical Factory, Guangzhou, China) to 1 dm^3 with distilled water and standardised by an iodimetric method.[26] The standardised formaldehyde solution was further diluted with ethanol. A known amount of formaldehyde in ethanol was used. A 0.5% solution of MBTH (Aldrich, Milwaukee, WI, USA) was prepared by adding an appropriate amount of MBTH to distilled water. An oxidising reagent solution was prepared by dissolving 0.8 g of sulfamic acid (Acros Organics, Geel, Belgium) and 0.5 g of iron(III) chloride hexahydrate (Aldrich) in distilled water and diluting to 100 cm^3. A dilute solution of HCHO was freshly prepared before the experiments.

Instrumentation

Absorption measurements were performed on a UV–visible spectrophotometer (Cary 100 UV–VIS, Varian Australia Pty., Mulgrave, Victoria, Australia). The air-sampling device was the same as that used in our previous studies[20] and was composed of a micro-cartridge holder and a battery-operated constant flow pump (Model GilAir-5, Gilian Instrument Corporation, West Caldwell, NJ, USA). Glass fibre filters containing MBTH were loaded in the micro-cartridge holder. The flow rate of sampled air was measured by a mass flow controller (Model Bubble Generator, Gilian Instrument Corporation).

Preparation of filter for active sampling

A 50 μL aliquot of 0.5% MBTH solution was transferred to a Gelman Type AE 13 mm diameter glass fibre filter (Supelco, Bellefonte, PA, USA). The filters were then allowed to dry under vacuum for 30 min and stored in a closed brown bottle which was placed in a desiccator.

Sampling and analysis

A typical volume (15 L) of the air sample (25 min at a calibrated flow rate of 0.6 L min^{-1}) was drawn through the micro-cartridge by the battery-operated pump. After sampling, the filter was taken out from the micro-cartridge and immersed in 2.0 cm^3 of distilled water for 20 min. Then, 2.0 cm^3 of oxidising reagent were added. Absorption measurement was immediately carried out at 628 nm after the mixture solution had been allowed to stand for 20 min.

Collection experiment

The collection experiments were conducted based on the injection of a known amount of HCHO in ethanol into a glass tube through a septum inlet, after which about 9 L of HCHO-free air of known relative humidity were drawn through the glass tube (100 × 7 mm id) at a flow rate of 0.6 L min^{-1}. The glass fibre filters containing MBTH were used in micro-cartridge holders.

Results and discussion

Desorption of the resulting azine

According to the reaction principle, it is necessary for the adduct to be desorbed from the filter by water due to the water soluble properties of the adduct before the oxidation reaction has taken place. In order to determine the optimum desorption time of the proposed method, an exact known amount of HCHO in a 10 μL aqueous solution was pipetted onto MBTH-coated glass fibre filters with 1.3 μg per filter. The desorption time was monitored. The absorption of the solution at 628 nm increased with the increase in desorption time and reached a constant value at desorption times longer than 20 min (Fig. 1). Thus, the optimum desorption time was chosen to be 20 min.

Effect of MBTH concentration

The glass fibre filters as solid sorbents were coated with MBTH by transferring 50 μL of various concentrations of MBTH solution onto them. Then, 10 μL of a solution containing an exact amount of HCHO were added to each filter with 1.3 μg HCHO per filter. Higher MBTH concentrations favoured the complete reaction, resulting in higher absorbance values (Fig. 2). However, this can also cause, to some extent, an increase in the reagent blank absorption. As a result, for compromise

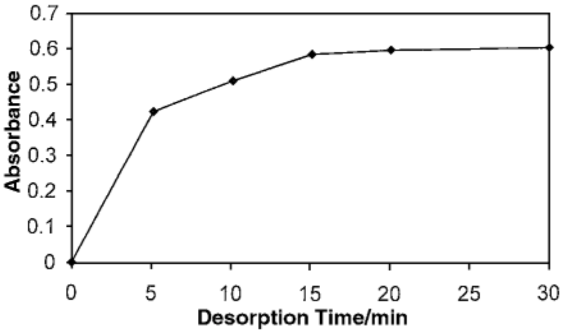

Fig. 1 Effect of desorption time on extraction of formaldehyde–MBTH product from glass fibre filter into water; 1.3 μg HCHO per filter was used.

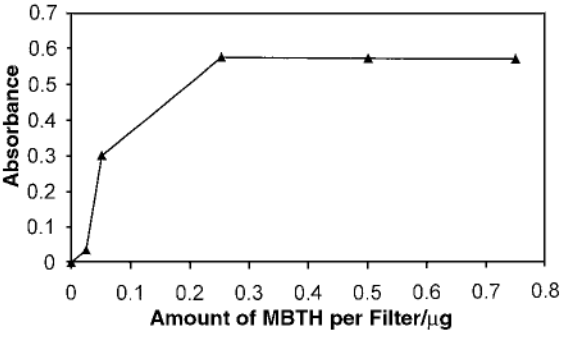

Fig. 2 Effect of MBTH concentration on the reaction of HCHO and MBTH; 1.3 μg HCHO per filter was used.

experimental conditions, the filter was coated with 0.5% MBTH, corresponding to 0.25 μg MBTH per filter. The oxidation reaction of the azine to the cationic dye is complete in about 20 min for 0.1–10 μg HCHO. The blue dye formed is very stable in solution for at least 3 h.

Collection efficiency and recovery of the glass fibre filter

The collection efficiency of formaldehyde was investigated on two coated glass fibre filters in series. Table 1 shows the collection efficiency of HCHO on two filters. By comparison with the absorbance values for the same amount of HCHO directly applied onto the filters, the collection efficiency of the MBTH coated-filters was found to be 88–105% for the first filter under the experimental conditions. With an injected formaldehyde content greater than 2.6 μg, breakthrough from the first filter was evident.

The recovery test was performed by injecting a known amount of HCHO into a glass tube through a septum inlet, with a stream of ambient air at a flow rate of 0.6 L min^{-1} for 25 min passing through the glass fibre filter. Table 2 shows the results of the recovery test. Recoveries from 87 to 102% were obtained.

Analytical characteristics

Under the optimum experimental conditions, the determination of HCHO was established. The absorption spectra of the cationic dye obtained from various amounts of HCHO are displayed in Fig. 3. The calibration graph at 628 nm was linear from 0.065 to 2.9 μg per filter with a correlation coefficient of 0.995. The corresponding linear regression equation is $A = 0.069 + 0.3147 \times m_{HCHO}$, where A is the absorbance value and m_{HCHO} is the mass of formaldehyde (μg) collected. The detection limit of the method was determined to be 0.05 μg HCHO based on twice the absorbance value for a blank solution. Furthermore, potential interference experiments were conducted by adding various amounts of HCHO and interferent solutions to the MBTH-coated filter. Acetone showed no interference but there were some major interferences from the other aliphatic aldehydes. When a 10% interference limit was set as a measure to estimate the interference effect, and with 0.39 μg HCHO adsorbed on the filter, interference was observed from 1 μg acetaldehyde, 2.8 μg propionaldehyde and 4 μg butyraldehyde, respectively. The interference decreases with an increase in the carbon chain length of the aldehyde. Fortunately, the levels of other aliphatic aldehydes are generally much lower than that of HCHO.[27] Hence, their interference on airborne HCHO determination will not be a major cause for concern using the proposed method.

Table 1 Collection efficiency of formaldehyde on glass fibre filters coated with 0.5% MBTH using active sampling mode with a stream of HCHO-free air at a flow rate of 0.6 L min^{-1}

Sample	Amount of formaldehyde injected into glass tube/μg	Relative humidity (%)	Collection efficiency (%)[a]		RSD (%)
			1st filter	2nd filter	
1	0.07	79	105	—	10
2	0.7	79	98	—	7
3[b]	0.7	74	93	—	5
4	1.3	70	94	3	7
5	2.6	70	90	9	6
6	2.9	74	88	10	6

[a] Average value of six determinations. [b] At a sampling flow rate of 0.2 L min^{-1}.

Table 2 Recovery of formaldehyde on glass fibre filters coated with 0.5% MBTH using active sampling mode with a stream of ambient air flow rate of 0.6 L min^{-1}

Sample	Amount of formaldehyde added/μg	Relative humidity (%)	Recovery (%)[a]	RSD (%)
1	0.07	77	90	11
2	0.7	75	102	7
3	2.0	81	87	5

[a] Average value of six determinations.

Determination of formaldehyde in indoor and outdoor air

The proposed method was applied to air sample analysis. The air was sampled at a flow rate of 0.6 L min^{-1}. The sampling times for indoor and outdoor samples were 25 min and 1 h, respectively. Typical indoor air samples were chosen from offices and chemical laboratories in the Science Tower of our University. The HCHO levels found are listed in Table 3. In addition, an 8 h variation of the HCHO content in an office is depicted in Fig. 4. For further comparison purposes, outdoor air

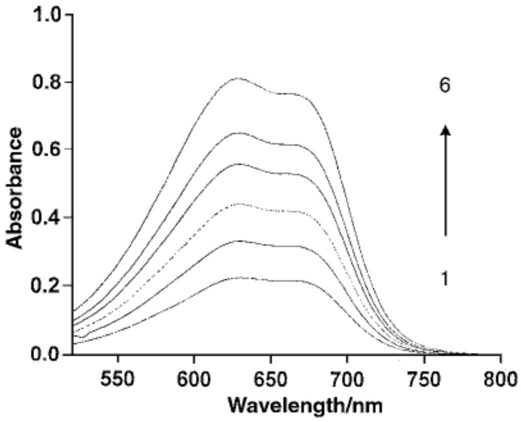

Fig. 3 Absorption spectra of the cationic dye formed from various amounts of HCHO. (1) 0.5; (2) 0.8; (3) 1.2; (4) 1.5; (5) 1.8; (6) 2.4 μg HCHO.

Table 3 Levels of formaldehyde in indoor air at a sample flow rate of 0.6 L min^{-1}

Sample No.	Location	Sampling time/min	Relative humidity (%)	HCHO concentration[a]/ μg m^{-3}
1	Office 1	25	74	14.4 ± 1.5
2	Office 2	25	80	17.8 ± 2.4
3	Chem. lab. 1	25	82	6.6 ± 0.9
4	Chem. lab. 2	25	76	7.5 ± 1.2

[a] Average value of three determinations.

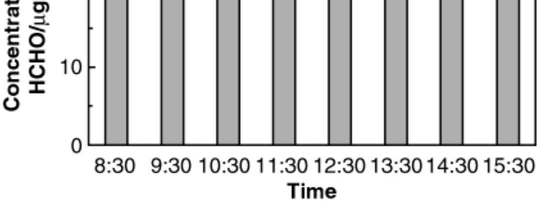

Fig. 4 An 8 h variation of the indoor formaldehyde level in an office.

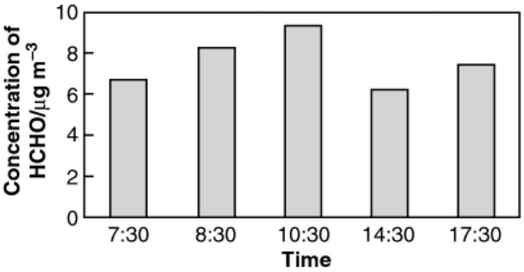

Fig. 5 Level of formaldehyde in outdoor air.

samples were also taken and measured. The HCHO levels are displayed in Fig. 5. It can be seen that the HCHO level in indoor air is considerably higher than that in outdoor air. The results are in agreement with those of other investigations.[20,28]

Conclusion

A simple method for the spectrophotometric determination of airborne HCHO has been established. The proposed method has certain advantages over conventional methods such as ease of use, short sampling time and high analytical sensitivity. It can be used to determine trace amounts of airborne HCHO and was successfully applied to the determination of HCHO in indoor and outdoor air.

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