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Institute for Regulatory Science

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EDITORIAL

Greenhouse Effect, Tropical Rain Forests and Environmental Colonialism ✓

The world news media has finally recognized the existence of the greenhouse effect. The steady increases in the concentration of carbon dioxide and the climatological consequences of these increases are now discussed by the printed as well as by the media press globally. At the same time, the press, the political leaders and, most notably, the environmental advocacy organizations complain about the conversion of tropical rain forests for agricultural and other uses at an increasing rate. It is being argued that tropical rain forests are not only a sink for carbon dioxide but also the habitat for many unique species of animals.

The environmental scientific community has long provided the evidence in support of most of these arguments. For example, the late Leona Libby guest-edited a multiple issue of *Environment International* (Vol. 2, issues 4–6, 1979) dedicated to the topic of carbon dioxide and climate. Many other scientific periodicals have published similar information providing solid evidence that the increases in carbon dioxide may have adverse climatological effects and rain forests are potential sinks for carbon dioxide.

About two-thirds of the tropical rain forests are located in Brazil, Indonesia and Zaire. The remainder of these forests are scattered around the world and are principally located in developing countries. These countries would like to use the wood much like developed countries have done for the last few centuries. They also need the land for agricultural and industrial development. Although, in the long run, the tropical rain forests may prove to be economically more viable than these uses of tropical rain forests, those who are suffering from poverty rightfully reject a long-term benefit because they may not live long enough to see them. A person suffering from malnutrition, disease, and whose children cannot survive the first year of life, cannot be persuaded to worry about protection of endangered species or increases in global temperature by 0.4° regardless of their long-term or global impact.

There is another important aspect of the problem. Carbon dioxide is produced principally from combustion of fossil fuels for energy generation. Coal is used mostly in power plants for electricity generation and petroleum is used as a fuel for automobiles, home heating and electricity generation. Carbon dioxide is also produced in the chemical industry, mostly from petroleum, and as a consequence of a number of other activities. About three-fourths of the carbon dioxide emissions originate from developed countries and are associated with energy production and other activities that are responsible for a high living standard in these countries.

Brazil, Indonesia, Zaire and other developing nations are under strong pressure from environmental organizations to stop the deforestation of tropical rain forests. They are being asked to help the global environment and the humanity, yet they are those who can least afford it.

It has been proposed that developed nations should purchase the land from these countries and declare it an international park. The generated funds could be used to pay for the debt that many of these nations have accumulated. This proposal has certain similarities with colonial practices of yesteryears. In effect, a nation is being asked to surrender its sovereignty under duress for reasons that primarily benefit others and are not necessarily advantageous to its immediate well-being. What if large new deposits of minerals are found in these forests? What price would one ask for a forest that today is not commercially valuable but in the future may be of great value to a nation for reasons that may not be apparent today? Who decides the price of the land and who negotiates on behalf of a nation that has not developed sufficient democratic institutions for the people to participate in the decision? No one should be surprised that the proposal has not found many takers, neither those who provide the money nor those who are to sell the forest. There is already the accusation that environmental colonialism is replacing the conventional colonialism. This is a legitimate issue requiring discussion at national and international levels and whose resolution must be satisfactory not only to current but also to future generations of the nations involved.

What is the solution? If one accepts the notion that those who generate a waste must provide for its disposal, one must accept that those who produce carbon dioxide must pay for the maintenance of carbon dioxide sinks. One possible solution would consist of the formation of an International Climate Fund (ICF). For every unit of carbon dioxide, the ICF would receive a fee. For example, for every tonne of CO_2 (or an equivalent quantity of chemicals with an impact on climate), a contribution would be made to the ICF. The ICF, in turn, would pay those who are to maintain the tropical rain forests. The retention or formation of forests would not be limited to countries such as Brazil, Indonesia and Zaire. Every country would have to establish and maintain forests. A minimum of land (expressed in percent of the total territory) in every country would be dedicated to forests.

Paying for the waste generated by a segment of the industry is not new. In the U.S., the nuclear power industry is taxed specifically for the treatment and disposal of nuclear waste. It is just as logical to ask that the petroleum and coal producers pay for the removal of carbon dioxide from the atmosphere.

Clearly, the best method for avoiding the greenhouse effect is reducing the generation of CO_2. Electrical energy can be produced by means other than fossil fuels and the generated energy can be used more efficiently.

The environmental scientific community has known for at least a decade or longer that increasing carbon dioxide concentrations in the atmosphere may have deleterious effects on the well-being of mankind. It is true that the scientific community is not uniquely qualified to provide solutions to societal problems. However, it is equally true that the scientific community has an obligation to point out problems that are based on science and yet originate from political and advocacy interests.

The global climate is an important problem. The environmental scientific community welcomes the attention of political leaders and the news media. However, it is imperative that solutions are sought that survive political upheavals and can withstand the legitimate desires of every nation now and in the foreseeable future.

A. Alan Moghissi

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DETERMINATION OF NICKEL-63

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The research of activation products in the environment is often centred on cobalt-60 or other gamma emitters, since pure beta emitters require time consuming separations to be counted. However, some beta emitters must be checked because they have a build up in the environment, leading to potential hazards. Among these nuclides, there is nickel-63 which is a pure, soft beta emitter (67 keV) with a long half-life (100 years). A chemical separation, providing good results, was developed. Such a separation is based upon nickel carrier addition in the sample then DMG complex formation and isolation; after elimination of solvent, DMG complex is destroyed. Chemical yield is determined by flame atomic absorption measurement and nickel-63 counted by liquid scintillation. The described procedure allows the determination of low-level activities in different samples (soils, effluents, etc.). Detection limits are close to 0.1 Bq per sample.

1. Introduction

Nickel-63 is produced in nuclear reactors by activation of nickel-62 which is present in inconel or structural stainless steel, following the reaction.

$$^{62}\mathrm{Ni} \xrightarrow{(n,\gamma)} {}^{63}\mathrm{Ni}.$$

The natural abundance of Nickel consists of:

^{58}Ni	67.8%
^{60}Ni	26.2%
^{61}Ni	1.2%
^{62}Ni	3.7%
^{64}Ni	1.1%

Other activation reactions may occur, such as:

$$^{58}_{28}\mathrm{Ni} \xrightarrow{(n,\gamma)} {}^{59}_{28}\mathrm{Ni}$$

$$^{58}_{28}\mathrm{Ni} \xrightarrow{(n,p)} {}^{58}_{27}\mathrm{Co}$$

$$^{60}_{28}\mathrm{Ni} \xrightarrow{(n,p)} {}^{60}_{27}\mathrm{Co}$$

Cobalt isotopes are well characterized and are easy to measure by their gamma emissions; on the other hand, both nickel 63 and nickel 59 remain difficult to determine: they do not emit gamma rays.

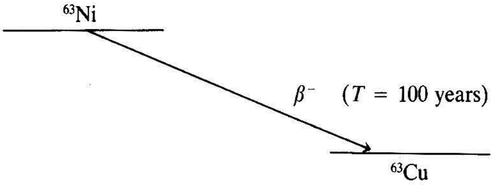
Moreover, these two nickel isotopes have rather long half lives.

^{59}Ni $T\,1/2 = 8 \times 10^4$ years.

^{63}Ni $T\,1/2 = 100$ years

and may lead to a build up in the environment — Nickel-59 production competes with cobalt-58; this competition leads to less nickel-59 present. Only nickel-63 measurement seems worthwhile. This nuclide represents a hazard for biological systems because of its continuous production and long half-life.

Due to its radioactive property (nickel-63 is a pure soft beta emitter, $E_{\max} = 67$ keV), there are no external radiation risks.



To measure nickel-63, liquid scintillation counting is required after specific nickel separation.

To reach this goal, different procedures have been developed. Complexation with dithiocyanate has been reported (Harvey and Sutton, 1970). A majority of authors use dimethylglyoxime (DMG) but only the separation procedure differs. Chloroform (Motojima *et al*, 1967) or toluene (Yonezama *et al*, 1983; Radwan *et al*, 1981) is used as extractant; other authors prefer a DMG precipitation (Kramer, 1984; Bhat *et al*, 1976). A method based on DMG complexation and chloroform extraction, then concentration, has been developed for different types of samples. A detection limit of 0.1 Bq may be attained with liquid scintillation counting.

Experimental

Reagents

- Ni carrier solution is 10g/L (i.e., 49 g/L of Ni SO_4, 7 H_2O).
- Dimethylglyoxime solution (DMG) 1 g of dimethylglyoxime obtained from FLUKA was dissolved in 100 ml of ethanol.
- Scintillation cocktail: LUMAGEL from KONTRON ANALYTIC.

Apparatus

A LKB 1219 rack beta liquid scintillation counter was used to measure ^{63}Ni. An atomic absorption apparatus 875 from varian was used to determine nickel concentrations; the main parameters were:

- nickel lamp with intensity adjusted to 3.5 mA.
- wave length for measurement: 232 nm.
- slit width: 0,2 nm.
- flame air + acetylene.

Sample preparation

Vegetation and organism samples are dried and ashed; soils are dried and powdered, 100 g of soil and 10 g of ash may be taken for nickel isolation.

To the sample in a 500 mL beaker, 100 mL of 14 N nitric acid are added. The sample is evaporated to dryness, then 100 mL of 4 N nitric acid are added and the solution is filtered. At this step, the nickel concentration is determined by atomic absorption. Should the concentration be lower than 1 mg/L, 0.1 mL of carrier solution is added. To avoid interference, cobalt solution should be added at the same concentration as nickel. The sample is stirred and 50 mL of 10% ammonium citrate solution added. Finally the solution is made pH 10 with concentrated ammonia; then 25 mL of DMG solution are added and this mixture is transfered in a 500 mL extraction vial.

The mixture is shaken with 20 mL of chloroform for about 2 minutes and allowed to settle. The aqueous phase is again shaken with 10 mL of chloroform. A total of four extractions is necessary; this leads to a final volume of 50 mL of chloroform.

To eliminate chloroform, the solution is heated gently in a water bath; then, 5 mL of concentrated nitric acid are added. This fraction is heated until half the volume is eliminated, then allowed to cool and adjusted with deionized water to 10 mL.

In a scintillation vial, (depending upon the activity) a known volume of solution is introduced (from 1 to 9 mL). This solution is gently heated in order to remove nitric acid. When the vial is dry, 1 or 2 mL of deionized water and 10 mL of scintillation cocktail are added. The vial is shaken then kept in the dark for one hour. It is then counted in a liquid scintillation counter. The counting time depends upon ^{63}Ni activity, but half an hour should be enough at a counting efficiency of 30%. One mL of the remaining nitric acid solution is adjusted to 100 mL in order to check the nickel concentration by atomic absorption. Generally, the yield is close to 100%; therefore, the nickel concentration reaches 10 mg/L.

Efficiency determination

Prior to any determination, a standard curve is established in order to correlate the activity to the quenching value. The following calibration was made using standard solutions of nickel-63 (LMRI-FRANCE).

100 Bq of nickel-63 were introduced into a scintillation vial with 10 mL of scintillation cocktail, then this standard solution was counted three times, 10 minutes each time; counts per minute and quenching figures are recorded.

Sample extraction	Gross CPM (With background)	Actual CPM	Efficiency	Calculated activity Bq
1	21	3	55	0.09
2	20	2	50	0.006
3	21	3	52	0.09
4	19	1	48	0.03
5	21	3	52	0.09
6	22	4	54	0.12
			mean	0.08 ± 0.05

Fig. 1. Results for detection limit approach.

Sample g	Nickel concentration	^{63}Ni value MBq/g	Specific activity MBq/g	Weight ratio mg/kg ^{63}Ni/Ni
0.276	72.1%	16.8 ± 2.5	23.3	8.8
0.284	58 %	13.6 ± 2.2	23.4	8.8

Fig. 2. Results for nickel-63 determination in inconel.

To establish a quenching curve versus efficiency 0.1 mL of nickel solution (10 g/L) was added step by step to total of 1.5 mL.

Determination of detection limit

The limitation for the measurement of low activities is the background of the liquid scintillation counter and more precisely, its reproductibility. The background was 18 ± 2 cpm with quenching figures corresponding to 50% efficiency.

To check the detection limit the whole procedure of nickel separation was followed. A solution with an activity of 0.1 Bq, which theoretically corresponds to 3 cpm (at 50% efficiency) was used. Six standard solutions (one liter each) were prepared, each containing 10 mg of nickel and 0.1 Bq of nickel-63.

Results listed on (Fig. 1), approximately, confirms a detection limit close to 0.1 Bq per sample, at two sigma confidence limit.

Application of procedure

The separation of nickel-63 was tested on various samples such as irradiated alloys, effluents, nuclear wastes, etc.

Inconel

This materials was submitted to neutron flows in a simulated loop reactor; two types of inconel, with different nickel concentration, were irradiated.

The sample was dissolved in aqua regia and the volume adjusted to one liter with deionized water. Nickel concentration was determined by flame atomic absorption; 1 mL was taken for nickel separation and nickel measurement: no carrier was added.

Results (Fig. 2) display values of nickel-63 per gram of sample, and also the values of specific activity of nickel; moreover, a calculation permitted the weight ratio determination of nickel-63 and total nickel.

Nuclear waste

From embedded thermosetting resins which were fully mineralized by acid attack, nickel was separated from other activation products. Results are listed on (Fig. 3) indicating that specific activities were consistent.

Effluent from nuclear power plant before rejection

Sampling was made in a tank before the effluents were rejected in a river. Nickel carrier was added since nickel concentration was lower than 0.01 mg/L. Results were lower than specification: nickel-63 measurement was 44 ± 8 Bq/L.

Discussion

The separation of nickel-63 was tested in samples which contained various activation products or fission products. The procedure resulted in excellent separation from these nuclides: DMG has a high complexant power; it is possible to separate one part per million (1

Sample g	Nickel value mg/g	^{63}Ni MBq/g	^{63}Ni/Ni mg/kg
2.00	0.88	1.00	436
2.38	0.89	0.99	430
1.78	0.95	1.05	420
1.27	0.90	0.90	413
1.84	0.90	0.95	403

Fig. 3. Results for nickel-63 determination in thermosetting resins.

		3 EXTRACTIONS mg/L	4 EXTRACTIONS mg/L
AQUEOUS PHASE	Co	5.00 ± 0.05	5 ± 0.05
	Ni	0.09 ± 0.02	< 0.01
CHLOROFORM PHASE	Co	< 0.01	< 0.01
	Ni	5.90 ± 0.05	6.00 ± 0.05

Fig. 4. Extraction of Ni-DMG complex initial concentrations were: Ni = 6 mg/L; Co = 5 mg/L.

mg/L) of nickel in solution (Kramer, 1984). This complex is stable between pH 3 and pH 10. Another could be used, such as, thiocyanate pyridine (Bhat *et al*, 1976) but this compound is not desirable for liquid scintillation counting.

Palladium is extracted by DMG; however, this nuclide is not present in the environment; moreover, all palladium isotopes have short half-lives (longest lived ^{103}Pd; $T\ 1/2 = 17$ days).

To get a good separation, it is necessary to have enough nickel present, which may require the addition of nickel carrier. This addition of this carrier must be limited because the colored nickel cation has a quenching effect on liquid scintillation counting.

Red DMG complex can be extracted by several organic solvents but chloroform seems to meet all the requirements:

- low solubility of water in chloroform.
- higher specific gravity than water ($d = 1.526$); this leads to an immediate extraction.
- low boiling point (61.2 °C).

This last characteristic allows an easy elimination of chloroform in order to obtain a "dry" Ni-DMG complex. To get a very high chemical yield, it is necessary to carry out four extractions (see Fig. 4). This test was done with cobalt in order to measure the effect of this element. Six samples were tested.

Once the number of extraction has been determined, a radiochemical separation, between nickel-63 and cobalt-60, has been done; this was in order to check potential interferences since radioactive contamination is much more critical. It was demonstrated that, from a solution containing 1 k Bq/L of cobalt-60 and 5 k Bq/L of nickel-63, decontamination factor was greater than 100, cobalt-60 was not detected in nickel phase; it would have greatly affected the liquid scintillation counting.

The destruction of DMG-nickel complex is important, since the red coloration must be removed. However, it is dangerous to destroy this complex by heating: DMG-Ni sublimes at 250 °C. The best way to recover nickel is by nitric acid attack of the complex. Nitric acid is easily eliminated by heating and this allows concentration of the final liquid sample. This also permits solubilization of nickel and consequently, is favourable both for liquid scintillation counting and atomic absorption measurement.

Conclusion

The described procedure allows a fairly good isolation of nickel isotopes in different types of samples. The most interesting isotope, nickel-63, has a long half-life (100 years) and is a pure soft beta emitter, which is not easy to measure by direct spectrometry.

Using the described separation procedure coupled with liquid scintillation counting, the detection limit, which can reasonably be reached, is close to 0.1 Bq per sample.

This procedure permits the determination of low level activities with a high confidence level, which is necessary for environmental monitoring.

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INCIDENCE OF ANTIBIOTIC RESISTANT BACTERIA IN UNDERGROUND WATER

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Bacteria other than fecal coliform were isolated from the negative Eijkman test tubes by streaking on eosin methylene blue agar plates. A total of 101 isolates from underground water pumped from three water works in Cairo were classified into genera or groups according to their morphological, cultural and physiological characters and tested for their resistance towards four commonly used antibiotics namely chloramphenicol, tetracycline, neomycin, penicillin and one chemotherapeutic agent namely 2-sulfanilamide pyrimidine. Results showed that 77 and 64 isolates were resistant to penicillin and 2-sulfanilamide pyrimidine and in addition, 32 isolates were resistant to tetracycline. Only 18 and 8 isolates were resistant to chloramphenicol and neomycin, respectively. It was also found that 19 isolates belonging to 6 genera or groups were sensitive towards all of the tested compounds.

Introduction

In recent years, the usage of low concentrations of antibiotics in animal feeds to promote growth and the greater emphasis by the medical professions on antibiotic therapy for treating a wide-spectrum of infectious bacteria is frequently considered. Previous studies proved that inadequately treated sewage and wastes are the main sources of antibiotic-resistant bacteria in the environment. For example, Mare (1968) studied the effect of five antibiotics on 582 different bacterial isolates. The author found that 57 isolates were drug-resistant Gram-negative bacteria. The high level of drug-resistance of some isolates is suggestive of R-factor mediated resistance, none of the 57 drug-resistant isolates transmitted resistance to the sensitive recipients. The detection of antibiotic-resistant bacteria in water resources was studied by many investigators. Feary *et al.*, (1972) reported that the incidence of antibiotic-resistance among total and fecal coliforms reached more than 40% in potable water samples from the tested spring and wells, while it was increased to 60% in streams and seawater samples. The presence of antibiotic resistant bacteria was found among standard plate count population of chlorinated drinking water from two districts in Cairo (El-Zanfaly *et al.*, 1987). Most strains appeared to be ampicillin resistant (89.7%) followed by sulfaguanidine resistant (78.1%) and streptomycin (56.9%). The multiple antibiotic resistant strains (MAR) represented 62.4 to 98% of the total isolates. Gram-positive rods were dominant among the MAR strains. Gram-negative fermentative-rods, gram-positive cocci and gram-negative nonfermentative rods represented the second, third and fourth group of the identified MAR strains.

In the present work, 101 bacterial isolates from underground water pumped in three water works in Cairo were examined for their ability to resist five commonly used drugs in Egypt.

Materials and Methods

Sixty-five ground water samples were taken from 13 wells under use in three water works (Mustrod, El-Marg and El-Maadi) in Cairo. Wells provide water treatment plants with water which pumped to the consumer after mixing with treated surface water at both Mostrod and El-Maadi, while it pumped directly through the distribution system at El-Marg. Pumping water is continuous and water samples obtained from special tap for sampling during operating hours. Water and associated microflora are representative of the aquifer itself. Water samples were aseptically collected from wells in sterile 1-litre bottles and analysed within 4 hrs. Aliquots of 10 mL were inoculated in test tubes containing 10 mL

MacConkey broth (double strength). Formation of acid and gas production after 48 hrs incubation at 37°C was assumed to be presumptive positive for the presence of coliforms. Then all positive tubes were inoculated in EC broth (Difco Manual, 1953) and incubated in a circulating water bath for 24 hrs at 44.5 ± 0.2°C. For obtaining bacterial isolates, MacConkey tubes which produced acid and gas at 37°C but not at 44.5°C (nonfecal types) were streaked on Eosin Methylene Blue agar (Levine, 1918) taking into consideration that selection basis are the morphology and color of colonies produced on the medium. The purified strains were examined for cell morphology, Gram stain, motility, catalase and oxidase reactions, indol formation, glucose oxidation or fermentation and classified into genera or groups according to the scheme given by LeChevallier *et al.*, (1980). The scheme includes four main classes of bacteria namely: Gram-negative, nonfermentative rods; Gram-negative, fermentative rods; Gram-positive cocci and finally Gram-positive rods.

Resistance to chloramphenicol, tetracycline hydrochloride, neomycin sulfate, penicillin G-sodium salt and 2-sulfanilamide pyrimidine was studied. Nutrient agar melted and cooled to 48–50°C was provided with a known volume of membrane filter sterilized solution of the antibacterial agent to give final concentration of 50 μg or International Unit (I.U.)/mL. Five plates containing different antibiotics or the chemotherapeutic sulfadiazine were streaked in parallel raws with test organisms and incubated at 37°C for 48 hrs. However, the control plates containing no antibiotic were inoculated consecutively to confirm successful inoculation of preceding plates. An organism was considered resistant to the agent in use only if it grew as well on the antibiotic plate as on the control plate.

Results

Bacteria other than fecal coliforms were isolated from the negative Eijkman test tubes by streaking on Eosin Methylene Blue agar plates. A total of 101 isolates representing flora from 13 wells in three water works were purified. The majority of isolates were found to belong to Gram-negative nonfermentative rods (47.5%) while only 8 strains (8.9%) were Gram-positive rods. The classified strains were tested for their resistance to four antibiotics (chloramphenicol, tetracycline, neomycin, and penicillin) as well as sulfanilamide pyrimidine. According to their resistance, bacterial isolates were divided into 3 groups (resistant to one antibiotic, resistant to more than one antibiotic, and the nonresistant strains). Results recorded in Table 1 sumarize the antibiotic resistance of the isolated strains to the individual compound. It becomes evident that the majority of the isolated strains (63%) are of multiple resistance ability towards two or more compounds (2R, 3R, 4R, and 5R) as appears in Table 1.

Table 1. Antibiotic resistance patterns for strains isolated for well water.

	Antibiotic Resistance						
Location	Cm	Tet	Neo	Pen	Sulf	No. Isolates	% of Individual Well Isolates
Mostrod	−	−	−	−	−	7	31.8
	−	−	−	+	−	3	13.6
	−	−	−	−	+	3	13.6
	+	−	−	+	−	1	4.5
	−	+	−	+	+	3	13.6
	+	+	−	+	+	3	13.6
	+	+	+	+	+	2	9.1
El-Maadi	−	−	−	−	−	4	6.3
	−	−	−	+	−	11	17.4
	−	+	−	−	−	1	1.6
	−	−	−	+	+	29	46.0
	+	−	−	+	+	3	4.7
	−	+	−	+	+	4	6.3
	+	+	−	−	+	1	1.6
	−	+	+	+	+	4	6.3
	+	+	−	+	+	4	6.3
	+	+	+	+	+	2	3.2
El-Marg	−	−	−	−	−	8	50.0
	−	+	−	+	−	2	12.5
	−	+	−	+	+	4	25.0
	+	+	−	+	+	2	12.5

− sensitive + resistant
Cm: Chloramphenicol Tet.: Tetracycline Neo.: Neomycin
Pen.: Penicillin Sulf: Sulfanilamide pyrimidine

For the sufficient diversity within such genera, it is possible to note that within a specific genus, some species (or strains) may be sensitive to the aforementioned antibiotics while others belonging to the same genus were resistant to one or more of these compounds (Table 2). Most strains (76.2%) appeared to be penicillin resistant. These were followed by sulfanilamide pyrimidine (63.3%), tetracycline (31.6%), chloramphenicol (17.8%), and finally neomycin (7.9%) (Table 1).

Results revealed that 19 strains belonging to 6 genera or groups were sensitive to all of the tested compounds,

Table 2. Antibiotic resistance pattern for some strains isolated from underground water.

Genera of Groups	No. of Isolates	Antibiotic Resistance				
		Cm	Tet	Neo	Pen	Sulf
Bacillus	2	−	−	−	+	−
	2	−	−	−	−	−
	1	−	−	−	−	+
Moraxella	2	−	−	−	+	−
	2	−	−	−	−	−
Pseudomonas	7	−	−	−	+	−
	4	−	−	−	−	−
Micrococcus	1	−	−	−	−	+
	1	−	+	−	−	−
	8	−	−	−	−	−

+: Resistant −: Sensitive
Cm: Chloramphenicol Tet: Tetracycline Neo: Neomycin
Sulf: Sulfanilamide pyrimidine
Pen: Penicillin

while the remaining isolates could resist one or more of them. Only 18 isolates belonging to 7 genera and one group were resistant to only one compound; tetracycline, penicillin, or sulfanilamide pyrimidine (Table 2).

The identities of the MAR phenotypes (64/101 strains) are presented in Table 3. Four major groups were identified. Generally, gram-negative nonfermentative rods constituted the largest portion of MAR phenotypes isolated from El-Maadi wells and represented 63.8% of the isolates. Gram-negative fermentative rods represented 33.3, 19.1 and 62.5% of the MAR identifed strains isolated from Mostrod, El-Maadi, and El-Marg wells, respectively (Table 3). Gram-positive cocci represented 55.5, 10.6 and 31.5% of the MAR isolates from Mostrod, El-Maadi, and El-Marg wells, respectively. Finally, Gram-positive rods represented 11.1 and 6.3% of the MAR isolates from Mostrod and El-Maadi, respectively.

Discussion

The frequent occurrence of sizable numbers of antibiotic resistant bacteria in drinking water has recently led to close examination and assessment of the significance of these organisms. It is known from the literature that several antibiotic resistant strains isolated from ground water samples belong to genera that may pose a hazard to public health (Lamka *et al.*, 1980; LeChevallier & Seildes, 1980). In the present study, the number of the isolates examined are representative of the diversity in the bacterial populations at the three different sites. It was found that among the isolated bacteria (101 isolates representing 13 examined wells located at three water works) the majority (63.3%) are of multiple resistance ability towards more than one of the commonly used drugs in Egypt (chloramphenicol, tetracycline, neomycin, penicillin and sulfanilamide). Of the total screened antibiotic resistant strains, the percentages of doubly, triply, quadraply and quintuply resistant strains are 31.7%, 14.9%, 12.9% and about 4%, respectively.

Mostrod plant is located 100 m away from Ismailia Canal on a heavy clay soil. A pond of wastewater exists near the wells. The depth of wells is 75–95 m. The soil at El-Marg area is clay and an open drain of high load of organic wastes exists 40 m away from the wells. The depth of the wells is ranged between 45 and 65 m. El-Maadi water works was constructed on a clay loamy soil, 100 m away from the eastern bank of the River Nile. Each of the tested wells is 55–65 m depth. So, differences in depth, hydrogeologic formation, sources of possible pollution are sufficient to separate the date according to the location from which the strains are identified. For the previous reasons one can expect that difference in MAR frequency in bacteria from wells sampled at the 3 sites must exist. Our data confirmed this expectation. The isolation of gram-negative nonfermentative rods from El-Maadi wells and not from wells at the other two locations may be due to the low numbers of isolates examined from both Mostrod and El-Marg wells.

A high incidence of certain patterns of resistance involving penicillin, sulfanilamide pyrimidine and tetracycline was observed. The patterns are believed to be a reflection of drugs frequently used in clinical therapy. In another study carried out by Armstrong *et al.* (1982) on bacterial isolates from wells in Oregon in the United States, they observed higher levels of resistance to carbenicillin, streptomycin, and sulfanilamide.

Table 3. Identities of MAR strains isolated from well water.

	Mostrod		El-Maadi		El-Marg	
Identity	No. of isolates	% of total MAR	No of isolates	% of total MAR	No. of isolates	% of total MAR
Gram-negative nonfermentative rods:		0		63.8		0
Moraxella spp.	0		10		0	
Flavobacterium spp.	0		1		0	
Pseudomonas/Alcaligenes	0		19		0	
Gram-negative fermentative rods:		33.33		19.1		62.5
Aeromonas	2		4		0	
Enterobacteriaceae	1		5		5	
Gram-positive cocci:		55.55		10.6		37.5
Micococcus spp.	1		1		0	
Staphylococci	4		4		3	
Gram-positive rods:		11.11		6.3		0
Bacillus spp.	1		3		0	
Total MAR	9		47		8	

The high incidence of MAR bacteria among standard plate count population of chlorinated River Nile water was mentioned before by El-Zanfaly *et al.* (1987). The authors reached the conclusion that MAR strains represented 62.4 to 98.0% of the total isolates. The use of disinfectants such as chlorine for MAR bacteria control was investigated (Armstrong *et al.*, 1982). They reported that disinfection of water was found to select for antibiotic resistant bacteria in the environment.

It was mentioned in the literature that the widespread concern that the proliferation of antibiotic resistant bacteria may hamper the efficacy of antibiotics in chemotherapy (Armstrong *et al.*, 1981). In addition, we add that any source of antibiotic resistant bacteria must be viewed with concern and consideration of the data on MAR bacteria should be made in future water quality deliberations and in regulating effluent quality discharges.

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THE EFFECT OF HOME CONSTRUCTION ON INDOOR RADON IN VIRGINIA AND MARYLAND

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The levels of indoor radon in approximately 500 homes located in two contiguous counties of northern Virginia and southern Maryland have been measured during four consecutive, three month seasonal intervals using alpha-track detectors. These two counties represent an area of about 700 square miles. Results from the winter period show that the indoor radon levels were about twice as high as anticipated. In some areas, more than 50% of the homes had winter indoor radon levels above 4 pCi/liter, the EPA's recommended action level. For the spring and fall periods, indoor radon levels showed a considerable drop with approximately 35% of the homes above 4 pCi/L. Summer values were even lower with approximately 25% of the homes above 4 pCi/L. Indoor radon can be related to the weather, but home construction demonstrably determines indoor radon levels.

Introduction

The natural radioactive decay series beginning with ^{238}U is the major source of natural radiation exposure in the environment. Uranium occurs widely in nature and locally occurring high levels of uranium are due in large part to its solubility in an oxidizing medium and its precipitation in a reducing medium (Levinson, 1980). The most significant uranium daughter is ^{226}Ra with a half-life of 1600 years. Radium's daughter, radon, is a radioactive noble gas and is widely dispersed in the environment. The dispersion of a gas that forms in the earth is only limited by that soil's permeability.

The dangers of the natural radioactive nuclide ^{222}Rn, and its progeny, notably ^{218}Po and ^{214}Po in air are well documented in the literature from studies of uranium miners (Steinhausler, 1988; Mercer, 1975; NIOSH, 1985). Studies have shown that inhalation of these nuclides in the environment can result in radiation doses which exceed by far all other doses from natural radiation sources (Cliff *et al.*, 1983; Steinhausler *et al.*, 1983).

Homes with high levels of indoor radon have recently been discovered in the northern part of the Appalachian Mountain system (Sextro *et al.*, 1987; George and Eng, 1983). It is becoming evident that several factors related to seasonal weather and home construction can combine to produce elevated indoor radon levels (Cohen and Gromicko, 1988; Alter and Oswald, 1987). State and county reports in Virginia and Maryland using measurements of only a few hours or a few days yielded results that suggested that approximately 10–30% of the homes would have radon levels above 4 pCi/L (Va Department of Health, 1987; Fairfax County Health Department, 1987).

To determine if elevated indoor radon levels are a problem in the central Appalachians, the Center of Applied Science at George Mason University is conducting an in-depth regional survey in Virginia and Maryland. This paper describes the indoor radon situation as it existed in the contiguous Fairfax County in northern Virginia and Montgomery County in southern Maryland.

Method

We report on our results for a winter interval, November 1986 through January 1987, a spring interval February through April 1987, a summer interval May through July 1987, and a fall interval August through October 1987. The number of homeowners participating in this study is continually increasing, and from the start of the study in the fall of 1986, approximately 1500 homes have now been entered into the study. The goal of the project is to report on 1% of the total area homes. Approximately 500 homes were measured. Of these, approximately 350 returned all four seasonal monitors. Each month about 100 new homes are added, and the present number of participants account for about 0.5% of the total homes in Fairfax County and 0.1% of the homes in Montgomery County.

Homeowners in Virginia and Maryland were informed of the testing program through announcements by area newspapers, radio and television stations. All homeowners who expressed interest were sent a package of literature about radon and about the testing program. All the homeowners who subsequently requested to join the study were accepted, probably because those with potentially low indoor radon (occupants who live more than one story above the ground) were self-screened from the study. Most joined because of newspaper coverage. The preliminary questionnaire showed that only about 10% of the test participants had a radon measurement before joining the study. A separate analysis of only these homes showed radon levels about 20% higher than the levels characteristic of the entire group reported upon in this paper. Exclusion of these homes from the data sets does not significantly alter the conclusions.

Participation in the test series requires that the homeowner participate in the entire four season testing period. Each radon measurement costs the homeowner $25.00. The homeowner answers a questionnaire at the start of the testing program which describes the construction of the home. At the end of each measurement interval, the homeowner answers another questionnaire about the monitor location and about the use of the home during the interval. The homeowners were allowed to place their radon monitors at any location in their home, but were advised that a basement is probably the location of the greatest radon concentration. About 90% of the homes had basements, and of these homes, about 90% of the homeowners placed the monitors in a basement location.

The conclusions are based on three month indoor radon measurements using alpha-track radon monitors provided by Terradex Corporation of Illinois. The measurement intervals start and end on particular days (Feb. 1, May 1, Aug. 1, and Nov. 1) so as to estimate the relationship between indoor radon and seasonal weather. After the exposure period, the indoor monitors are returned to Terradex for analysis.

Accuracy and Precision

The data reported in this paper are all from the interval during Round 4 of the U.S. Environmental Protection Agency Proficiency Program. Terradex alpha-track monitors of the type used in this study were examined by the Proficiency Program, and the results indicated that the monitors should carry a +/− 25% uncertainty at the 90% confidence level (Table 1). Terradex claims a +/− 25% uncertainty at one standard deviation for about 30–40 pCi/L-days.

To evaluate these estimates of precision, Terradex monitors were placed in the home of one of the authors (Mose) under reasonably constant "closed home" conditions for an entire year. A series of four, three month monitors were suspended on a wall in a basement room without ventilation, except for air exchange through a stairwell; a group of three was placed on a basement recessed shelf during the fall season (Table 2). The basement wall monitors yielded an average radon concentration of 5.7 +/− 0.8 pCi/L (2 standard deviations). Considering that the measurements were made during different seasons, the standard deviation is surprisingly small. The fall season basement shelf monitors yielded an average radon concentration of 5.1 +/− 0.6 pCi/L (2 S.D.). Perhaps the slightly lower measurements for the recessed shelf monitors are due to decreased circulation, but the difference between the open wall and recessed shelf monitors is actually quite small. These estimates of uncertainty from the Table 1 data correspond to about 10–15% of the average radon measurements, and are reasonably similar to the manufacturer and the EPA estimates of uncertainty.

In the following discussions, we regard +/− 25% to be a conservative estimate of uncertainty. We have

Table 1. U. S. Environmental Protection Agency, round 4 results.

Ratio of Measured Values To EPA Target Values	Number of Measurements	Range of Measured To Target Ratios	Percentage of Tests
0.5 to 0.599	1	0.9 to 1.099 (1 +/−10%)	44%
0.6 to 0.699	9	0.8 to 1.199 (1 +/−20%)	74%
0.7 to 0.799	51	0.7 to 1.299 (1 +/−30%)	95%
0.8 to 0.899	53	0.6 to 1.399 (1 +/−40%)	99%
0.9 to 0.999	64	0.5 to 1.499 (1 +/−50%)	100%
1.0 to 1.099	49		
1.1 to 1.199	25		
1.2 to 1.299	4		
1.3 to 1.399	1		
1.4 to 1.499	2		

Note: A compilation of the EPA data can be obtained from Tech/Ops Landauer, 2 Science Road, Glenwood, Illinois 60425.

Table 2. Study of radon monitor uncertainty.

Winter	(11/86–1/87)	Basement Wall 5.3 pCi/L
Spring	(2/87–4/87)	Basement Wall 5.6 pCi/L
Summer	(5/87–7/87)	Basement Wall 5.7 pCi/L
Fall	(8/87–10/87)	Basement Wall 6.3 pCi/L
		Average = 5.7 ± 0.8 pCi/L (2 S.D.)
Fall	(8/87–10/87)	Basement Shelf 5.3 pCi/L
Fall	(8/87–10/87)	Basement Shelf 4.8 pCi/L
Fall	(8/87–10/87)	Basement Shelf 4.8 pCi/L
		Average = 5.1 ± 0.6 pCi/L (2 S.D.)

seen no evidence that suggests that these measurements are analytically biased towards too-high or too-low results. These considerations lead us to believe that individual homeowners may have obtained some measurements that were significantly higher or lower than their actual concentrations, and for that reason we advise homeowners to measure indoor radon over several seasons. The random nature of the possible inaccuracies lead us to believe that the compilations obtained for large groups of homes such as are presented later in this paper are reasonably correct. We are encouraged in this belief by noting that when the geology and weather in the contiguous Fairfax and Montgomery Counties are studied separately, their radon characteristics are similar.

Discussion

The indoor radon situation in Fairfax County in northern Virginia is similar to the situation in Montgomery County in southern Maryland because both areas have the same geological provinces containing the same geological units. Almost all of the homes are built on soil derived from the rocks. For this reason, and because both areas have essentially the same weather and the same spectrum of home construction, the indoor radon statistics noted in the following discussion are similar for both counties. Since most of Virginia and Maryland are likewise similar, the results are thought to be representative of the central Appalachian states.

The three Appalachian provinces that comprise the terrane of northern Virginia, (Froelich, 1985), southern Maryland, (Weaver, 1964), and the adjacent District of Columbia, (Johnson, 1964), are the Coastal Plain, the Culpeper Basin, and the Piedmont. The Coastal Plain Province is located along the eastern edge of the study area. It consists of poorly cemented clastic sedimentary strata, mostly layers of clay and sand, that were deposited during the opening of the modern Atlantic Ocean. These deposits were formed between about 130 million years ago and the present. The western margin of the study area is part of the Culpeper Basin, a fault-bounded valley containing terrestrial clastic rocks (siltstone, sandstone, conglomerate) along with extrusive and intrusive igneous rocks (diabase) that were all deposited during the Mesozoic Era, about 190–150 million years ago. The Piedmont Province extends from Maine to Georgia, and rock units of this province underlie most of the central part of the Maryland and Virginia study area. These rock units are composed of metamorphic and igneous rocks that were formed when the Appalachian Mountains were created during the Paleozoic Era, about 600–300 million years ago.

Approximately 350 homes in the study have been measured for indoor radon during all four seasons. Table 3 shows that in most homes, indoor radon is at its maximum concentration during the winter. This is presumably because homes are more often sealed for protection against the weather in the winter. Under these conditions, outside air with its relatively low radon concentration cannot easily enter to dilute the radon which has entered through soil-facing walls and floors.

The results of the testing intervals are shown in Table 4. Perhaps the most important observation is that winter radon concentrations were about 50% greater than summer concentrations, both in the basements and on the first floors. Spring and fall tend to have intermediate radon concentrations and therefore would be the best times to estimate the annual radon concentration with a single three month testing interval.

The results of our study over approximately 700 square miles were also correlated with home construction. Table 5 is a comparison of basement radon concentration with the composition of the basement walls. The integrity of basement wall construction is important because soil radon is generally about 100 to 1000 times more concentrated than indoor radon, so even small cracks and porous areas can facilitate the passage of radon into the basement. Table 5 shows that basement rooms with concrete block walls tend to have greater radon concentrations during the winter than basement rooms with poured concrete walls. We suspect that this is because the concrete block walls more easily develop cracks and porous areas.

More important differences concern the radon concentration on the first floor above ground level. In general, first floor radon concentrations are usually less

Table 3. Season with the highest indoor radon concentration.

Radon in Fairfax County		Radon in Montgomery County	
Season	% of Homes	Season	% of Homes
Winter	49%	Winter	63%
Spring	19%	Spring	11%
Summer	9%	Summer	0%
Fall	23%	Fall	26%
299 Homes Provided Four Seasonal Measurements		46 Homes Provided Four Seasonal Measurements	

Table 4. Seasonal summary of indoor radon levels

Seasonal Radon Concentrations in Fairfax County (Basement Data)

Season	Median pCi/L Rn	% Over 4 pCi/L	% Over 10 pCi/L	Number
Winter	3.7 pCi/l	44%	8%	420 Homes
Spring	2.9 pCi/l	32%	6%	480 Homes
Summer	2.5 pCi/l	22%	2%	448 Homes
Fall	3.2 pCi/l	37%	2%	387 Homes

Seasonal Radon Concentrations in Fairfax County (First Floor Data)

Season	Median pCi/L Rn	% Over 4 pCi/L	% Over 10 pCi/L	Number
Winter	2.5	27%	3%	70 Homes
Spring	1.6	16%	4%	75 Homes
Summer	1.5	11%	1%	79 Homes
Fall	1.9	20%	0%	60 Homes

Seasonal Radon Concentrations in Montgomery County (Basement Data)

Season	Median pCi/L Rn	% Over 4 pCi/L	% Over 10 pCi/L	Number
Winter	4.4 pCi/l	52%	18%	65 Homes
Spring	3.4 pCi/l	42%	12%	67 Homes
Summer	2.6 pCi/l	30%	3%	63 Homes
Fall	3.3 pCi/l	42%	11%	45 Homes

Seasonal Radon Concentrations in Montgomery County (First Floor Data)

Season	Median pCi/L Rn	% Over 4 pCi/L	% Over 10 pCi/L	Number
Winter	3.2	33%	17%	12 Homes
Spring	1.8	17%	8%	12 Homes
Summer	2.6	28%	0%	18 Homes
Fall	3.3	33%	0%	12 Homes

than the basement concentrations (see Table 4). It is thought that the greater radon concentration in basements is a result of the site of radon origin. Radon enters the home primarily from soil immediately adjacent to basement floors and walls. Subsequently, radon enters the above ground floors from air circulation by the home heating or cooling system, and by diffusion. Table 6 shows that first floor rooms above concrete block basements tend to have greater radon concentrations that first floor rooms above a basement with poured

Table 5. Comparison of basement indoor radon and basement wall construction.

Fairfax County, Basement Data

Wall Construction	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Concrete Block	Winter	3.8	43%	8%	282 Homes
	Spring	3.0	35%	6%	309 Homes
	Summer	2.5	23%	2%	288 Homes
	Fall	3.2	38%	2%	246 Homes
Poured Concrete	Winter	3.3	38%	7%	129 Homes
	Spring	2.7	27%	6%	154 Homes
	Summer	2.2	19%	1%	144 Homes
	Fall	3.1	33%	3%	120 Homes

Montgomery County, Basement Data

Wall Construction	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Concrete Block	Winter	4.5	53%	19%	47 Homes
	Spring	3.2	39%	15%	46 Homes
	Summer	2.5	24%	4%	45 Homes
	Fall	3.2	45%	10%	31 Homes
Poured Concrete	Winter	4.6	62%	15%	13 Homes
	Spring	5.0	64%	7%	14 Homes
	Summer	3.4	43%	0%	14 Homes
	Fall	3.5	33%	17%	12 Homes

Table 6. Comparison of first floor radon and basement wall construction.

Fairfax County, Floor Above Ground Level Data

Wall Construction	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Concrete Block Basement Walls	Winter	3.1	36%	6%	36 Homes
	Spring	2.4	19%	3%	32 Homes
	Summer	2.4	22%	3%	37 Homes
	Fall	2.6	24%	0%	29 Homes
Homes That Have No Basement	Winter	2.2	23%	0%	22 Homes
	Spring	1.4	14%	0%	29 Homes
	Summer	1.0	4%	0%	28 Homes
	Fall	1.8	17%	0%	23 Homes
Poured Concrete Basement Walls	Winter	2.3	11%	0%	9 Homes
	Spring	1.3	9%	9%	11 Homes
	Summer	1.5	0%	0%	11 Homes
	Fall	1.5	17%	0%	6 Homes

Montgomery County, Floor Above Ground Level

Wall Construction	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Concrete Block Basement Walls	Winter	8.8	60%	40%	5 Homes
	Spring	5.0	50%	25%	4 Homes
	Summer	4.1	30%	0%	10 Homes
	Fall	3.6	43%	0%	7 Homes
Homes That Have No Basement	Winter	2.3	25%	0%	4 Homes
	Spring	1.8	0%	0%	4 Homes
	Summer	1.7	0%	0%	5 Homes
	Fall	—	—	—	2 Homes
Poured Concrete	Winter	2.2	0%	0%	3 Homes
	Spring	1.7	0%	0%	4 Homes
	Summer	2.9	50%	0%	4 Homes
	Fall	3.4	33%	0%	3 Homes

Table 7. Comparison of basement indoor radon and home heating systems.

Fairfax County, Basement Data

Type of Heating	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Combustion of Oil or Gas	Winter	3.4	45%	8%	209 Homes
	Spring	2.9	33%	5%	232 Homes
	Summer	2.3	19%	0%	220 Homes
	Fall	3.2	33%	0%	203 Homes
Electrical Heat	Winter	4.0	50%	11%	127 Homes
	Spring	3.0	37%	8%	152 Homes
	Summer	2.8	29%	4%	143 Homes
	Fall	5.2	49%	6%	113 Homes

Montgomery County, Basement Data

Type of Heating	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Combustion of Oil or Gas	Winter	3.7	48%	15%	46 Homes
	Spring	3.5	43%	14%	44 Homes
	Summer	2.7	37%	5%	41 Homes
	Fall	4.0	48%	10%	31 Homes
Electrical Heat	Winter	5.7	100%	33%	3 Homes
	Spring	6.1	75%	25%	4 Homes
	Summer	4.2	50%	0%	4 Homes
	Fall	—	—	—	1 Home

concrete walls. In homes without any basement, the first floor radon concentrations are similar to concentrations in homes with poured concrete basements. Apparently, the reduced radon characteristics of basements with poured concrete walls has a significant effect on the radon circulation to higher levels in a home.

The type of heating system in a home also seems to control to a measurable degree the concentration of indoor radon. Homes with electrical heating systems, which are mostly homes with heat pumps, tend to have greater radon concentrations than homes with conbustion heating systems, mainly oil and gas, in the basement (Table 7) and on the first floor (Table 8). The reason for this difference may involve the air circulation patterns during cold and warm intervals. Rising hot air escaping out of the top of a home is presumably active for any heating system in the winter. However, homes with combustion heating systems presumably create a greater partial vacuum in the home as hot air escapes through the chimney of the heating system. This is probably important because the "chimney effect" is absent in electrical heating system homes. The lower indoor radon concentrations during the winter associated with combustion heating systems compared to homes with electrical heating systems may occur because a greater amount of out-of-doors air is drawn into the combustion system homes due to the "chimney effect."

During the summer, home heating systems are rarely used in the study area, and one might predict that the indoor radon signature of homes with combustion heating systems would be the same as that of homes with electrical systems. However, the data show that homes with electrical heating systems tend to have greater radon concentrations in the summer in both the basement (Table 7) and on the first floor (Table 8). We suspect that because most of the electrical heating systems are actually heat pumps, these homes are often closed up to utilize the convenient whole-home cooling function of the heat pump. As a result, summer radon in homes with heat pumps show greater radon concentrations than in homes with combustion heating systems.

One advantage of identifying factors that can contribute to elevated indoor radon is that the factors can be combined. Tables 5 and 7 showed that homes with concrete block basement walls and an electrical heating system tend to have elevated indoor radon. By combining these factors (Tables 9 and 10), it can be seen that homes with both electrical heating systems and concrete block basement walls tend to have higher indoor radon concentrations than with only one contributory factor. Our study of other factors is not complete, but we expect to find useful correlations between indoor radon and the age of the home, the amount of insulation and weatherization, the size of the home and the presence of visible cracks in the basement floor and walls. Taken together, these factors could facilitate the determination of radon potential for a home, in situations where a meaningful (i.e., long-term) estimate of the annual radon concentration is not available.

Conclusions

The problem of indoor radon and its progeny has been well documented. Many studies of the indoor radon problem have concentrated on large geographical areas with a random selection of test sites. The present

Table 8. Comparison of first floor indoor radon and home heating systems.

Fairfax County, Floor Above Ground Level Data

Type of Heating	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Combustion of Oil or Gas	Winter	2.6	23%	0%	43 Homes
	Spring	1.6	12%	2%	50 Homes
	Summer	1.5	8%	2%	51 Homes
	Fall	1.7	12%	0%	51 Homes
Electrical Heat	Winter	2.1	28%	0%	18 Homes
	Spring	1.5	23%	0%	13 Homes
	Summer	1.6	19%	0%	16 Homes
	Fall	3.4	33%	0%	9 Homes

Montgomery County, Floor Above Ground Level Data

Type of Heating	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
Combustion of Oil or Gas	Winter	3.2	30%	10%	10 Homes
	Spring	1.8	22%	11%	9 Homes
	Summer	2.0	27%	0%	15 Homes
	Fall	2.5	33%	0%	9 Homes
Electrical Heat	Winter	—	—	—	1 Home
	Spring	—	—	—	0 Homes
	Summer	—	—	—	0 Homes
	Fall	—	—	—	0 Homes

Table 9. Correlation between basement wall construction and indoor radon in homes with electrical heating systems.

Wall Construction	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
		Fairfax County, Basement Data			
Concrete Block	Winter	4.7	54%	15%	59 Homes
	Spring	3.8	48%	10%	67 Homes
	Summer	3.4	37%	6%	63 Homes
	Fall	4.4	52%	7%	46 Homes
Poured Concrete	Winter	3.7	45%	7%	67 Homes
	Spring	2.9	29%	6%	84 Homes
	Summer	2.6	24%	3%	79 Homes
	Fall	3.6	45%	5%	64 Homes
		Montgomery County, Basement Data			
Concrete Block	Winter	—	—	—	1 Home
	Spring	—	—	—	2 Homes
	Summer	—	—	—	2 Homes
	Fall	—	—	—	1 Home
Poured Concrete	Winter	—	—	—	1 Home
	Spring	—	—	—	1 Home
	Summer	—	—	—	1 Home
	Fall	—	—	—	0 Homes

study, to overcome the radomness of widely varied measurements, concentrated on achieving results from 1% of the homes in two contiguous counties. Indoor radon values are a serious problem in northern Virginia and southern Maryland. Observed radon values in the present study have been correlated with the seasonal weather, but home construction is also an important factor.

Winter measurements were higher than any other season due to the decreased influx of outside air in the colder season. Basements with concrete block walls tend to have higher radon concentrations than base-

Table 10. Correlation between home heating systems and indoor radon in homes with concrete block basement walls.

Type of Heating	Season	Median Rn pCi/L	% Over 4 pCi/L	% Over 10 pCi/L	Number
		Fairfax County, Basement Data			
Combustion of Oil or Gas	Winter	3.6	43%	8%	159 Homes
	Spring	3.0	33%	5%	178 Homes
	Summer	2.4	20%	0%	168 Homes
	Fall	3.3	37%	0%	152 Homes
Electrical Heat	Winter	4.7	54%	15%	59 Homes
	Spring	3.8	48%	10%	67 Homes
	Summer	3.4	37%	6%	63 Homes
	Fall	4.4	52%	7%	46 Homes
		Montgomery County, Basement Data			
Combustion of Oil or Gas	Winter	4.5	53%	18%	34 Homes
	Spring	3.4	45%	18%	33 Homes
	Summer	2.6	29%	6%	31 Homes
	Fall	3.9	50%	9%	22 Homes
Electrical Heat	Winter	—	—	—	1 Home
	Spring	—	—	—	2 Homes
	Summer	—	—	—	2 Homes
	Fall	—	—	—	1 Home

ments with poured concrete walls, presumably because concrete block is more likely to be permeable and to develop fractures. Superimposed on this variation is the observation that basements tend to have greater radon concentrations than first floor rooms, and first floor rooms tend to have more radon if the home has a concrete block basement. Homes with electrical heating systems tend to have higher indoor radon than homes with combustion system heating. It is obvious that the owners of presently occupied homes can be alerted to a potential indoor radon problem if the effects of climate is reasonably well understood, but an analysis of home construction is an equally important consideration.

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HEAVY METAL CONCENTRATIONS ALONG THE LOUISIANA COASTAL ZONE

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Cores were taken from seven locations in southern Louisiana and analyzed for concentrations of heavy metals. Sedimentation rates for the locations were determined using the ^{137}Cs dating technique. Correlations of metals with depth were calculated using absolute, aluminum normalized, and iron normalized concentrations. Correlations indicated recent increases at several sites (Lake Palourde, Manchac Pass, and Wax Lake Outlet) for several metals (Pb, Cd, Cr, Ni, Zn) when profiles were normalized to aluminum. Metal profiles from rapidly-accreting areas (Atchafalaya and Four League Bay) did not show historical increases comparable to areas accreting less rapidly (e.g., Wax Lake Outlet, Manchac Pass, and Lake Palourde).

Introduction

High concentrations of toxic heavy metals in the sediments of coastal and estuarine ecosystems have been widely documented (Bruland *et al.*, 1974; Butterworth *et al.*, 1972; Grieg and McGrath, 1977; Schell and Nevissi, 1977). These coastal areas are often centers of population and industry in addition to serving as depositional regions for metal-laden rivers. The Gulf Coast of the United States is one such area with a large development of oil exploration, refining, and petrochemical industries over the past 50 years. In addition, the Mississippi River carries and deposits large quantities of toxic heavy metals into this ecosystem, mostly in particulate form (Presley *et al.*, 1980).

The Louisiana coastal region includes the largest coastal wetland ecosystem in the United States. Many researchers (Sloey *et al.*, 1978; Simpson *et al.*, 1983) have suggested that wetland systems act as water "purifiers," removing toxic material such as heavy metals from contaminated water. At present, the Louisiana Gulf Coast wetland system is undergoing severe deterioration. Large areas of land-loss are resulting from a complex interaction of eustatic sea-level rise, sediment deprivation from the leveed Mississippi River, and other factors (Salinas *et al.*, 1986). There is concern over these processes because metal input into the Gulf of Mexico is partially dependent on scavenging processes which occur in Louisiana's coastal wetlands.

At present, there is inadequate information on metal concentrations in Louisiana's coastal environment. Presley *et al.* (1980) have documented historical Zn, Pb, and Cd increases in the sediments of the rapidly-accreting modern Mississippi delta. Presley has hypothesized that historical increases of other metals in the rapidly accreting delta are being masked by the large quantities of deposited sediment. It is unclear if sediments of Louisiana wetland areas which are accreting more slowly will reflect recent increases of a wider group of metals. Little or no data exists which establishes metal concentrations in other Louisiana coastal areas, particularly in areas which are accreting slowly.

The aim of this research is to establish concentrations for toxic heavy metals in Louisiana's coastal zone. Differences in metal profiles between rapidly and slowly accreting regions will be discussed in light of ^{137}Cs-derived sedimentation rates from these areas. This data is important in identifying areas of heavy metal input into the Gulf and in understanding the effect of changes in sedimentation on metal profiles.

Methods and Materials

Sample collection

Multiple cores were taken from each of the sites in Fig. 1. Core samples from Lake Palourde, Four League Bay and Atchafalaya Bay were taken in bottom sedi-

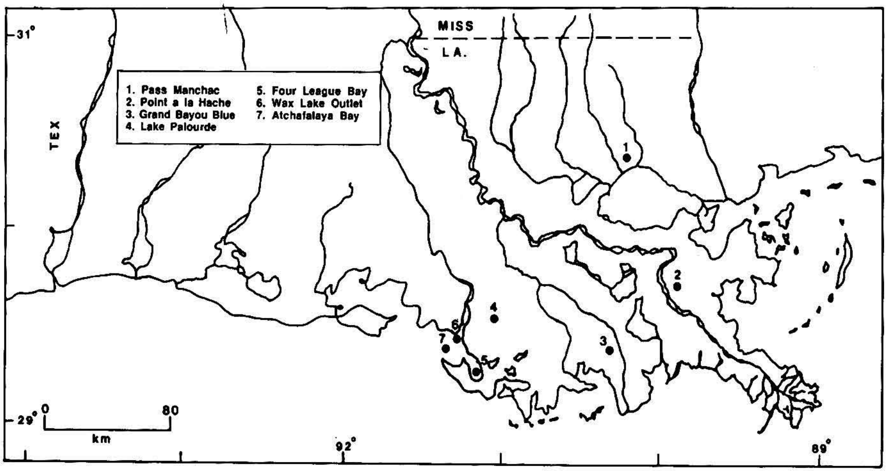

Fig. 1. Locations sampled in southern Louisiana.

ment. Cores from the remaining sites were taken in the marsh. Cores were taken by twisting a thin aluminum cylinder, 15 cm in diameter and 50 cm in length, into the sediment surface. Compaction from sampling ranged from 2 to 3%. Cores were sectioned into 3 cm intervals.

Metal analysis

Core sections were dried (100°C), ground, and thoroughly mixed prior to analysis. Sediment samples were digested using a nitric-perchloric acid digestion procedure (Standard Methods, 1975). The digested samples were diluted to volume and analyzed using Inductively Coupled Argon Plasma spectrophotometry (ICAP). The Zn channel was not available for analyzing Atchafalaya Bay or Four League Bay sediment. Data were compiled and statistical analyses performed using SAS (Statistical Analysis System, Cary, NC) on an IBM PC-AT.

Sedimentation rates

Vertical accretion was determined from the ^{137}Cs distribution in the profile using the method of DeLaune *et al.* (1978). ^{137}Cs is a man-made fission isotope that first entered the environment in the early 1950s as a result of fallout from atomic testing. Peak fallout occurred in 1963 (Pennington *et al.*, 1973). The 1963 peak was used to calculate sedimentation rates. ^{137}Cs activity in each section was determined by gamma counting of the oven-dried sample, using a lithium-drifted germanium detector.

Results and Discussion

Surface and depth-integrated metals data from each of the seven sites along with ^{137}Cs sedimentation rates are presented in Table 1. Metal concentrations below the surface section are presented as averages over the depth of ^{137}Cs penetration. Because of the comparatively high sedimentation rates of the Louisiana Gulf Coast region cores of this length represent a 40–50 year record. Sample ^{137}Cs profiles from a rapidly-accreting bay site and a marsh site are presented in Fig. 2. The higher sedimentation rate of the bay site is obvious. Input of smaller amounts of reworked ^{137}Cs-containing sediment in the bay after 1963 accounts for the relatively high ^{137}Cs baseline since the 1963 peak.

Correlation coefficients for the metals with sediment depth were calculated for the sites. These correlations will determine any linear increase or decrease in metal concentration over the years penetrated by this core. Two normalization methods, one using aluminum concentration ratios {[metal]/[Al]} and one using iron concentration ratios {[metal]/[Fe]}, were used to adjust metal profiles for correlation coefficient calculations. Correlation coefficients for these ratios with depth are also given in Table 2. The use of ratios between trace metals and conservative elements (e.g., Fe or Al) has been used as a method of removing variability of sediment parameters between cores at different sites (Kemp *et al.*, 1976; Bruland *et al.*, 1974; White and Tittlebaum, 1984).

Correlations of metals with depth differed significantly with the method used to normalize metal concentrations. Correlations based on absolute concentrations in the cores indicated recent increases (negative correlation) in certain metals at several sites (Atchafalaya Bay, Grand Bayou Blue, and Lake Palourde). At two of these sites, Atchafalaya Bay and Grand Bayou Blue, aluminum and iron normalization changed the correlation pattern significantly. At other sites (e.g., Manchac Pass, Point La Hache and Wax Lake Outlet)

Table 1. Concentrations of heavy metals, iron, and aluminum along the Louisiana Coastal Zone.

	%		µg/g						
depth (cm)	Fe	Al	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Location: **Atchafalaya Bay** ($n = 4$) Sedimentation rate: >2.0 cm/yr									
0–3	1.2 ± 0.31	1.8 ± 0.50	2.6 ± 0.62	17.2 ± 7.4	8.0 ± 2.3	14.7 ± 3.3	59.1 ± 16.7	160.7 ± 29.9	—
3–30 (Avg.)	1.1 ± 0.20	1.6 ± 0.30	2.3 ± 0.50	18.4 ± 3.5	7.4 ± 1.0	13.6 ± 1.8	46.9 ± 9.5	138.8 ± 27.8	—
Location: **Four League Bay** ($n = 6$) Sedimentation rate: >1.5 cm/yr									
0–3	1.9 ± 0.80	3.9 ± 1.0	4.4 ± 1.0	27.1 ± 4.4	15.5 ± 3.8	26.2 ± 3.5	114 ± 32	320 ± 96	—
3–51 (Avg.)	2.3 ± 0.30	3.9 ± 0.6	4.8 ± 0.9	31.7 ± 4.9	16.8 ± 2.6	28.7 ± 4.6	118 ± 19	330 ± 54	—
Location: **Grand Bayou Blue** ($n = 5$) Sedimentation rate: 0.86 ± 0.15 cm/yr									
0–3	1.1 ± 0.13	2.6 ± 0.3	4.4 ± 0.6	35.1 ± 6.4	17.1 ± 4.0	19.0 ± 2.5	111.4 ± 21.0	74.0 ± 13	54 ± 13
3–51 (Avg.)	1.0 ± 0.33	2.7 ± 0.72	4.5 ± 0.8	35.4 ± 9.4	17.1 ± 2.6	19.2 ± 4.6	112 ± 23	75 ± 15	51.5 ± 15
Location: **Lake Palourde** ($n = 3$) Sedimentation rate: 1.1 cm/yr									
0–3	3.3 ± 0.3	5.5 ± 0.3	7.6 ± 0.7	65.7 ± 5.9	28.1 ± 1.4	40.8 ± 4.2	159 ± 9.0	106 ± 9	133 ± 13
3–51 (Avg.)	3.5 ± 0.3	5.7 ± 0.5	8.2 ± 0.7	61.1 ± 5.6	30.3 ± 4.1	41.6 ± 4.2	162 ± 14	112 ± 9.3	114 ± 9
Location: **Manchac Pass** ($n = 2$) Sedimentation rate: 1.07 cm/yr									
0–3	3.2 ± 1.1	5.5 ± 1.4	9.7 ± 1.7	54.2 ± 4.1	24.7 ± 4.3	39 ± 10	205 ± 43	135 ± 37	100 ± 29
3–42 (Avg.)	2.0 ± 0.20	5.1 ± 0.50	7.6 ± 0.40	51.1 ± 5.2	22.9 ± 1.5	30.3 ± 2.7	195 ± 15	125 ± 8.6	83 ± 4
Location: **Point La Hache** ($n = 5$); Sedimentation rate: 0.73 cm/yr									
0–3	2.0 ± 0.3	3.6 ± 0.6	6.3 ± 0.7	47.3 ± 6.7	20.2 ± 1.5	28.7 ± 2.5	141 ± 21	91 ± 15	84 ± 11
3–42 (Avg.)	2.1 ± 0.3	4.1 ± 0.6	6.9 ± 0.6	47.8 ± 4.6	21.9 ± 3.4	29.4 ± 3.4	151 ± 20	103 ± 13	76 ± 9
Location: **Wax Lake Outlet** ($n = 4$) Sedimentation rate: 1.4 ± 0.40 cm/yr									
0–3	3.2 ± 0.4	5.1 ± 0.9	7.9 ± 1.1	44.8 ± 19	26.4 ± 0.9	41.3 ± 6.6	156 ± 25	106 ± 18	111 ± 29
3–42 (Avg.)	2.9 ± 0.1	6.1 ± 0.7	8.2 ± 0.5	36.3 ± 5	29.2 ± 1.6	43.0 ± 3.1	193 ± 20	128 ± 15	110 ± 7

significant correlations emerged only after normalization with aluminum or iron. Similar changes in the correlations occurred at every site except Lake Palourde. There was little agreement between the use of iron or aluminum as a normalizing agent. The use of these conservative elements assumes a constant flux to the sediments. Iron, however, can post-depositionally migrate in wetland soils and therefore its use as a "constant" element may not be applicable to this system.

Metal profiles in rapidly-accreting areas (e.g., Atchafalaya and Four League Bay) were less likely to show significant increases (normalized) than areas that are accreting less rapidly (e.g., Wax Lake Outlet, Manchac Pass, and Lake Palourde). Examination of the data from two of the sites, Wax Lake Outlet and nearby Atchafalaya Bay, representing different sedimentation rates demonstrates that concentrations of metals are generally an order of magnitude higher in the area of lower sedimentation (Wax Lake Outlet). This supports the idea that historical increases of metals may be masked in areas of high sedimentation. Metal profiles from areas of high sedimentation in the region (e.g., bay bottoms such as Atchafalaya Bay) are diluted with larger amounts of sediments. Any changes in metal input which may be reflected in the sediment profile are diluted out by the larger quantity of incoming sediment.

It is important to note that metal profiles of this type cannot distinguish between local and regional inputs of toxic metals. Particulate input from Mississippi River sediment is an example of a regional input while a point source of metal pollution is an example of a local input. In rapidly-accreting areas metal input is likely dominated by regional input and smaller local point sources input may have little effect on metal profiles.

More research is necessary to determine the full impact of heavy metal input on Louisiana's Gulf Coast region. The sediments of this area could serve as a large reservoir of toxic metals subject to remobilization and resuspension processes. In addition, a deteriorating wetland system may serve as an inefficient buffer for

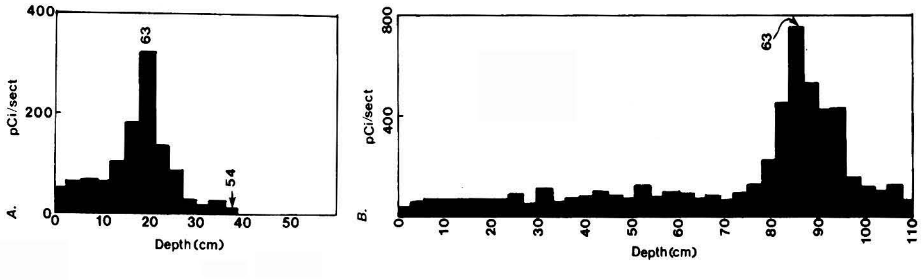

Fig. 2. ^{137}Cs profiles from a marsh (A.) and rapidly accreting bay bottom (B.) in southern Louisiana.

Table 2. Correlations of heavy metals, iron, and aluminum with depth from cores taken in southern Louisiana.

Location	Sedimentation Rate (cm/yr)	Negative Correlation With Depth ($P \leq 0.05$)	Positive Correlation With Depth ($P \leq 0.05$)
Atchafalaya Bay	>2.0	Al, Fe, Ni, Pb, Sb[a]	—
(bottom sediment)		(–)[b]	(Cr, Ni)
		[Cd, Pb][c]	[Cr]
Four League Bay	>1.5	—	Fe, Cr, Ni, Pb, Sb
(bottom sediment)		(–)	(Fe, Ni, Pb, Sb)
		[–]	[–]
Grand Bayou Blue	0.86 ± 0.15	Fe, Cd, Cu, Zn	–
(salt marsh)		(–)	(–)
		[–]	[Al, Cd, Cr, Cu, Ni, Pb, Sb]
Lake Palourde	1.11	Cr, Ni, Pb, Zn	–
(bottom sediment)		(Cr, Pb, Zn)	(–)
		[Cr, Ni, Pb, Zn]	[–]
Manchac Pass	1.07	–	–
(fresh marsh)		(Fe, Cd, Ni)	(–)
		[–]	[Al, Cr, Cu, Ni, Pb, Sb]
Point La Hache	0.73	–	Al, Cd, Cu, Sb
(brackish marsh)		(Cr, Pb)	(–)
		[–]	[–]
Wax Lake Outlet	1.4 ± 0.40	–	Al, Pb, Sb
(fresh marsh)		(Fe, Cd, Cu, Ni, Zn)	(–)
		[–]	[Al, Cd, Cu, Ni, Pb, Sb]

[a] Correlation based on absolute metals concentrations.
[b] Correlation based on aluminum normalized metals concentrations.
[c] Correlation based on iron normalized metals concentrations.

metal input into coastal fisheries. These data should provide a base for monitoring future metal inputs into this region.

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AN APPRAISAL OF ATMOSPHERIC POLLUTION BY ALUMINIUM FUMES EMANATING FROM SMELTER WORKS IN WESTERN NORWAY

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Material including birch leaves, twigs, soil, and grass was collected from various sites around the Øvre Årdal aluminium smelter in Western Norway. Samples were analysed by means of electron probe X-ray microanalysis to ascertain the relative amounts of deposited aluminium. The prevailing wind together with the steep sided valleys controlled the fate of the pollutant, and material was found to sediment out from the atmosphere in lowland sites particularly to the north-east, north-west, and east of the industrial complex; most deposition occurred within several kilometers of the plant. Some effects of aluminium on plant surfaces are discussed.

Introduction

Aluminium, an important metal, constitutes approximately 8% of the earth's crust. It was first extracted by a chemical method in 1825 by Ørsted, as reported in the Årdal og Sunndal Verk report (1971). Later, work by Wøhler and Sainte-Claire DeVille resulted in the production of aluminium on a commercial scale in 1855.

In 1886, Héroult and Hall independently invented a process for producing aluminium by the electrolysis of alumina (aluminium oxide) dissolved in molten cryolite (Na_3AlF_6); subsequently, smelters were developed in France, Germany, and the USA and, by 1900 world production of aluminium was in excess of 7,000 tonnes per annum.

It was in 1908 that the first Norwegian smelter was initiated at Stongfjord, Sunnfjord and, in 1909 one was also developed near Kristiansand. In 1947 A/S Årdal og Sunndal Verk were established and developed from plants initiated by the Germans during the last War. Energy is efficiently provided by cables from the major power stations (hydro-electric) situated at Fortun and Tyin. The plants (Figs. 1 and 2) are located in Western Norway to the south of the mountainous Jotunheimen area, with its important National Park (Fig. 2) and are located in the towns of Årdalstangen and Øvre Årdal (Figs. 2 and 3). Årdalstangen possesses excellent docking facilities at the northern end of the Årdalsfjord; this fjord joins the Sognefjord, q.v., and thence leads to the sea. The works at Årdalstangen receives alumina from ships; in addition the plant at Årdalstangen also produces the electrode paste and prebaked carbon for anodes and cathodes for the pots employed in the production process. Material is then transferred to the smelting and other facilities of Øvre Årdal (Fig. 4) some 15 km to the north. The plants possess techniques for the removal of pollutants (such as aluminium fume and fluorine) from emissions emanating from the smelting plant.

According to the A/S Årdal og Sunndal Verk report (1971), in 1970 the production capacity exceeded 500,000 tonnes which made Norway the fifth largest producer of aluminium in the world.

The group has a number of major smelters including Årdal, Sunndal Verk (Sunndalsøra), Høyanger Verk (Høyanger), and mines including Surnadal and Lassedal.

Boehlen (1968) noted that the most important extraneous substances in the atmosphere resulting from alumina reduction are inorganic fluorine compounds, alumina, tar, carbon, sulphur dioxide, and carbon monoxide. McCabe (1955) described the electrolytic reduction of alumina — the oxygen liberated in the cryolite bath combines with the carbon of the anode yielding carbon dioxide. As the carbon dioxide rises through the blanket of alumina covering the electrolytic cells, small amounts of alumina dust and fluorides become entrained. He noted the evolution of heat and stressed

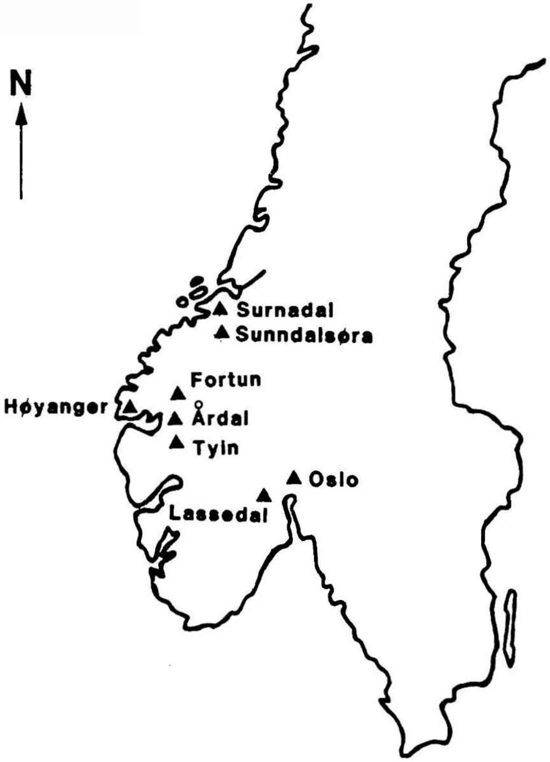

Fig. 1. Western Norway; the Sognefjord.

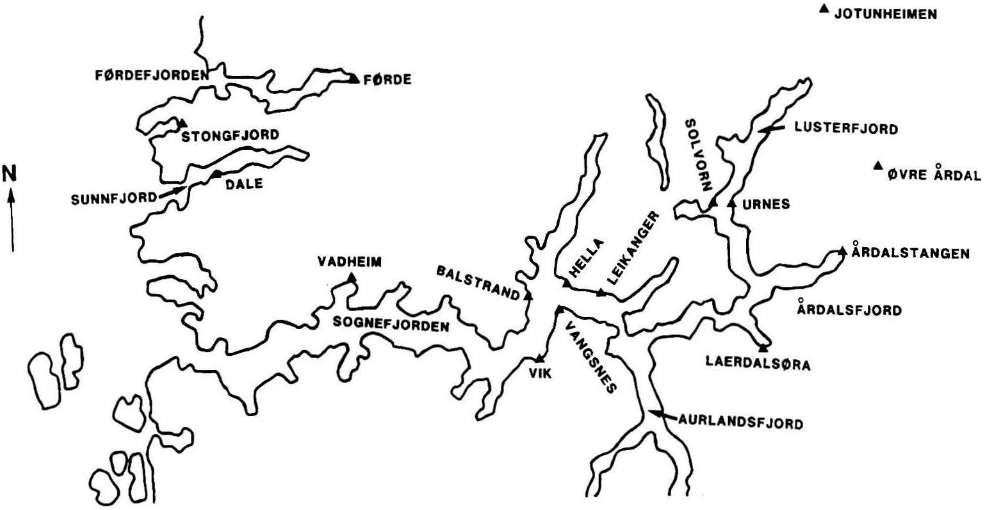

Fig. 2. The Årdalstangen and Øvre Årdal region; the smelter occurs at Øvre Årdal to the east.

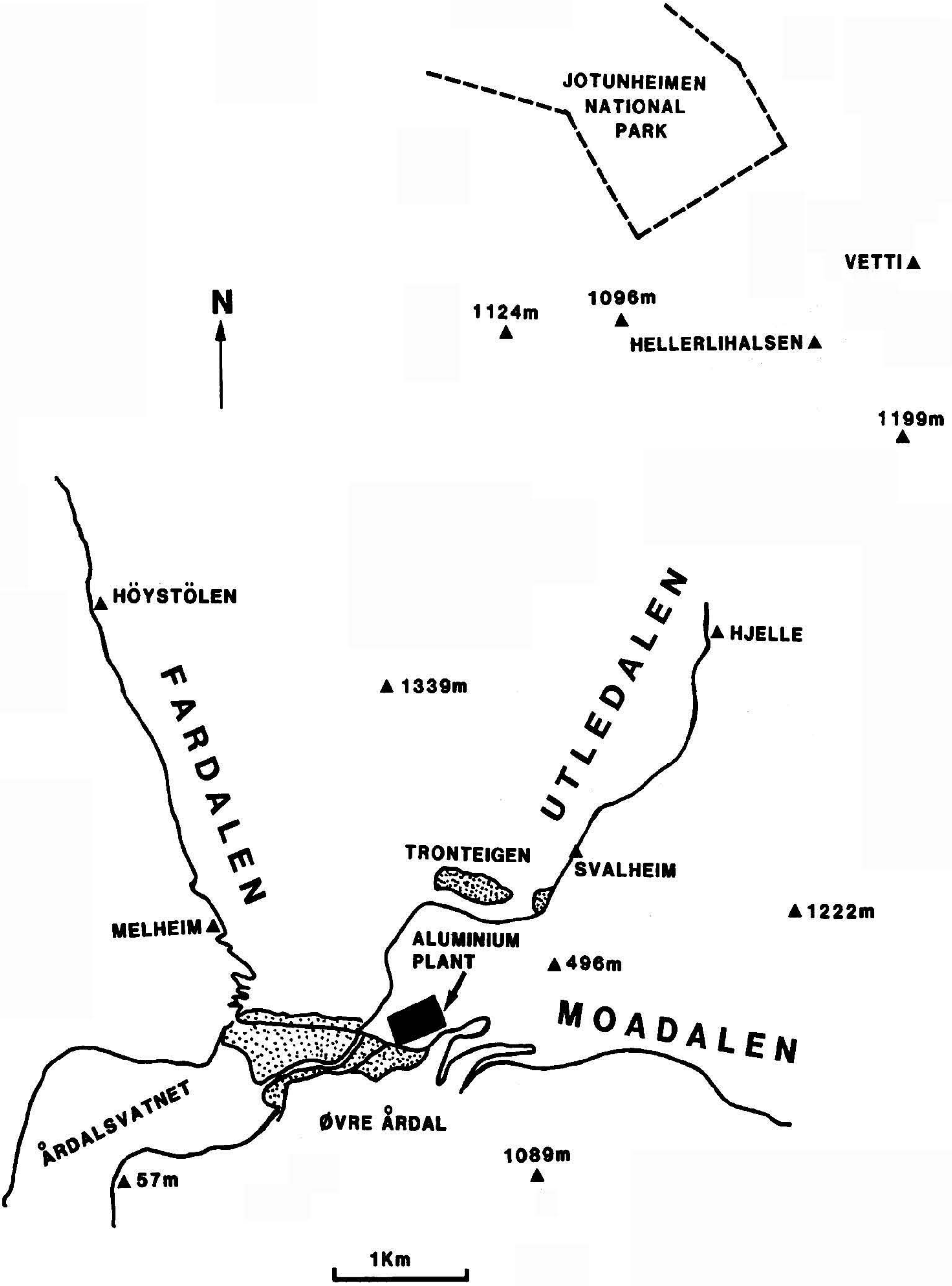

Fig. 3. Øvre Årdal and associated valleys at the northern end of Årdalsvatnet.

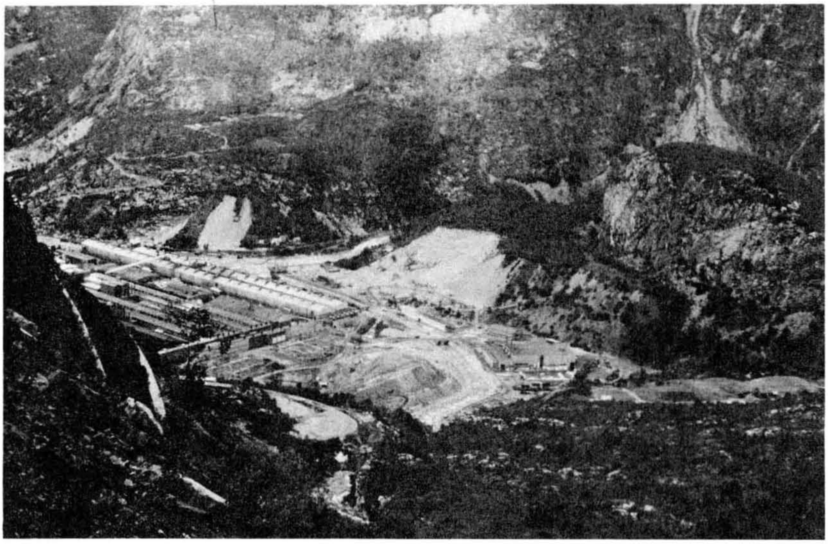

Fig. 4. The plant at Øvre Årdal (viewed from east).

the need for adequate ventilation in pot rooms; however, he indicated that the high velocities of an induced draught will lift dust from the top of the pots.

The Ministerium für Arbeits report (1972) examined emissions in nonferrous industries in North Rhine-Westphalia and noted that, in the aluminium industry, the following quantities of pollutants were produced:

gaseous fluorine componds: 0.8–1.5 kg/tonne
aluminium- and fluorine-bearing dust: 9–20 kg/tonne
sulphur dioxide: 3–15 kg/tonne, and carbon monoxide.

It should, however, be stressed that the plant at Øvre Årdal has the advantage of hydro-electric power.

Less and Waddington (1971) investigated the nature of aluminium reduction cell fume and found that the particulate matter exhibited a bimodal size distribution with one fraction consisting mainly of dust particles witha diameter greater than 5μm, and the other of material with a diameter smaller than 1 μm. The coarse fraction included alumina, carbon, and cryolite droplets, whilst they describe the fine fraction as consisting mainly of condensed fluoride vapour approximating in composition to chiolite ($5NaF. 3AlF_3$) and that this fine particulate accounted for approximately 35% of the total fluorine emission from the cells.

Location of Sampling Sites

Årdalstangen lies at the north-eastern end of Årdalsfjorden; this fjord, to the west joins Lustrafjorden and Lœrdalsfjorden and then leads ino the Sognefjorden. To the north of the town lies the lake Årdalsvatnet which terminates at Øvre Årdal. The latter is located in a steep sided valley which leads into valleys including Fardalen (to the north-west), Utledalen (to the north-east), and Moadalen (approximately to the east); these are illustrated in Fig. 3. The restricting topography and wind direction are factors which will have major effects on the fate of atmospheric pollutants in this region.

The population of Årdalstangen and Øvre Årdal is approximately 7,000. Industrial activity in the latter town dates back to the early eighteenth century when this represented an important site for copper mining. With these towns are situated a number of smaller communities including Fardal, Utladal, Seimsdal, Nadvik, Ofredal, and Vetti; some of these are shown in Fig. 3.

North and north-east of these sites is the mountainous Jotunheimen region characterized by glaciers such as Storbreen, Smörstabbreen, and Tverråbreen, and mountain peaks including Galdhöpiggen (2469 m), and Glittertind (2452 m). West lies the Hurrungane with glaciers such as Styggesdalsbreen; associated glaciers include Jervvassbreen (to the east), Maradalsbreen (to the south-east), Slingsbybreen (to the south), and Skardstölsbreen (to the south-west). Peaks in the region include Fannaråki (1068 m), Storen (2403 m), and Styggedalstindane (2387 m).

In Utladalen, near Vetti (Fig. 3), is situated the famous Vettisfossen; a major waterfall possessing a 275 m free fall. This area, like many other sites in this region has vegetation exhibiting severe effects of fluorine pollution; the aluminium (q.v.) appears to have a more limited sphere of influence.

Field Work and Experimental Procedures

Samples were collected in clean plastic screw top containers during the course of ecological field work in the summer of 1987. They were obtained during dry weather and carefully harvested, subsequently air dried and thence transferred to the laboratory. In the various sites selected, the following material was collected (when available):

1. Birch (*Betula*): leaves and twigs — all at a height of 2 m.
2. Soil: samples were collected with a nonmetal tool from the top 5 cm of the soil.
3. Grass: this was in each case an approximately equal mixture of *Agrostis*, *Festuca*, and *Deschampsia*.

In addition, from a few sites were collected cores of birch or cores of Norway Spruce (*Picea abies*); these were obtained by means of a Pressler borer.

Preparation and analysis

Each sample was mounted on a 13 mm diameter carbon stub and held in place using conductive carbon cement. The samples were given a light coating of Duron Spray (an antistatic material produced by Hansawerke of Bremen-Hemelingen) to eliminate problems caused by electrostatic charges and when dry placed in a Cambridge Stereoscan 600.

Samples were analysed by means of electron probe X-ray microanalysis with a Link System 860 series 2 computer using a ZAF-4 program, (where *Z* is the atomic number, *A* the absorption, and *F* the fluorescence). In this process of X-ray microanalysis, an electron beam strikes the solid specimen and a number of interactions occur including the production of X-rays. These X-rays are detected by a lithium drifted silicon detector and are passed on to a multi-channel analyser. Suitable areas on each sample (10,000 μm^2) were selected for analysis using the microscope visual display monitor and analysed at a magnification of 500X for 100 seconds of live time at 25kV (electron beam energy).

The quantitative accuracy of this technique on biological material may be restricted to ±10% relative of the true value (Goldstein *et al.*, 1984). The results may be influenced by a combination of factors:

1. The variable geometry of the sample surface,
2. The sample itself may be a cause of contamination,
3. The majority of elements in biological material (i.e., carbon, oxygen, nitrogen, hydrogen), are not detected by the type of detector used, as the energy they generate is too low.

The technique is otherwise highly accurate; to maintain maximum acccuracy of data 10 random areas were examined in each case.

Leaf material was also examined microscopically in an attempt to determine whether stomatal penetration and accumulation of particulates had occurred or whether deposition of particulates was confined to cuticular surfaces.

Results and Discussion

The results are presented in Tables 1 and 2 and three sample results are given in Figs. 5, 6, and 7. It must be stressed that the technique only records elements higher than sodium; replicates were used throughout.

The print out will list a variety of elements; thus, for example, one of the birch twig samples near Svalheim gave (in simplified format):

Table 1. An example of a printout of elements.

Element	% element
Mg	0
Al	33.232
Si	6.967
P	0
S	10.110
K	4.685
Ca	36.586
Mn	0
Fe	7.031
Zn	1.398

Aluminium will be represented as Al as indicated above, but also as Si in, for example, the form of aluminosilicates (e.g., in the soil). Thus, soil samples will include in their percentage occurrence values not just aluminium from any pollution sources but also aluminium from the normal soil sources.

In this article, little emphasis is placed on the soil samples and all data will only be examined in a comparative manner.

Particulate pollution by aluminium fume was confined to sites close to the smelter (Table 2). To the north-east they occurred within 8 km of the works, to the north-west within 5 km, and, to the east, within 3 km. The fate is affected, as noted by Bovay and Bolay (1965), working on fluoride pollution, by the direction and nature of air movement, but also the topography of the area is important. The valley above the smelter is steep sided and consequently low altitude winds moving in from Sognefjord (and the west) will largely move any atmospheric pollutants into one of the three major valley systems emanating from Øvre Årdal (i.e., Utledalen, Fardalen, and Moadalen). Of these, the former appears to be the major sink for such pollutants as the access into the valley is not steep as is the case with Fardalen and Moadalen. In fact, this is reflected by the results expressed in Table 2.

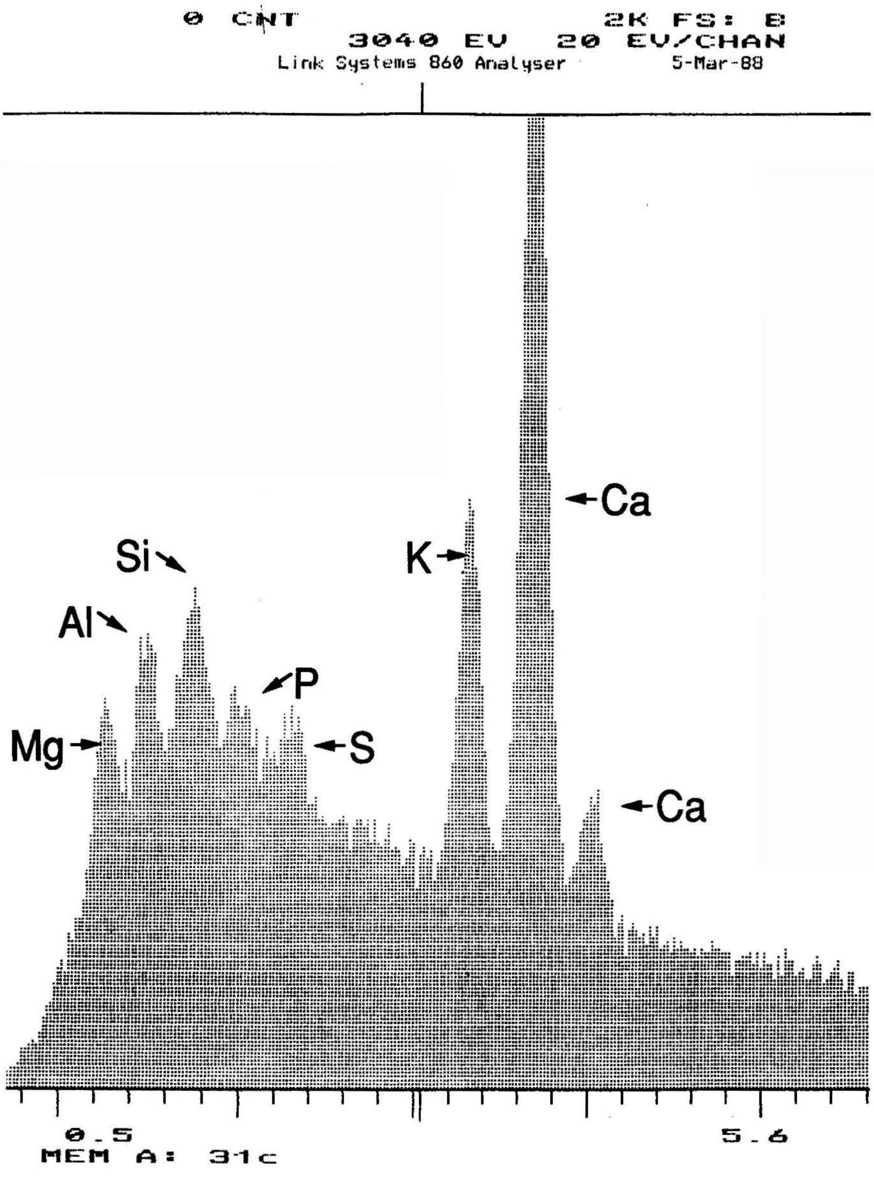

Fig. 5. Major elements in a sample of birch leaves.

The Øvre Årdal sites located approximately 100 m from the plant had aluminium contamination of *Betula* twigs, leaves, and soil; note the earlier comments about soil aluminium values. The birch leaves carried more aluminium than the twigs and the average birch value (twigs and leaves) amounted to 7.0%.

The site near Svalheim (altitude approximately 50 m) is located in the low altitude valley Utledalen at approximately 2.5 km north-east of the plant. The results indicate major deposition of aluminium in this area which will reflect not only atmospheric pollution but also such processes as soil erosion, etc. The birch twigs here had a much higher load than the birch leaves and the average birch value amounted to 19.68%.

Samples of birch cores were also removed to ascertain whether measureable quantities of aluminium had been accumulated in the woody tissues of this tree; in addition, twigs from which the bark had been removed

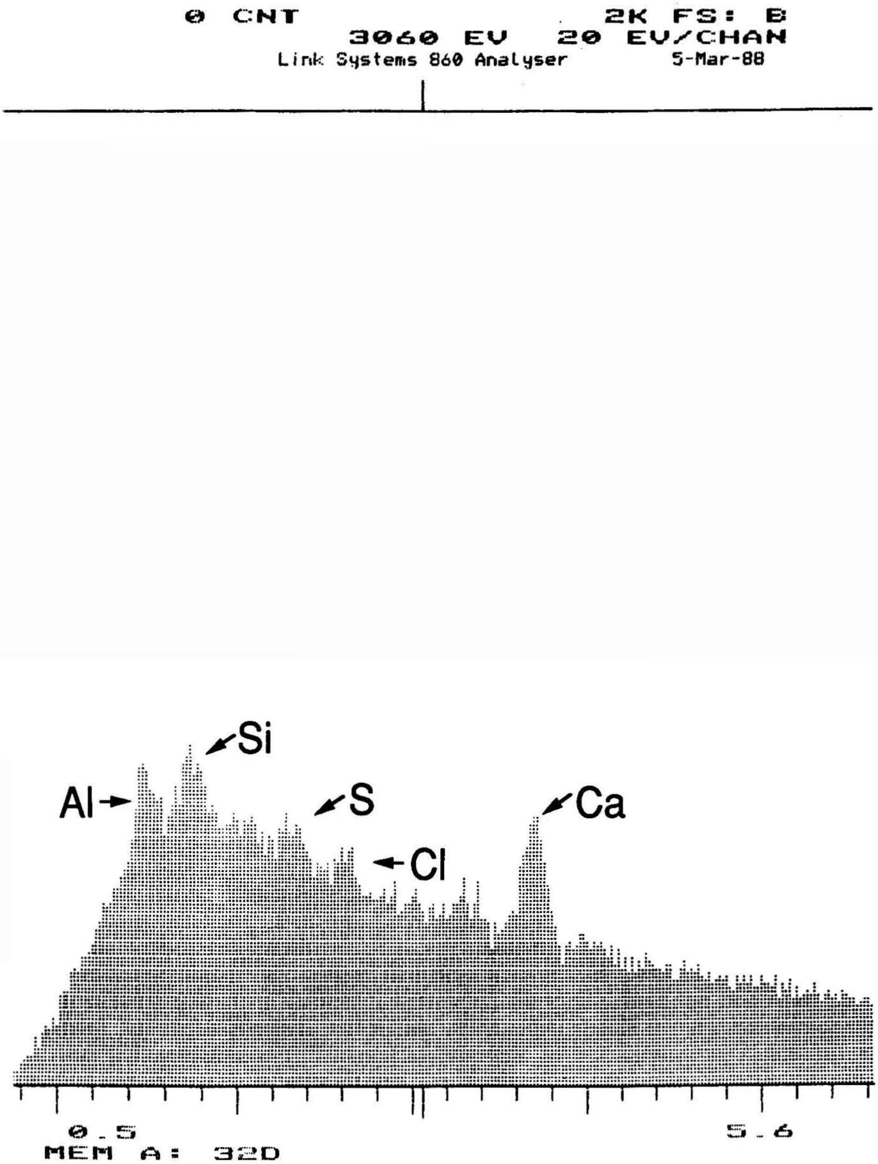

Fig. 6. Major elements in a sample of birch twigs.

were also examined. Aluminium was not found to be accumulated (in any age wood) from the atmosphere into the tissue or indeed from the soil system into the tissues of the stem or twigs.

The grass samples contained no aluminium and this conceivably can result from various factors such as; (a) the grass is sheltered topographically from wind carrying particulates (would not apply during still conditions when particulate sedimentation would occur); (b) leaf presentation, as noted by Pyatt (1973) is not conducive to accumulation of particulate pollutants; (c) some of the grass can be sheltered by adjacent taller species in a stratified system — the sampling procedure avoided this; and (d) grass grows constantly from a basal meristem and replaces portions (which might be contaminated) removed by processes such as grazing pressure or indeed by cutting.

The final sites in Utledalen (at approximately 8.0

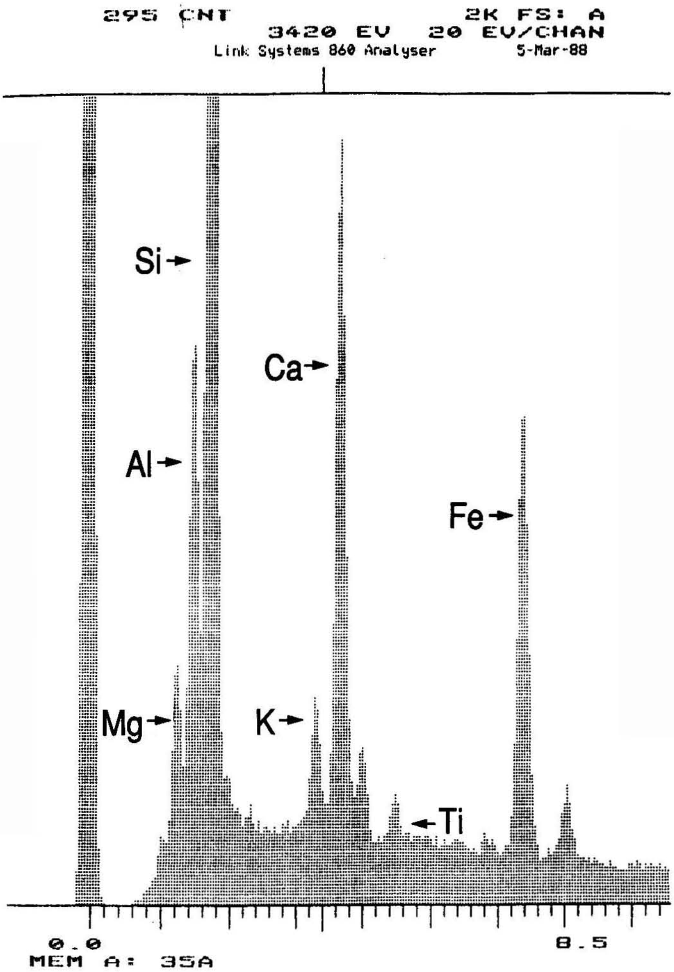

Fig. 7. Major elements in a sample of soil.

and 9.0 km from the plant) had vegetation which did not carry any aluminium deposits; the particulates, thus sediment out or impact well before these areas are reached.

To the north-west of the plant two sites were examined as indicated. These sites, on the steep valley side, were at altitudes of approximately 274 m (Melheim) and 535 m (Höystölen). From Table 2 it is apparent that only birch leaves and twigs in Melheim showed contamination; it appears that the dense particulates from the relatively low altitude emission sources (works are on the valley floor at approximately fjord level) do not generally reach sites with an altitude much in excess of that found at Melheim. The same applied to sites to the east of the works with altitudes of approximately 325 m and 525 m.

Birch twigs then are a good indicator of pollution of this type. They have the advantage over the leaves, that

Table 2. Aluminium content of samples (dry weight) from various sites in the vicinity of the Øvre Årdal smelter.

Approximate Site Location	Approximate Distance From Centre of Smelter	Compass Bearing	Material	Average Al[a] Content (of 10 random areas) mg/g
Øvre Årdal	100 m	N	birch twigs	61.5
			birch leaves	78.5
			soil	169.5
Svalheim (Utledalen)	2.5 km	NE	birch twigs	291.9
			birch leaves	101.7
			soil	111.9
			grass	0
			birch cores	0 (throughout)
			birch twigs without bark	0
Hellerlihalsen (Utledalen)	8.0 km	NE	birch twigs	0
			birch leaves	0
			soil	0
Vetti (Utledalen)	9.0 km	NE	birch twigs	0
			birch leaves	0
			soil	0
			grass	0
Melheim (Fardalen)	2.0 km	NW	birch twigs	152.5
			birch leaves	104.2
			grass	0
			birch cores	0 (throughout)
Höystölen (Fardalen)	5.0 km	NW	birch twigs	0
			birch leaves	0
			grass	0
			soil	0
East of Works	0.5 km	E	birch twigs	84.6
			birch leaves	38.0
			soil	0
			grass	0
			birch cores	0 (throughout)
Tyin Road (Moadalen)	3.0 km	E	birch twigs	0
			birch leaves	0
			soil	0
			grass	0

[a] The average aluminium contents are expressed in terms of a weight per unit area of sample; 10 replicates being employed in each case.

despite a relatively low surface area to volume ratio, of being exposed to the atmosphere throughout the year. Also, as can be seen from Fig. 8 factors, including fluorine pollution, in the area have resulted in massive Birch defoliation — this can lead to the twigs being more exposed and consequently more accessible to atmospheric pollutants.

The leaf samples from Svalheim in Utledalen were examined to assess particulate distribution. It was noted that 60 — 84% of the particulates were associated with the upper leaf surface; this is in agreement with Pyatt (1973) and Gilbertson, Kent, and Pyatt (1985). Sections through the leaves, and direct leaf examination, revealed that particulate matter of the smaller diameters had penetrated the stomatal openings; also cuticular accumulation was well represented. This conceivably can limit productivity and also may affect herbivores on leaf surfaces and ultimately decomposers after leaf fall.

Soil samples from the sites furthest from the works contained no aluminium (below detectable level of the instrument); it appears then that long-term processes of climatic weathering have mobilised this aluminium. However, the occurrence of aluminium in sites near the

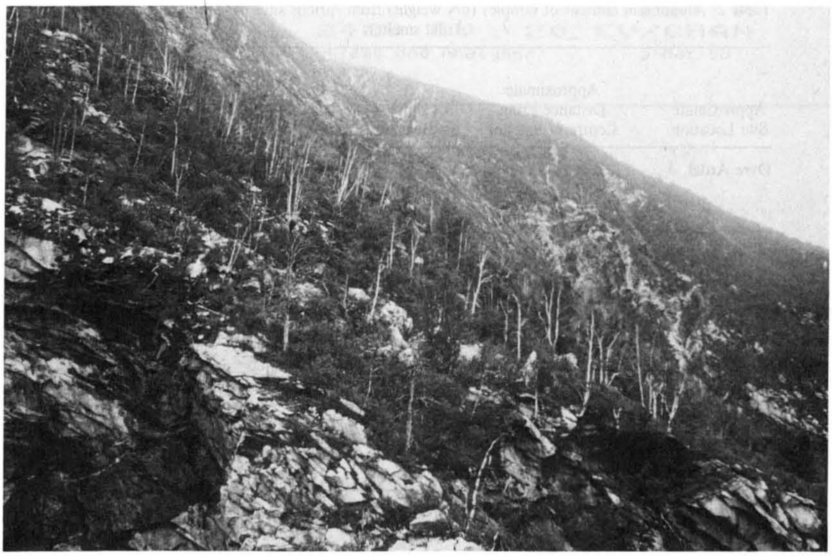

Fig. 8. Birch woodland, approximately 500 m, to east of plant; note severe defoliation which is to some extent the result of fluorine pollution.

works would indicate atmospheric deposition of aluminium has exceeded the rate of climatic weathering.

Acknowledgements — We thank Mr. Martin Hutchings for assistance in preparing the diagrams and Mrs. Joan Witter for typing the manuscript.

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A REVIEW OF THE ANALYSIS OF ORGANOMETALLIC COMPOUNDS IN THE ENVIRONMENT

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This review is concerned with the analytical methods that have been devised for the determination of organometallic compounds in the environment. For the purposes of this review the environment includes water, air, plants, crops, fish and crustacae and biological materials. The requirements in this field of analysis are very demanding and are becoming increasingly so. Regarding sensitivity, analysis is now commonly required at the microgram level and frequently at the nanogram or subnanogram levels. The ability to speciate organometallic compounds occurring in the environment is another searching requirement which is of rapidly growing importance and which is being met to a large extent by refinements in chromatographic techniques. This review demonstrates that success in these areas will only be achieved by adopting the most advanced analytical techniques and stretching their capabilities to the limit.

Introduction

A surprisingly large number of organometallic compounds occur in the environment. In this context the environment means inland waterways, potable water supplies, the oceans and also sedimentary matter, vegetation and animal life in inland waterways and the oceans. Some of the more volatile organometallic compounds are found in plant material, crops and biological materials such as fish, animal and human tissues and body fluids. Thus, organometallic compounds occur widely throughout the environment principally as compounds of mercury, tin, lead, arsenic and magnesium and, to a lesser extent as compounds of germanium, antimony, copper, silicon, manganese and nickel. The distribution of these compounds throughout the environment—air, water, food has toxicological implications which are of concern from the point of view of the health of humans, animals, fish, insects, bird-life, who, in one way or another, are all subject to contamination by organometallic compounds and who are all part of a food chain.

Considerations, other than toxicological, are involved in a consideration of the occurrence of organometallic compounds in the environment. These include the present and future roles of organometallic compounds in the biotechnologies that open industrial and regulatory options for bioremediation of unwanted toxic metal releases, recovery of precious metals, controls over bioactive and essential metals for agriculture and horticulture, biomining, and bioseparations of key industrial waste species subject to biotransformations by either endo- or exocellular organylation processes.

In all these areas, there is a growing recognition that high analytical sensitivity, alone, is insufficient. There is also a requirement from a detailed insight into the speciation of organometallic compounds occurring in the environment in order that a complete understanding can be obtained in processes occurring in nature. An example of such quantitative structure is the activity relationships illustrated, for example, by considering in the case of lead and tin, the effect of structure on human and mamalian toxicity.

Organometallic compounds enter the environment by three main routes. The first path is represented by the organometallic compounds produced by man such as those of lead and mercury. Lead enters chiefly as alkyl-lead compounds, used as an additive in gasoline which enters the air via gasoline spillages and possibly, to some extent, from automobile exhausts and then contaminates waterways and consequently river sediments and fish and plant life and also enters crops and animals in the fields. Similar comments can be applied to organomanganese compounds which to some extent are displacing lead as a petroleum additive and to organotin compounds which enter the environment, as for example, in antimoluscicide paints used on the hulls of ships and in harbour works.

The second source of organometallic compounds concerns inorganic substances such as industrial effluents and sewage introduced into the environment by man, and which are subsequently converted in nature to organometallic compounds. Classic cases of this are the inorganic mercury compounds and arsenic compounds, which in the environment or in animal tissues can be converted by bacteria to methylmercury and methylarsenic compounds. Probably the chief source of organomercury contamination is inorganic mercury entering rivers as an effluent from industries such as chloralkali works and industries which use alkalies in large quantities such as paper-making. It is believed that tin entering the environment via industrial effluents or mining operations as inorganic tin can be similarly converted in nature to organotin compounds. Certainly, we are only on the perifery of understanding what biotransformations occur when metal contaminated sewage sludge is disposed of as a fertilizer to agricultural land or to the oceans.

The third group of organometallic compounds which occur in the environment are those that are produced in waterways from naturally occurring metals. These include methylarsenic compounds produced by methylation of inorganic arsenic in fish or on sediment deposits, and probably include other elements such as antimony and selenium.

The list of organometallic compounds found in trace amounts in the environment has increased dramatically over the past few years and has necessitated the development of analytical methodology both for the purposes of first identifying new compounds and, secondly, of monitoring the concentrations of such compounds so that trends can be followed and working hypotheses developed. The occurrence of organometallic compounds in the environment is now systematically discussed.

The most powerful tools that are emerging to satisfy the needs of sensitivity and speciation are various combinations of chromatography, coupled with element specific detectors such as atomic absorption spectrometry or mass spectrometry, linked at the outlet end of the chromatography. These techniques have the advantages of being extremely sensitive, of providing a separation of sample components to meet the speciation needs and of confirming the metal and organic structure present by the specificity of the technique. Under these conditions nanogram quantities of each component can be identified and determined and, indeed, if sample preconcentration techniques are available, then subnanogram analysis becomes feasible.

The automation of techniques as exemplified by continuous lead in air monitoring programmes and the provision of on-line analysers in the biotechnology industries are areas in which rapid future developments are expected.

Before starting a discussion of the analytical procedures, the limited knowledge available to date concerning origins and toxic effects of organometallic compounds is discussed below.

Occurrence and Toxic Effects of Organometallic Compounds

Organomercury compounds

Certain organomercury compounds are more toxic than elemental mercury (Uthe and Armstrong, 1971, Griefenstein *et al.* 1958; Davies and Beech, 1960) and inorganic mercury forms and when present in the environment, may cause serious illness in extremely polluted areas (Backmann, 1982).

A growing public interest in environmental quality has lead to the development of analytical techniques for the monitoring of environmental pollutants. Due to its chronic toxicity and its tendency to bioaccumulate, mercury is of prime interest. Being volatile in the organic and elemental forms, mercury is well dispersed in the atmosphere. The activity of certain bacteria, molds, and enzymes in the soil or sediment can produce methylated mercury from elemental or inorganic mercury (Ridley *et al.* 1977; Imura *et al.* 1971; Wood *et al.* 1968; Jenson and Jernelöv, 1969; Ridley *et al.* 1977). The organic mercury compounds produced, primarily dimethylmercury and methylmercury halides, are potentially more toxic than inorganic mercury forms. Therefore, recent studies of environmental mercury have been concerned with its chemical speciation to determine not only the amounts of mercury present but the chemical forms as well. More extensive data in this area will assist in determining the role of organic mercury in the global cycling of the element. It has been reported that organomercury compounds are significantly concentrated in fish (Westoö, 1966; 1967; 1968; Bache and Lisk, 1971; Jones and Nickless, 1978; Collett *et al.* 1980; Vostal, 1972) predominantly as methylmercury compounds. The syntheses of methylmercury compounds by micro-organisms in freshwater sediments have been investigated by some workers (Jensen and Jernelöv, 1969; Wood *et al.* 1968).

Although methylmercury has been found in aquatic organisms, its origin is not in all cases clearly known. It is generally assumed that methylmercury exists in natural waters and that the organisms concentrate it, because it has been detected in many aquatic organisms. The methylation of inorganic mercury in sediments has been reported by several investigators (Jensen and Jernelöv, 1969).

Organotin compounds

These compounds have been the subject of environmental studies for two obvious reasons. First, is the increasing world-wide use of inorganic and organotin compounds in many industrial, chemical and agricultural areas, very little being known about their environmental fate; secondly, there is a great difference in toxicity of the various organotin compounds according to the variation of the organic moiety in the molecules.

There is a special interest in the biotic and abiotic methylation of tin compounds (Guard *et al.* 1981) and the fate of some industrial organotins in the aquatic ecosystems. One possible route is the dealkylation of the trialkyltin species eventually to Sn(IV) and the microbial methylation of Sn(IV) to the various methyltin species. Increasing methylation concentrations with increasing anthropogenic tin influxes has been noted in the Chesapeake Bay (Jackson *et al.* 1982).

Rapsomankis and Weber (1985) examined the environmental implications of the methylation of tin(II) and methyltin(IV) ions in aqueous samples in the presence of manganese dioxide.

Their studies were carried out with particular reference to the mechanisms involved and the role of a dimethylcobalt complex carbanion donor, the carbocation donor iodomethane, and the oxidizing agent manganese dioxide. The yields of the various methyltin ions were estimated, some preliminary results were also presented on the further methylation of monomethyltin, dimethyltin, and trimethyltin, which indicated that the presence of a naturally occurring donor such as methylcobalamin would result in formation of volatile tetramethyltin and this would account for the global occurrance of methyltin compounds.

Van Nguyen *et al.* (1984) carried out an investigation of the fate in an aqueous environment of three organotin compounds (triphenyltin acetate, triphenyltin hydroxide and triphenyltin chloride) used in antifoulant paint compositions. The organotin compounds were leached from paint panels by shaking with distilled water for up to 2 weeks at room temperature, and the water and undissolved residues were then examined by infrared spectroscopy and thin-layer chromatography. The results suggested that the organotin compounds ionized in aqueous media; a simple model was developed to explain the process.

Organolead compounds

The use of tetraalkylleads as antiknock additives/ octane enhancers for automotive gasolines has been reduced in the United States, although not elsewhere.

The high toxicity of tetraalkylleads is attributed to their ability to undergo the following decomposition in the environment (Grove, 1980):

$$R_4Pb \longrightarrow R_3Pb^+ \longrightarrow R_2Pb^{2+} \longrightarrow Pb^{2+}$$

The formation of alkyllead salts, probably associated with proteins, arising in tissues from rapid metabolic dealkylation of tetraalkyllead compounds is of toxicological importance in evaluating exposure to tetraalkylleads.

The possibility of biomethylation of lead or organolead ionic species by microorganisms (Wong *et al.*, 1977); Schmidt and Huber, 1976) reversing the decomposition mechanism given above, may add to environmental lead problems, although the area is presently much disputed (Reisinger *et al.* 1981).

Organically bound lead is a minor but important contribution to total lead intake by humans and animals. Alkyllead salts such as trialkyllead carbonates, nitrites and/or sulfates arising in tissues from rapid metabolic de-alkylation of tetraalkyllead compounds are of low toxicity.

Recently, a renewed interest in the speciation of lead in environmental samples has resulted from several diverse lines of investigation. Organolead compounds have been detected in cod, lobster, mackerel and flounder meal (10 to 90% of the total lead burden) (Sirota and Uthe, 1977), and in freshwater fish) (Chau and Wong, 1980), Reamer *et al.* (1978). There is also evidence for the chemical (Reisinger, 1981) and biological (Chau and Wong, 1980; Wong *et al.* 1977; Thayer, 1978) alkylation of organolead salts or of lead (II) salts.

Speciation of alkyllead compounds, including ionic, volatile and solvated forms has become important and in demand for environmental studies. The highly polar dialkyl and trialkyl forms in particular are more important species because of their toxicity to mammals and as a result of degradation of tetraalkyllead in aqueous medium (Grove, 1980).

Organoarsenic compounds

Organoarsenic species are known to vary considerably in their toxicity to humans and animals (Webb, 1966). Large fluxes of inorganic arsenic into the aquatic environment can be traced to geothermal systems (Stauffer *et al.*, 1980), base metal smelter emissions and localized arsenite treatments for aquatic weed control. The methylated arsenicals have entered the environment either directly as pesticides or by the biological transformation of the inorganic species (Andreae, 1977; Wong *et al.*, 1977).

Organoarsenical pesticides such as sodium methylarsenate and dimethylarsinic acid are used in agriculture as herbicides and fungicides. It is possible that these arsenicals enter soil, plant, and consequently humans. On the other hand, arsenic is a ubiquitous element on the earth, and the presence of inorganic arsenic and several methylated forms of arsenic as monomethyl-, dimethyl-, and trimethylarsenic compounds in the environment has been well documented (Braman, 1975). The occurrence of biomethylation of arsenic in microorganisms (Cox, 1975), soil (Von Endt *et al.*, 1968), animals and humans (Lasko and Peoples, 1975) has also been demonstrated. Therefore, further investigation of the fate of arsenicals in the physical environment and living organisms requires analytical methods for the complete speciation of these arsenicals.

It has been shown that arsenic is incorporated into both marine and freshwater organisms in the form of both water-soluble and lipid-soluble arsenic compounds (Chapman, 1926). Recent studies to identify the chemical forms of these arsenic compounds have shown the presence of arsenite (As-III), arsenate (As-V), methylarsonic acid, dimethylarsinic acid and arsenobetaine (Andreae, 1977). Methylated arsenicals also appear in the urine and plasma of mammals, including man, by biotransformation of inorganic arsenic compounds, (Lasko and Peoples, 1975). Several methods have been devised to characterize these arsenicals.

Organomercury compounds in natural and potable waters

Classical methods

Mercury in water samples can exist in inorganic or organic forms or both. Preliminary degradation of organomercury compounds in the sample to inorganic mercury preparatory to analysis is often necessary because the normal methods of reducing inorganic mercury compounds to elemental mercury with reagents such as stannous chloride do not work with organomercury compounds and hence organomercury compounds are not included in such determinations. Owing to the conversion of Hg^{2+} to CH_3Hg^+ in natural water, it is often observed that a high percentage of the mercury is present in the form of organic compounds. Some organic mercurials like CH_3HgCl and $(CH_3)_2$ Hg may be reduced by a combination of cadmous chloride and stannous chloride, but this method requires large quantities of reductants and the use of strong acid and strong alkali (Magos, 1971).

Organic mercury compounds can be decomposed by heating with strong oxidizing agents such as potassium dichromate or nitric acid-perchloric acid, followed by reduction of the formed divalent mercury to mercury vapour (Kimura and Miller, 1962).

Both methods are rather time-consuming and not readily suitable for automation. Potassium persulphate has also been used successfully to aid the oxidation of organomercury compounds to inorganic mercury and this forms the basis of an automated method (Environmental Protection Agency, 1972).

Sulphuric acid acidified potassium permanganate has also been used to decompose organically bound mercury, prior to reduction with stannous chloride and determination of the evolved mercury by atomic absorption spectroscopy.

Bennett *et al.* (1972) showed that acid-permanganate alone did not recover three methylmercuric compounds, while the addition of a potassium persulfate oxidation step increased recoveries to 100%. El-Awady *et al.* (1976) confirmed the low recoveries of methylmercury by acid-permanganate. They showed that only about 30% of methylmercury could be recovered by this method, while the use of potassium persulfate produced complete recovery.

Umezaki and Iwamoto (1971) differentiated between organic and inorganic mercury in river water samples. They used the reduction-aeration technique. By using stannous chloride solution in hydrochloric acid only inorganic mercury is reduced whereas stannous chloride in sodium hydroxide medium and in the presence of Cu^I reduces both organic and inorganic mercury. The mercury vapour is measured conventionally at 254 nm. Ions that form insoluble salts or stable complexes with Hg^{II} interfere.

Becknell *et al.* (1971) first converted the organomercury to mercuric chloride using chlorine. The mercury was then concentrated by removal as $HgCl_4^{2-}$ by passing the sample solution (500 mL) adjusted to be 0.1M in hydrochloric acid through a paper filter-disc loaded with SB-2 ion-exchange resin. The paper, together with a mercury standard, is then heat-sealed in Mylar bags and analysed by neutron activation analyses using the 77-keV x-ray photo-peak from the decay of ^{197}Hg.

Braun *et al.* (1981) showed that polyurethane foam loaded with diethylammonium diethyldithiocarbamate is suitable for concentration of trace amounts of organic mercury from potable water samples prior to analysis. Organomercury compounds studied included phenylmercury and methylmercury species. The polyurethane discs were then analysed by x-ray fluorescence spectrometry. Preconcentration of mercury prior to the measurement has also been achieved by amalgamation with noble metals (Muscat *et al.*, 1972; Olafsson, 1974; Jones and Nickless, 1978).

Potentiometric titration with standard solutions of dithiooxamide at pH 5–6 has been used to estimate less than 100 pg mercury in water samples (Rubel and Lugowoka 1980). The precision in the range 0.5–1.0 mgL^{-1} mercury is about 4%. The first derivative could be used for end-point determination. A wide variety of ions can be tolerated but silver, copper and chloride interfere, and must be separated in a preliminary step.

Ke and Thibert (1973) have described a microdetermination of down to 50 μgL^{-1} of inorganic and organic mercury in river water and sea water. Mercury is determined by use of the iodide-catalysed reaction between Ce^{IV} and As^{III} which is followed spectrophotometrically at 275 nm.

Stary and Prasilova (1976a, 1976b, 1976c, 1976d) have described a selective radiochemical determination of phenylmercury and methylmercury. These analytical methods are based on the isotope exchange reactions with the excess of inorganic mercury-203 or on the exchange reactions between phenyl-mercury and methylmercury chloride in the organic phase and sodium iodide-131 in the aqueous phase. The sensitivity of the methods (0.5 μgL^{-1} in 5-mL sample) is, however, insufficient to determine organomercurials in natural waters.

Stary developed a preconcentration-radioanalytical method for determining down to 0.01 μgL^{-1} of methyl and phenyl mercury and inorganic mercury using 100–500 mL samples of potable or river water. Extraction chromatography and dithizone extraction were the most promising methods for the concentration of organomercurials in the concentration range 0.01 to 0.1 μgL^{-1}. The dithizone extraction method was used for the preconcentration of inorganic mercury.

Atomic absorption spectrometry

Various workers have made contributions to the determination of organically bound mercury compounds and inorganic mercury in potable and natural waters by atomic absorption spectrometry (Baltislanger and Knudson, 1974; Umezaki and Iwamoto, 1971; Stainton, 1971; National Institute of Drug Abuse, 1978; Done *et al.* 1978; Doherty and Dorsett, 1971; Simpson and Nickless, 1977; Lutze, 1979; Goulden and Anthony, 1980; Kiemenis and Kloosterboer, 1976; Farey *et al.*, 1978; Minagawa *et al.* 1980; Yamagami *et al.*, 1980; Oda and Ingle, 1981a, 1981b; Hawley and Ingle, 1975; Christman and Ingle, 1976).

The Water Research Council UK (1978) have described a method for the determination of mercury in water in which all forms of mercury are converted to inorganic mercury using prolonged oxidation with potassium permanganate. Elemental mercury is then released using stannous chloride and mercury estimated by cold vapour atomic absorption spectrometry at 253.7 nm. Many of the potential interferences in the atomic absorption procedure are removed by the preliminary digestion-oxidation procedure. The most significant group of interfering substances are volatile organic compounds which absorb radiation in the ultraviolet. Most of these are removed by the pretreatment procedure used and the effect of any that remain are overcome by preaeration. Substances which are reduced to the elemental state by stannous chloride and then form a stable compound with mercury may cause interference (e.g., selenium, gold, palladium and platinum). The effects of various anions, including bromide and iodide were studied. These are not likely to be important interferers. Excellent performance characteristics are presented for this method.

Sampling techniques are described in detail including methods of cleaning sample bottles and fixing the sample with a solution of potassium dichromate in nitric acid. Farey *et al.*, (1978) compared this method with a method in which the sample is brominated to quantitatively convert alkyl and aryl mercury compounds to mercuric bromide. Recoveries of inorganic mercury from distilled water spiked with phenylmercury(II) chloride, tiomersal, ethylmercury(II) chloride, methylmercury(II) chloride, phenylmercury(II) acetate and p-tolymercury(II) chloride were greater than 95%.

When identical conditions of treatment were used on 50 mL samples of tap water and various river waters and sewage effluents, all with added methylmercury(II) chloride there were similar recoveries after 5 min reaction with bromine reagent.

Farey *et al.* (1978) claim that their pretreatment compares favourably with an established permanganate—sulphuric acid method. An advantage of the technique is that it can easily be carried out while sampling onsite. The sample is collected in glass bottles containing hydrochloric acid and the bromate—bromide solution is added. A bromination reaction time is then provided from the collection of the sample to the analysis in the laboratory and this is far in excess of that necessary to decompose the organic mercury. In addition as aqueous mercury(II) solutions are stabilised by strong oxidising agents, the oxidising conditions so created will help to preserve the inorganic mercury formed.

Abo-Rady (1979) has described a method for the determination of total inorganic plus organic mercury in nanogram quantities in natural water, fish, plants and sediments. This method is based on decomposition of organic and inorganic mercury compounds with acid permanganate, removal of excess permanganate with hydroxylamine hydrochloride, reduction to elemental mercury with tin and hydrochloric acid, and transfer of the liberated mercury in a stream of air to the spectrometer. Mercury was determined by using a closed, recirculating air stream. Sensitivity and reproducibility of the "closed system" were better, it is claimed, than those of the "open system." The coefficient of variation was 13.7% for water, 1.9% for fish, 4.9% for plant and 5.6% for sediment samples.

Doherty and Dorsett (1971) analysed environmental water samples by separating the total organic and inorganic mercury by electro-deposition for 60 to 90 min. on a copper coil in 0.1 M nitric acid medium and then determined it directly by flameless atomic-absorption spectrophotometry. The precision and accuracy are within ±10% for the range 0.1 to 10 μgL^{-1}. The sensitivity is 0.1 μgL^{-1} (50 mL sample).

Ultraviolet irradiation of the sample prior to analyses is another means of decomposing organomercury compounds to the inorganic form. Goulden and Afghan (1980) have used ultraviolet irradiation as a means of sample decomposition. After the photochemical oxidation, the formed inorganic mercury is reduced to metallic mercury in the usual way by stannous chloride. This method reduces the consumption of oxidising agents and thus diminishes considerably the risk of contamination; it also leads to shorter analysis times. Determinations with and without irradiation enable the separate determination of total and inorganic mercury, respectively.

Kiemenes and Kloosterboer (1976) have described an improvement on the Goulden and Afghan photochemical decomposition of organomercury compounds in the μgh^{-1} range in natural water prior to determination by cold vapour atomic absorption spectrophotometry. The decomposition of the organomercurials is carried out by means of ultraviolet irradiation at a suitable wavelength from small low-pressure lamps containing either Hg, Cd or Zn or a mixture of these metals in their cathodes. These lamps have the strongest lines, respectively at 254, 229 and 214 nm and the cadmium 229 lamp was chosen as the best compromise between high quantum efficiency and avoidance of background absorbance due to naturally occurring organic contaminants in water samples. The formed inorganic mercury is determined in the usual way by cold vapor atomic absorption after reduction of divalent mercury to mercury vapour. Comparison of the photochemical with a wet-chemical method (Table 1) showed that the results of prolonged irradiation compare well with the results obtained after complete wet-chemical destruction.

Jackson and Dellar (1979) attained a detection limit of 0.1 μgL^{-1} total mercury in potable and natural waters using ultraviolet irradiation—atomic absorption spectrometry.

The reproducibilities for inorganic mercury and methylmercury were similar. At the 0.33 μgL^{-1} level, the 95% confidence interval is approximately 0.1 μgL^{-1} and at the 2.00 μgL^{-1} level it is approximately 0.30 μgL^{-1}. The limit of detection based on the variation of results when estimating low levels is 0.1 μgL^{-1} for a single estimation. Hence, levels of about 0.1 μgL^{-1} may be estimated for 95% confidence intervals to the nearest 0.1 μgL^{-1} up to 0.5 μgL^{-1} and over this figure to the nearest 20%.

Jackson and Dellar (1979) emphasize that to obtain results for concentrations of mercury present in water at sampling time the container and water itself must be stabilized to avoid loss or gain of mercury. Acidic potassium dichromate is believed to be the best preservative (Feldman, 1974). Any particulate matter present in a water is likely to absorb dissolved mercury.

Direct cold vapour atomic absorption spectrometry with a reduction-aeration technique gives reproducible results down to levels of about 0.5 μgL^{-1}. This sensitivity is not enough to monitor background levels of mercury in unpolluted areas or to meet for example, the proposed World Health Organisation requirement for total mercury in potable water of 1 μgL^{-1} where it would be necessary to be able to determine mercury at one tenth of this limit (World Health Organisation), 1971, 1975). Consequently, a preconcentration step is necessary which also separates the mercury from interfering substances. Two types of preconcentration steps have been studied, those involving amalgamation with noble metals such as silver and gold and those involving preconcentration on resins. An example of the former technique is one in which concentrated nitric acid is used to decompose organomercury compounds in water samples prior to estimation by flameless atomic absorption spectroscopy. Stannous chloride was used to liberate elementary mercury, which is then vaporised by passing a stream of air (1360 mL per min.) through the solution. The air stream passes over silver foil, where mercury is retained by amalgamation and other volatile substances pass out of the system. The foil is heated at 350°C in an induction coil, and the air stream carries the mercury vapour through a cell with quartz windows. The atomic absorption at 253.65 nm is measured and the mercury concentration (up to 0.02 μgL^{-1}) is determined by reference to a calibration graph. In addition to improving specificity, this method has the additional advantage of improving sensitivity due to the concentration factor achieved in collecting the mercury from a large volume a sample on the silver foil.

Table 1. Comparison of photochemical and wet chemical decomposition of mercury compounds in an acidified natural water sample (River Wall).

Sample treatment		Hg found, μgL^{-1}	
Unirradiated		0.3	
Irradiated	10 min	1.01	1.00
(ZnCdHg lamp)	30 min	1.15	1.11
	30 min	1.05	1.12
Stored with KMn04	2% KMn04	0.98 (0.06)	1.02 (0.03)
	4% KMn04	1.04 (0.08)	0.97
	4% KMn04	1.07	1.01
Stored with KMn04	2% KMn04	1.00 (0.24)	1.06 (0.23)
partly evaporated and rediluted	4% KMn04	1.07 (0.27)	1.06 (0.31)

Yamagami *et al.* (1980) applied diethiocarbamate type chelating resins to the determination of μgL^{-1} of mercury in water. The samples were adjusted to pH 2.3 and passed thrugh a column packed with 5 g of the resin, at a flow rate of 50 ml per min. The resin is then refluxed with concentrated nitric acid, and the mercury is determined by atomic absorption spectrophotometry, using the reduction-aeration technique. The method is relatively simple and inexpensive and the detection limit is 10 ng mercury in water samples as large as 10 litres i.e., 0.1 μgL^{-1} thereby meeting the regulation requirements of the World Health Organisation (1971, 1975). Minagawa *et al.* (1980) use dithiocarbonate resin preconcentration on a column to determine traces of inorganic and organic mercury down to 0.2 μgL^{-1} in fresh water samples. River water and the other fresh waters were sampled in a 20–1 high density polyethylene bottle which was rinsed three times with the water sampled before the sample was taken. The sample was adjusted to pH 2 with concentrated nitric acid, 1 mg of $HAuCl_4$ being added as preservative. Samples of water should be analysed within one week of collection to avoid losses of mercury by adsorption and vaporization.

The apparatus used for preconcentration consisted of a column (15 mm i.d., 5 cm long) for the resin and a 20-L high density polyethylene bottle as reservoir for the samples. The 20–50 mesh wet dithiocarbamate treated resin was packed in the column. Each polyethylene bottle was cleaned by soaking in (1 + 9) nitric acid for 2 days and then rinsed throughly with distilled deionized water before use. Collected mercury is readily eluted with a slightly acidic aqueous 5% thiourea solution. The resin can then be reused.

For the determination of inorganic mercury, the 10 mL aliquot of well-mixed effluent was placed in the reaction vessel, 10 mL of 30% (w/v) potassium hydroxide was added followed by 2 mL of the tin(II) chloride solution and the air flow was started immediately. This mixture was allowed to react for 30 s, during which time the mercury vapour generated passed through the quartz gas cell in an atomic absorption spectrometer.

For the determination of total mercury, the same procedure was used, except for reduction with the tin(II) chloride Cd(II) chloride mixture (10%–1%), instead of tin(II) chloride alone. The peak heights were again measured. The total mercury minus the inorganic mercury gives an estimate of the organic mercury.

The total blank was determined by carrying out the complete procedure of analysis with 20 litre of distilled-deionized water. Five replicate measurements gave mean blanks of 0.07 ± 0.05 ngL^{-1} and 0.15 ± 0.06 ngL^{-1} for inorganic and total mercury, respectively.

Typical mercury contents found in unfiltered samples of Japanese rivers by this method were in the range 9 to 15 ngL^{-1} with a standard deviation of about 0.4 ngL^{-1}, 35% to 50% of which was organically bound. In excess of 90% recovery was obtained in spiking experiments in which mercuric chloride and methylmercuric chloride were added to river water samples.

Possible interferences are other ions, amino acids and naturally-occurring chelating agents which could affect the preconcentration, desorption and reduction steps. No interference was produced in the determination of 0.1 pg of mercury(II) by the presence of at least 1 ng of each of the following ions or substances added to 5- L aliquots of river water: Cr^{3+}, Mg^{2+}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Au^{3+}, Fe^{3+}, Al^{3+}, Zn^{2+}, $PO_4{}^{3-}$, Cl^-, $CO_3{}^{2-}$, $NO_3{}^-$, $SO_4{}^{2-}$, silicate, cysteine and humic acid.

Oda and Ingle (1981a) have described a method which with a detection limit of about 5 MgL^{-1} using a 1 mL sample for the determination of both forms of mercury. The inorganic and organic mercury are selectively reduced by stannous chloride and sodium borohydride and volatilized elemental mercury determined by cold vapour atomic absorption spectrometry. This procedure is much faster than other procedures because no time-consuming sample extraction, sample decomposition, or chromatographic separation steps are required.

The accuracy of organomercury determination is better than in many procedures because the organomercury concentration is not determined by difference which is difficult if most of the total mercury is inorganic mercury.

These workers showed that nitric acid is not suitable for fixing samples between sampling and analysis as it alters the ratio of organic to inorganic mercury and, indeed, causes a 25% loss of total mercury during 8 days sample storage. For extended periods of sample storage a fixing reagent comprising 10 mg/L potassium chromate and 50 mL/L nitric acid should be used. Even with this reagent the organic to inorganic mercury ratio will alter during storage but total mercury remains unaltered. The information on speciation can be obtained only when the sample is analysed immediately after fixing.

Ahmed and Stoeppler (1986) used cold vapour atomic absorption spectrometry to carry out ultraviolet light stability studies on methylmercury in water.

Gas chromatography

Nishi and Horimoto (1968, 1970) determined trace amounts of methyl, ethyl and phenyl mercury compounds in river waters and industrial effluents. In this procedure the organomercury compound in 100–500 mL of sample is extracted with 0.1% L-cysteine solution, and recovered from the complex by extracting with 1 mL of benzene in the presence of hydrochloric acid and submitted to gas chromatography using a stainless-steel column (197 cm × 3 mm) packed with 5% of diethylene glycol succinate on Chromosorb W (60–80 mesh) with nitrogen as carrier gas (60 mL per minute) and an electron-capture detector.

The calibration graph is rectilinear for less than 0.1 μg of mercury compound per mL of the cysteine solution. This method is capable of determining mercury down to 0.4 μgL^{-1} for the methyl and ethyl derivatives and 0.86 μgL^{-1} for the phenyl derivative.

The above method has been modified by the addition of mercuric chloride to displace sulphuric bonded methylmercury groups for the determination of methylmercury(II) compounds in aqueous media containing sulphur compounds that affect the extractions of mercury. The modified method is capable of handling samples containing up to 1 μgL^{-1} of various organic and inorganic sulphur compounds.

Ealy *et al.* (1973) have discussed the determination of methyl, ethyl and methoxymercury halides in water and fish. The mercury compounds were separated from the samples by leaching with M-sodium iodide for 24 hours and then the alkylmercury iodides were extracted into benzene. These iodides were then determined by gas chromatography of the benzene extract on a glass column packed with 5% of cyclohexane—succinate on Anakron ABS (70–80 mesh) and operated at 200°C with nitrogen (56 mL/min) as carrier gas and electron capture detection. Good separation of chromatographic peaks were obtained for the mercury compounds as either chlorides, bromides or iodides. The extraction recoveries were monitored by the use of alkyl mercury compounds, labelled with 208 Hg.

Cappon and Crispin-Smith (1977) have described a method for the extraction, clean-up and gas chromatographic determination of organic (alkyl- and aryl-) and inorganic mercury in biological materials. Methyl-, ethyl-, and phenylmercury are first extracted as the chloride derivatives. Inorganic mercury is then isolated as methylmercury upon reaction with tetramethyltin. The initial extracts are subjected to thiosulfate cleanup, and the organomercury species are isolated as the bromide derivatives. Total mercury recovery ranges between 75 and 90% for both forms of mercury, and is assessed by using appropriate ^{203}Hg-labelled compounds for liquid scintillation assay. Specific gas chromatographic conditions allow detection of mercury concentrations of 1 μgL^{-1} or lower. Mean deviation and relative accuracy average 3.2 and 2.2% respectively.

Another application of gas chromatography to natural water analysis is that of Longbottom (1972) who uses a Coleman 50 Mercury Analyser System, as a gas chromatographic detector. A mixture of dimethyl, diethyl-, dipropyl- and dibutylmercury (1 ng of each) was separated on a 2 m column packed with 5% of DC-200 and 3% of QF-1 on Gas-Chrom Q and temperature programmed from 60° to 180° at 20° per min. The mercury detector system was used after the column effluent had passed through a flame ionisation detector; the heights of the resulting four peaks were related to the percentages of mercury in the compounds.

Dialkylmercury compounds in river waters were also separated in a glass column (1.86 m × 2 mm) packed with 5% of DC-200 plus 3% of QF-1 on Gas Chrom Q (80 to 100 mesh) and temperature programmed from 70° to 180° at 20° per min, with nitrogen as carrier gas (50 mL per min). The mercury compound eluted from the column was burnt in a flame ionisation detector, and the resulting free mercury was detected by a Colman Mercury Analyzer MAS-50 connected to the exit of the flame ionisation instrument; down to 0.1 ng of mercury could be detected. River water (1 L) was extracted with pentane-ethyl ether (4:1) (2 × 60 mL). The extract was dried over sodium sulphate evaporated to 5 mL and analysed as above.

Mushak *et al.* (1973) have described a gas chromatographic method for the determination of inorganic mercury in water, urine and serum. The inorganic mercury in the sample is reacted with lithium pentafluorobenzenesulphinate arylating reagent which converts inorganic mercury to arlymercury compounds. The arylmercury compounds as well as any other organomercury compounds present in the original sample are then determined by a technique based on that described by Westoo (1967, 1968) involving gas chromatography on columns of 10% of Dexsil-300 on Anakrom SD (70–80 mesh) and of Durapak Carbowax 400 on Porasil F (80–100 mesh). The recoveries and precision (standard deviations) were for water 70.5% (6.8), urine 81.4% (10.5) and serum 51% (9.4). The limit of detection of inorganic mercury achieved in this method was 20 μgL^{-1}.

Jones and Nickless (1973, 1974) have devised methods for the determination of inorganic mercury based on conversion to an organomercury compound with arene sulphinites and formation of the trimethylsilyl derivatives, both of which are amenable to gas chromatography.

Organomercury in sea water:
Classical methods

Fish frequently have 80–100% of the total mercury in their bodies in the form of methylmercury regardless of whether the sites at which they were caught were polluted with mercury or not. Methylmercury in the marine environment may originate from industrial discharges or be synthesised by natural methylation processes. Fish do not themselves methylate inorganic mercury, but can accumulate methylmercury from both sea water and food. Methylmercury has been detected in sea water only from Minamata Bay, Japan, an area with a history of gross mercury pollution from industrial discharge. It has been found in some sediments but at very low concentrations, mainly from areas of known mercury pollution (Olafssen, 1974). It represents usually less than 1% of the total mercury in the sediment and frequently less than 0.1% (Olsen and Cooper, 1976; Davies *et al.* 1979). Micro-organisms within the sediments are considered to be responsible for the methylation (Olsen and Copper, 1976), and it has been suggested that methylmercury may be released by the sediments to the sea water, either in dissolved form or attached to particulate material and thereafter rapidly taken up by organisms.

Compeau and Bartha (1983) studied the effects of sea salt anions on the formation and stability of methylmercury. The effect of different anions in sea water on the formation and stability of methylmercury was investigated. The extent of methylation was reduced in the presence of sulphide under anaerobic conditions and of bicarbonate under both aerobic and anaerobic conditions; other anions had no significant effect. In the dark monomethylmercuric chloride was chemically stable in the presence of all the anions tested.

Davies *et al.* (1979) set out to determine the concentrations of methylmercury in sea water samples much less polluted than Minamata Bay, viz the Firth of Fourth, Scotland. They described a tentative bioassay method for determining methylmercury at the 0.06 μg g^{-1} level. Mussels from a clean environment were suspended in cages. A small number were removed periodically, homogenized and analyzed for methylmercury. The rate of accumulation of methylmercury was determined, and by dividing this by mussel filtration rate, the total concentration of methylmercury in the sea water was calculated.

The methylmercury concentration in caged mussels increased from low levels (less than 0.01 μg g^{-1}) to 0.06–0.08 μg g^{-1} in 150 days giving a mean uptake rate of 0.4 ng g^{-1}d^{-1}. The average percentage of total mercury in the form of methylmercury increased from less than 10% after 20 days to 33% after 150 days.

Davies *et al.* (1979) calculated that the total methylmercury concentration in the sea water as 60 pg L^{-1} (i.e., 0.1–0.3% of the total mercury concentration), as opposed to 32 ng L^{-1} methylmercury found in Minamata Bay, Japan.

Stoeppler and Matthas (1978) have made a detailed study of the storage behaviour of methylmercury and mercuric chloride in sea water. They recommend that samples spiked with inorganic and/or methylmercury chloride be stored in carefully cleaned glass containers acidified with hydrochloric acid to pH 2.5. Brown glass bottles are preferred. Storage of methylmercury chloride should not exceed 10 days. Sipos *et al.* (1980) used subtractive differential pulse voltametry at a twin gold electrode to determine mercury levels in sea water samples taken from the North Sea.

Olsen (1977) has reported that up to 20% losses of mercury occur during storage of sea water samples for up to 96 h prior to analysis. They attributed losses to either a salting out effect which increased the volatilization of mercury or by chemical reactions which either increase the volatility of or precipitate mercury.

Atomic absorption spectrometry

Fitzgerald and Lyons (1973) have described flameless atomic absorption methods for determining organic mercury compounds in coastal and sea waters. These workers used ultraviolet light in the presence of nitric acid to decompose the organomercury compounds. In this method two sets of 100 mL samples of natural water are collected in glass bottles and then adjusted to pH 1.0 with nitric acid. One set of samples is analysed directly to give inorganically bound mercury, the other set is photo-oxidised by means of ultra-violet radiation to destroy organic material and then analysed to give total mercury. The element is determined by a flameless-atomic-absorption technique, after having been collected on a column of 1.5% of OV-17 and 1.95% of QF-1 on Chromosorb W-HP (80–100 mesh), cooled in a liquid-nitrogen bath and then released by heating the column. The precision of analysis is 15%. It was found that up to about 50% of the mercury present in river and coastal waters was organically bound or associated with organic matter.

A method developed by Dean and Rues (1978) is suitable for the determination of 10–100 ng L^{-1} dissolved inorganic mercury and those organomercury compounds which form dithizonates in saline, sea and estuary waters. In this method, inorganic mercury is extracted from the acidified saline water as its dithizonate into carbon tetrachloride. Organomercury compounds may also be extracted by the carbon tetrachloride, but not all these compounds form dithizonates and those which do not (e.g., dialkylmercury compounds) may not be determined by this method. Mercury is recovered from the organic extracts by back extraction with acid and determined by stannous chloride reduction followed by cold vapour atomic absorption spectrometry.

Millward and Bihan (1978) studied the effect of humic material on the determination of mercury by flameless atomic absorption spectrometry. In both sea and fresh water, association between inorganic and organic entities takes place within 90 min at pH values of 7 or above, and, consequently, the organically bound mercury is not detected by an analytical method designed for inorganic mercury. The amount of detectable mercury was related to the amount of humic material added to the solutions. However, total mercury could be measured after exposure to ultraviolet radiation under strongly acid conditions.

Agemian and Chau (1978) showed that organomercurials could be quantitatively decomposed by ultraviolet radiation and that the rate of decomposition of organomercurials increased rapidly in the presence of sulfuric acid and with increased surface area of the ultraviolet irradiation. They developed a flow-through ultraviolet digestor which had a delay time of 3 min to carry out the photooxidation in the automated system. The ultraviolet radiation has no effect on chloride. The method, therefore, can be applied to both fresh and saline waters without the chloride interference. With an atomic absorption spectrometric finish this method was capable of determining down to 0.02 $\mu g L^{-1}$ mercury.

Yamagami *et al.* (1980) evolved a technique involving amalgamation of methylmercury in sea water on to gold followed by atomic absorption spectrophotometry for the determination of picogram quantities of the organomercury compound. Samples of sea water, groundwater and river water were analysed for methylmercury and total mercury. Methylmercury is extracted with benzene and concentrated by a succession of three partitions between benzene and cysteine solution. Total mercury is extracted by wet combustion of the sample with sulphuric acid and potassium permanganate. The proportion of methylmercury to total mercury in the coastal sea water sampled was a round 1%.

Graphite furnace atomic absorption spectrophotometry has also been applied to the determination of trace levels of divalent mercury in inorganic and organomercury compounds in sea water. Filippelli (1984) has described a technique in which mercury is first preconcentrated using the ammonium tetramethylenedithiocarbamate (ammonium pyrrolidine-dithiocarbamate)—chloroform system and then determined by graphite furnace atomic-absorption spectrometry. The technique is capable of detection mercury(II) in the range 5–1500 ng in 2.5 mL of chloroform extract and can be adapted to detect subnanogram levels. Atmospheric pressure helium microwave-induced plasma emission spectrometry has been used as an element-selective detector for gas chromatography of organomercury compounds in sea water (Tanabe *et al.*, 1981).

Chiba *et al.* (1982), used atmospheric pressure helium microwave induced plasma emission spectrometry with the cold vapour generation technique combined with gas chromatography for the determination of methylmercury chloride, ethylmercury chloride and dimethylmercury in sea water following a 500 fold preconcentration using a benzene-cysteine extraction technique.

The analysis system consisted of a Shimsdzu QC-6A gas chromatograph, a chemically deactivated four-way valve for solvent ventilation, a heated transfer tube interface, a Beenakker-type TM_{010} microwave resonance cavity, and an Ebert-type monochromator (0.5 m focal length).

The dual column gas chromatograph was equipped with a thermal conductivity detector. The interface between the gas chromatograph and the discharge tube of the microwave-induced plasma detector is constructed from a chemically deactivated four-way valve and a heated transfer tube. The gas chromatographic columns and optimum operating conditions are summarized in Table 2. As is seen in Table 2, the diethylene glycol succinate column was used for the measurement of methylmercury chloride and ethylmercury chloride and the OV-17 column for that of dimethylmercury. The former column was treated with dimethylsilane and potassium bromide in order to deactivate the surface.

The TM_{010} microwave cavity is constructed from pure copper metal. The microwave generator, which provides 20–200 W of microwave power at 2.45 GHz, is run at 75 W forward power. The width and the height of both monochromator entrance and exit slits are 10 µm and 1 mm, respectively. A photomultiplier tube with low dark current and high gain over a wide wavelength region is used as a detector. The measurement of mercury is carried out at 253.7 nm mercury line.

The flow rate of carrier helium gas is adjusted at 80 mL min^{-1} for both columns, and then the plasma ignited. About 30 min later, the plasma and the temperature of the gas chromatograph stabilize. The adjustments of wavelength and observation position in the plasma are performed as follows. An appropriate concentration of methylmercury chloride standard solution (1–2 µL) is injected very slowly into the OV-17 column, and a broad mercury peak appears. During the appearance of the peak, wavelength and observation position (both vertical and horizontal) are adjusted quickly.

The chromatograms were detected with the thermal conductivity and the microwave-induced plasma detectors in series. When the microwave-induced plasma detector was used as a detector, the emission signals were monitored at 253.7 nm, and the solvent was vented through a four-way valve before reaching the microwave induced plasma detector.

The column packed with OV-17 used for the measurement of dimethylmercury was optimized in terms of carrier gas flow rate and column temperature.

Detection limit and standard deviation date obtained for these organomercury compounds without preconcentration are shown in Table 3.

The total extraction efficiency involved in the three stages of the extraction of methylmercury chloride from sea water by the cysteine-benzene extraction technique was reproducible at 42% for a 500 fold concentration giving a detection limit of 0.4 ngL^{-1} and a relative standard deviation of 6% at the 20 ngL^{-1} level (Table 4).

Summarizing, it can be seen that in natural and sea waters organomercury compounds can be speciated and determined in amounts down to 10 ng^{c}L^{-1}, thereby meeting even the work searching present day requirements.

Organomercury in soils and river sediments

In lakes, streams and rivers, mercury can collect in the bottom sediments, where it may remain for a long time. It is difficult to release this mercury from the matrices for analysis.

Mercury is also found in soil as a result of applications of mercury containing compounds, or sewage contaminated with traces of mercury.

Table 2. Operating condition for the gas chromatograph.

	Conditions for determination of	
	CH_3HgCl and C_2H_5HgCl	$(CH_3)_2Hg$
Column	Pyrex, 1 m × 3 mm i.d.	Pyrex 3 m × 3 mm i.d.
Column packing	15% DEGS[a] on 80/100 mesh Chromosorb W	3% OV-17on 80/100 mesh Uniport HP
Column Temp. °C.	160	70
Injector Temp. °C.	180	130
Detector Oven Temp °C.	180	130
Transfer tube Temp °C.	190	140
Carrier Gas	helium	helium
Carrier gas flow Rate mL/min.	80	80
Detector	Ratharometer	Ratharometer.

[a] DEGS = diethylene glycol succinate.

Table 3. Analytical figures of merit in the determination of alkylmercury compounds by the GC/MIP System.

Compound	Detection limit μgL^{-1}	rel std dev,[a] %	Dynamic range, decades
methylmercury chloride	0.09 (0.02 pg/s)	2.0	5
ethylmercury chloride	0.12 (0.02)pg/s)	2.0	5
dimethylmercury	0.40 (0.03 pg/s)	3.0	4.5

[a]Measured with 1 μgL^{-1} of mercury for each compound.

Classical procedures

In an earlier publication Kimura and Miller (1962) described a procedure for the determination of organomercury, (methylmercury, ethylmercury and phenylmercury compounds) and inorganic mercury in soil. In this method, the sample is digested in a steam bath with sulphuric acid (1.8 N) containing hydroxy-ammonium sulphate, sodium chloride and, if high concentrations of organic matter are present, potassium sulphate solution. Then 50% hydrogen peroxide is added in portions with vigorous mixing until the solution becomes blue-green to yellow in colour, then heating is continued to decompose excess hydrogen peroxide. Potassium permanganate is added until the pink colour persists for 15 min then the cooled solution reduced with hydroxyammonium sulphate dissolved in sodium chloride. Air is then passed through this solution to sweep out elemental mercury into an absorber containing potassium permanganate in dilute sulphuric acid and stannous chloride. Following reduction with hydroxy-ammonium sulphate and acidification with dilute sulphuric acid, mercury is determined in a chloroformic dithizone extract of this solution spectrophotometrically at 605 nm.

In a similar procedure (Society of Analytical Chemistry, 1965) the sediment is wet oxidized with dilute sulphuric acid and nitric acids in an apparatus in which the vapour from the digestion is condensed into a reservoir from which it can be collected or returned to the digestion flask as required. The combined oxidized residue and condensate are diluted until the acid concentration is 1 N and nitrate is removed by addition of hydroxylammonium chloride with boiling. Fat is removed from the cooled solution with carbon tetrachloride and the liquid is then extracted with a solution of dithizone in carbon tetrachloride. The extract is shaken with 0.1 N hydrochloric acid and sodium nitrite solution and, after treatment of the separated aqueous layer with hydroxylammonium chloride a solution of urea and then EDTA solution are added to prevent subsequent extraction of copper. The liquid is then extracted with a 0.01% solution of dithizone in carbon tetrachloride and mercury estimated in the extract spectrophotometrically at 485 nm.

Table 4. Analytical characteristics of the solvent extraction technique for methylmercury determination.

Sample Treatment	Sample Volume injected into GC, μL	detection limit, ng/L	extraction efficiency, %
without extraction	4	90	
with extraction	4	0.4	42

Kimura and Miller (1964) also described the following methods for the determination in soil samples of extractable organic mercury, total mercury and extractable ionic mercury.

Extractable phenyl- and alkylmercury compounds. Phenyl and alkylmercury compounds are extracted from about 1 g soil by shaking for 2 h with 25 ml 0.1 M phosphate pH 8 buffer containing 6 mg thiomalic acid, added just prior to use, and analysed after dilution of a 5 mL aliquot of the centrifuged extract with 5 mL water, and acidification with 5 ML 9 N hydrochloric acid containing 150 mg hydroxylammonium chloride. The final determination is made by the dithizone microprocedure of Miller and Polley (1954). Diphenyl- and dialkylmercury compounds are extracted from 1 g soil by shaking for 2 h with 10 mL chloroform and analysed by cleaving the disubstituted mercurial to give an aryl- or alkylmercury salt, using 9 N or 12 N hydrochloric acid, followed by the dithizone microprocedure (Polley and Miller, 1955).

Ionic mercury. Ionic mercury is extracted from about 1 g soil by shaking for 2 h with each of two 25 mL portions of 2 M sodium chloride. The combined centrifuged and filtered (using 1 M sodium chloride for washing) extract is analysed by the procedure of Polley and Miller (1955).

Total mercury. Total mercury is determined in soils containing phenylmercury acetate and or ethylmercury acetate using the method described by Polley and Miller (1955). Total mercury is determined in soils containing methylmercury chloride and methylmercury dicyanamide by the method described by Kimura and Miller (1962).

Kimura and Miller (1960) have also studied the decomposition of organic fungicides in soil to mercury vapour and to methyl- or ethylmercury compounds and devised methods for the determination of these compounds in the vapours liberated from the soil sample. The mixed vapours of mercury and organomercury compounds is passed successively through bubblers containing a sodium carbonate—diabasic sodium phosphate solution which absorbs 45–99% of organic mercury and through an acidic potassium permanganate solution to absorb inorganic mercury vapour. In both cases the mercury in the scrubber solution is determined photometrically at 605 nm with dithizone.

A disadvantage of all these procedures is that the lowest concentration of mercury that can be determined in the soil on sediment samples is of the order of 0.05-1 mg per kg. These high detection imits are in part due to high blanks caused by the multiplicity of digestion reagents used in the procedures. Several investigators have liberated mercury from soil and sediment samples by application of heat to the samples and collection of the released mercury on gold surfaces. The mercury was then released from the gold by application of heat or by absorption in a solution containing oxidizing agents (Leong and Ong, 1971).

Bretthaur *et al.* (1974) and Anderson *et al.* (1971) described a method in which samples were ignited in a high-pressure oxygen-filled bomb. After ignition, the mercury was absorbed in a nitric acid solution. Pillay *et al.* (1971) used a wet-ashing procedure with sulfuric acid and perchloric acid to digest samples. The released mercury was precipitated as the sulfide. The precipitate was then redigested using aqua regia.

Feldman (1974) digested solid samples with potassium dichromate, nitric acid, perchloric acid and sulfuric acid. Bishop *et al.* (1973) used aqua regia and potassium permanganate for digestion.

The approved U.S. Environmental Protection Agency (1974) digestion procedure requires aqua regia and potassium permanganate as oxidants.

These digestion procedures are slow and often hazardous because of the combination of strong oxidizing agents and high temperatures. In some of the methods, mercuric sulfide is not adequately recovered. The oxidizing reagents, especially the potassium permanganate, are commonly contaminated with mercury, which prevents accurate results at low concentrations.

Atomic absorption spectrophotometry

Earlier work on the determination of total mercury in river sediments includes that of Iskandor *et al.* (1972). Iskandor applied flameless atomic absorption to a sulphuric acid nitric acid digest of the sample following reduction with potassium permanganate, potassium persulphate and stannous chloride. A detection limit of 1 $\mu g\ kg^{-1}$ is claimed for this somewhat laborious method. Langmyhr and Aamodt (1976) determined amounts of organic mercury in river sediments using cold vapour atomic absorption spectrometry.

A method (AOAC, 1970) has been described for the determination of down to 2.5 $\mu g\ kg^{-1}$ alkylmercury compounds and inorganic mercury in river sediments. This method uses steam distillation to separate methylmercury in the distillate and inorganic mercury in the residue. The methylmercury is then determined by flameless atomic absorption spectrophotometry and the inorganic mercury by the same technique after wet digestion with nitric acid and potassium permanganate. The well known adsorptive properties of clays for alkylmercury compounds does not cause a problem in the above method. The presence of humic acid in the sediment did not depress the recovery of alkylmercury compounds by more than 20%. In the presence of metallic sulphides in the sediment sample the recovery of alkylmercury compounds decreased when more than 1 mg of sulphur was present in the distillate. The addition of 4 N hydrochloric acid, instead of 2 N hydrochloric acid before distillation completely eliminated this effect giving a recovery of 90 to 100% (Leong and Ong, 1971).

This excellent method was sufficiently sensitive to determine 0.02 mg kg^{-1} methyl mercury and 9 mg kg^{-1} inorganic mercury in river sediment samples.

Jirka and Carter (1978) have described an automated determination of down to 0.1 mg kg^{-1} total mercury in river sediment samples with a precision of 0.13 to 0.21 μg Hg kg^{-1} at the 1 mg Hg kg^{-1} level and with standard deviations varying from 0.011 to 0.02 mg Hg kg^{-1} (i.e., relative standard deviations of 8.4 to 12%). At the 17.2 to 32.3 mg Hg kg^{-1} level in sediments recoveries in methyl mercuric chloride spiking studies were between 85 and 125%. This method is based on the automated procedure of El Awady *et al.* (1976) for the determination of total mercury in waters and wastewaters in which potassium persulfate and sulfuric acid were used to digest samples for analysis by the cold-vapour technique. These workers proved that the use of potassium permanganate as an additional oxidizing agent was unnecessary.

Aromatic organic compounds such as benzene, which are not oxidized in the digestion, absorb at the same wavelength as mercury. This represents a positive interference in all cold-vapour methods for the determination of mercury. For samples containing aromatics (i.e., those contaminated by some industrial wastes), a blank analysis must be performed and the blank results must be subtracted from the sample results. The blank analysis is accomplished by replacing the potassium persulphate reagent and the stannous chloride reagent with distilled water and reanalyzing the sample.

Umezaki and Iwamoto (1971) have reported that organic mercury can be reduced directly with stannous chloride in the presence of sodium hydroxide and copper(II) the determination of organic mercury can be simplified, particularly if the reagent used for back-extraction does not interfere with the reduction of organic mercury. Matsumaya and Takahasi (1976) found that back-extraction with an ammoniacal gluthathione solution was satisfactory. In this method, contamination only from the ammoniacal glutathione solution is expected. However, any inorganic mercury in this solution will be adsorbed on the glass container walls with a half-life about 2 d (i.e., the blank value becomes zero if the solution is left to stand for more than a week). This method for mercury in sediments does not distinguish between the different forms of organomercury. Down to 0.2 $\mu g\ kg^{-1}$ mercury in sediments can be determined by this method with a standard deviation of 0.03 $\mu g \cdot$

kg^{-1}. In this method, a large weight of sample (10–20 g) is extracted with hydrochloric acid for two days and organic mercury then extracted from the filtrate with benzene. Mercury is back-extracted from the benzene with aqueous ammoniacal gluthatione. This extract is then added to an aqueous solution containing sodium hydroxide, cupric sulphate and stannous chloride and the elemental mercury released is swept off with nitrogen and, in a further concentration step is collected on gold granules. Finally, the granules are heated at 500°C to release mercury which is determined by flameless atomic absorption spectrophotometry at 253·7 nm.

Gas chromatography

Bartlett *et al.* (1977) used the method of Uthe *et al.* (1970, 1971) for determining methylmercury. Sediment samples of 2–5 g were extracted with toluene after treatment with copper sulphate and an acidic solution of potassium bromide. Methylmercury was then back-extracted into aqueous sodium thiosulphate. This was then treated with acidic potassium bromide and copper sulphate following which the methylmercury was extracted into pesticide grade benzene containing approximately 100 μgL^{-1} of ethyl mercuric chloride as an internal standard. The extract was analysed by electron capture gas chromatography using a Pye 104 chromatograph equipped with 65 Ni detector. The glass column (1 m × 0.4 cm) was packed with 5% neopentyl glycol adipate on Chromosorb G (AW-DMCS). Methylmercury was measured by comparing the peak heights with standards of methyl mercuric chloride made up in the ethylmercury benzene solution. The detection limit was 1–2 μg kg^{-1} (Table 5).

Ealy *et al.* (1973) determined methyl, ethyl and methoxyethyl mercury compounds in sediments by leaching the sample with sodium iodide for 24 hours and then extracting the alkylmercury iodides into benzene. These iodides are then determined by gas chromatography of the benzene extract on a glass column packed with 5% of cyclohexylenedimethanol succinate on Anakrom ABS (70 to 80 mesh) operated at 200°C with nitrogen (56 mL · min^{-1}) as carrier gas and electron-capture detection (^{3}H foil). Good separation of chromatographic peaks is obtained for the mercury compounds as either chlorides, bromides or iodides.

Table 5. Typical GLC retention times for organomercury dithizonates. (I) 2% polethyleneglycol succinate on Chromosorb G (acid-washed, DMCS-treated, 60–80 mesh) in glass column 1.5m long, 3mm I.D.; carrier gas, nitrogen.

	Column Temperature (°C)				
Dithizonate	140	150	160	170	180
Methylmercury	3.8	2.8	2.2	1.6	1.2
Ethylmercury	6.6	4.6	3.6	2.7	2.0
Ethoxyethylmercury	17.0	11.6	8.7	6.2	4.9
Methoxyethylmercury	17.4	12.0	8.7	6.2	4.9
Tolylmercury	—	—	—	29.0	19.5
Phenylmercury	—	—	—	42.0	27.0

Bartlett *et al.* (1977) observed unexpected behaviour of methylmercury containing river Mersey sediments during storage. They experienced difficulty in obtaining consistent methylmercury values; supposedly identical samples analysed at intervals of a few days gave markedly different results. They therefore followed the levels of methylmercury in selected sediments over a period of time to determine if any change was occurring on storage. They found that the amounts of methylmercury observed in the stored sediments did not remain constant; initially there is a rise in the amount of methylmercury observed and then, after about ten days, the amount present begins to decline to levels which in general only approximate to those originally present. They have observed this phenomenon in nearly all of the Mersey sediments samples they examined. It was noted that sediments sterilised, normally by autoclaving at approximately 120°C, did not produce methylmercury on incubation with inorganic mercury suggesting a microbiological origin for the methylmercury. A control experiment was carried out in which identical samples were collected and homogenised. Some of the samples were sterilised by treatment with 40 g L^{-1} solution of formaldehyde. Several samples for both sterilised and unsterilised sediments were analysed at intervals and all of the samples were stored at ambient room temperature (18°C) in the laboratory. There is a difference in behaviour between the sterilised and unsterilised samples. This work suggests that the application of laboratory-derived results directly to natural conditions could, in these cases, be misleading; analytical results for day 10 if extrapolated directly might lead to the conclusion that natural methylmercury levels and rates of methylation are much greater than in fact they really are. Work in this area with model or laboratory systems needs to be interpreted with particular caution.

Organomercury in Plants and Crops

Classical procedures

Gutermann and Lisk (1960) suggested a method of overcoming mercury losses during decomposition of mercury containing organic materials by adopting the Schöniger oxygen flask combustion technique. They determined mercury in apples by first drying the apple tissue on cellophane, in vacuo, overnight. The dry material is then combusted in an oxygen-filled flask and the combustion products absorbed in 0.1 N hydrochloric acid. Mercury is extracted with dithizone and determined spectrophotometrically. Recovery of 0.3–0.6 mg Hg kg^{-1} in apples by this procedure averaged 83.6%.

Atomic absorption spectrometry

Langmyhr and Aamodt (1976) have described a cold vapour atomic absorption spectrometric method for the determination of nanogram amounts of mercury in aquatic organisms.

Gas chromatography

Ealy *et al.* (1973) have discussed the determination of methyl, ethyl and methoxyethyl mercury(II) halides in environmental samples such as aquatic systems, seeds and fish. The mercury compounds were separated from the samples by leaching with M sodium iodide for 24 hours and then the alkylmercury iodides were extracted into benzene. These iodides were then determined by gas chromatography of the benzene extract on a glass column packed with 5% of cyclohexylene succinate on Anakrom ABS (70–80 mesh) and operated at 200°C with nitrogen (56 mL per min) as carrier gas and electron-capture detection. Good separation of chromatographic peaks were obtained for the mercury compounds as either chlorides, bromides or iodides. The extraction recoveries were monitored by the use of alkylmercury compounds labelled with 208 Hg.

Houpt and Compaan (1972) used emission spectrographic analysis for the identification of traces of organic matter containing halogens and mercury isolated from eggs and grass by gas chromatography. They transferred the gas chromatographic fractions sequentially, through a heated stainless-steel capillary tube, to a silica tube (3 mm id) in which they were submitted to a plasma discharge (2.45 MHz) in helium at 10 torr. The emission spectrum arising from the fragmentation, ionization and excitation of the organic molecule was then analysed with the aid of two monochromators, the intensities of the required analytical lines being measured photo-electrically. One monochromator was focused on a characteristic line (e.g., the 247.86 nm carbon line (as a chromatographic detector) and, when the intensity of this line is a maximum for any one fraction detected in the discharge-tube, a 10 s sweep over the range 200–600 mm was made by the other monochromator. Examination of the resulting complete spectrograms revealed the presence or absence of mercury, phosphorus, sulphur, chlorine, bromine, iodine. This method permits the determination of 5 pg of methylmercury in plant and biological samples.

Organomercury in Biological Materials

Classical methods

Earlier classical procedures are generally too insensitive and laborious and lack the specificity required to distinguish between different types of organomercury compounds and in many instances, do not even distinguish between organic mercury and inorganic mercury. Thus, in a typical method for determining mercury in biological tissue the tissue is digested with nitric and sulphuric acids and following the addition of sodium acetate and formalin the solution is electrolysed at 80°C using a zinc anode and graphite on copper cathode to collect the mercury. Following stripping of the mercury from the cathode with concentrated nitric acid, addition of slight excess of potassium permanganate and decomposition of excess permanganate with hydrogen peroxide the solution is treated with an excess of standard ferric alum solution:

$$Hg^{+} + Fe^{3+} \longrightarrow Hg^{2+} + Fe^{2+}$$

and excess ferric alum estimated by titration with 0.01 N ammonium thiocyanate. This method is capable of determining down to only 500 mg Hg kg^{-1} of tissue sample.

Various workers have described methods for the determination of mercury in tissues. Miller and Lillis (1958) have described methods for the determination of phenylmercury acetate in urine, kidney, liver, muscle, spleen and brain. For urine, the sample (containing 5–20 μg of phenylmercury acetate) is refluxed with N sodium hydroxide, cooled, and excess 5% potassium permanganate solution added. Then 30% hydroxylamine sulphate: aqueous ammonia (1:1) and 30% ammonium sulphamate solution are added. The mixture is cooled and sufficient 12 N hydrochloric acid added under the surface of the liquid with vigorous swirling to lower the pH to not greater than 1. After further cooling, the solution is shaken well with purified chloroform (11 mL) for one min., the chloroform layer washed with 1N hydrochloric acid and the washings rejected. The chloroform layer is separated, diluted with chloroform to 1 L mL and the extinction measured at 620 nm.

For kidney, liver, muscle or spleen, 1 g of the sample is treated as described above. Results obtained by these methods are accurate to within approximately ± 1 μg of the amount of phenylmercury compound present.

Gage (1961) has described a method for the trace determination of phenylmercury acetate in biological material. In this method an acidified aliquot of a 5% aqueous homogenizate of the tissue is extracted with benzene (20 mL). A 15 mL portion of the extract is shaken with 1% aqueous sodium sulphide solution and the evaporated aqueous layer is oxidized with potassium permanganate. To the oxidized solution, decolorized with hydroxyl-ammonium chloride solution, are added urea and EDTA; the pH is adjusted to 1.5. Chloroform is added and the solution is titrated with dithizone solution until the colour of the chloroform layer is intermediate between the orange of the mercury complex and the green of the dithizone solution. Recoveries of added phenylmercury salts and methylmercury salts from rat tissue and rat urine were low by up to 15% by this procedure, but concentrations down to 1 mg/kg can be measured. Inorganic mercury does not interfere.

Ashley (1959) has reviewed procedures for the determination of micro amounts of mercury in biological materials involving destruction of organic matter, use of dithizone for mercury extraction and the avoidance of the simultaneous extraction of copper. Ashley describes an absorptiometric method for determining the mercury-dithizone complex and also a photometric method in which the separated mercury is volatilized and its concentration in the vapour determined by means of a detector cell with a monochromatic light source, the output of a photocell being measured and referred to calibration measurements.

Miller and Wachter (1950) have used a procedure based on reduction and digestion with sulphuric acid for the determination of low concentrations of mercury in biological materials.

Stuart (1978) used ^{203}Hg-labeled methyl mercuric chloride for *in-vivo* labeling of fish to study the efficacy of various wet ashing procedures.

Atomic absorption spectrometry

Various workers have discussed the application of this technique to the determination of organomercury and inorganic mercury in various biological materials (Hatch and Ott, 1968; Goulden and Afghan, 1980) and in fish (Collett *et al.*, 1980; Stainton, 1971; U.S. Environmental Protection Agency, 1972; Hendzel and Jamieson, 1976; Agemian and Cheam, 1978). Methylmercury compounds have been specifically dealt with by various workers (Aspilia and Carron, 1980; Society for Analytical Chemistry, 1977; Davies, 1978; Jones and Nickless, 1978; Capelli *et al.*, 1979). Shum *et al.* (1979) carry out a toluene extraction of the fish, then treat the extract with dithizone to form methylmercury dithizonate which is then determined in amounts down to 0.08 mg Hg kg^{-1} by graphite furnace atomic absorption spectroscopy. The determination of organomercury in solid environmental samples such as fish requires low temperature preparation techniques to prevent losses of these volatile compounds. Thus, *Uthe et al.* (1970, 1971) use a sulphuric and nitric acid digestion at 58°C to extract mercury from fish tissue. After digestion the extract is treated with an excess of 6% potassium permanganate solution and left 18 hours. Precipitated manganese is then dissolved by addition of 30% hydrogen peroxide. Mercury is then released from the sample using the stannous sulphate hydroxylamine reduction system and estimated by flameless atomic absorption spectrometry. Application of this method to the determination of methyl mercuric chloride and mercuric chloride in fish samples showed that it was applicable to mercury levels down to 0.1 mg Hg kg^{-1} fish with a standard deviation of 0.008 at the 0.1 mg kg^{-1} level and 0.6 at the 9 mg kg^{-1} level. Other workers (Society for Analytical Chemistry, 1976, 1977; Agemian and Chau 1975) have used mixtures of hydrogen peroxide and sulphuric acid for the determination of organic matter prior to the determination of mercury by cold vapour atomic absorption spectrometry.

Whilst the method discussed above is sensitive enough in some applications, in many types of biological samples it is necessary to determine much lower levels of organomercury. Thus, whilst the environmental level of mercury in canned tuna or human hair is about 0.5 mg kg^{-1} the level in human urine is considerably lower (i.e., 0.5 μg kg^{-1}). Oda and Ingle (1981a) have described a procedure for the determination of these levels of organomercury and inorganic mercury in tuna fish, hair and urine. They describe a speciation scheme for ultra trace levels of mercury in which inorganic and organomercury are selectively reduced by stannous chloride and sodium borohydride, respectively. The volatilized elemental mercury is determined by cold vapour atomic absorption spectroscopy. The samples were first digested by heating in 2 dram capped vials at 90°C for 15–30 mins, urine (1 mL) or hair (20–60 mg) or tuna (0.1–0.3 g) with 2.5 mL 10 M potassium hydroxide.

After digestion, the resultant solutions were centrifuged to separate remaining particulates and the supernatant liquid was decanted into a 100 mL volumetric flask. The vials were washed three to four times with 1% (w/v) concentrated nitric acid with centrifuging before each decant. When the sample had been transferred, 7.5 mL of concentrated nitric acid and 1 mL of 1% (w/v) potassium dichromate were added and the remainder of the volume was diluted with 1% (w/v) sodium chloride. These results are tabulated in Table 6 which shows that the requirement of a detection limit of 0.5 μg kg^{-1} for mercury in urine has been met.

Total concentration of mercury in hair (relative standard deviations of 6–11%) was fairly consistent with existing data which indicated mercury concentrations in hair ranging from 1 to 25 mg kg^{-1} for samples from rural to industrial areas. About half of the mercury found was in the organic form concentrated by the body whilst the other half was probably in the form of externally absorbed Hg^{2+}.

Tuna samples showed about 0.5 mg kg^{-1} total mercury contamination which is approximately normal for canned tuna. This is also the upper limit allowed by the United States Food and Drug Administration. About 92% of the tuna appears as organomercury (probably

Table 6. Analysis of hair, urine and tuna.

Sample	Amount of Hg II ng/g Inorganic	Organic	Total
urine	3.2	1.1	4.3
urine	2.9	0.80	3.7
hair	2.1×10^3	1.9×10^3	4.0×10^3
hair	2.3×10^3	2.0×10^3	4.3×10^3
tuna	35	4.1×10^2	4.5×10^2
tuna	39	4.4×10^2	4.8×10^2

mainly methylmercury). Relative precisions were 18 and 7% for inorganic and organomercury, respectively. The relative precision for the urine measurements was about 5 and 10% for inorganic and organomercury, respectively. The inorganic form predominates as expected since most organomercury that is introduced to the body is absorbed or broken down before excretion. Vernon (1974) has discussed the application of microwave emission spectroscopy to the determination of volatile mercury compounds. Hanamura *et al.* (1983) applied thermal vapourization and plasma emission spectrometry to the determination of organomercury compounds and inorganic mercury in fish.

This method which operates at a plasma temperature of 5500 °K and utilizes the 253.65 nm mercury line has sufficient sensitivity to detect 0.1 μg mercury. The sample (0.25 mg) in a quartz crucible is heated over the range 25 to 450 °C at 15 °C min^{-1} and as each organomercury compound is volatilized it passes into a 2540 M H_2 plasma torch operated at 500W and it is determined.

The analytical results of the emission signal of the analyte species recorded as a function of the temperature of the sample, resulting in a plot similar to that obtained in differential thermal analysis. Because analyte species in the solid sample vaporize at different temperatures, each species produces a peak at a temperature characteristic of the analyte species and the sample type. The vapourized molecular species, introduced into the microwave induced plasma, appear as peaks at characteristic temperatures dependant primarily upon the molecular form and secondarily upon the sample composition.

Gas chromatography

This technique is essential if it is required to obtain an unequivocal identification of the type of organomercury compound occurring in a biological material as opposed to the total organic plus inorganic mercury content that is provided by atomic absorption spectrometry. An ideal combination is to use gas chromatography for separation of the organomercury compounds combined with a flameless atomic absorption or an inductively coupled plasma atomic absorption spectrometer as a detector system. Much of the original work on the application of gas chromatography to the identification and determination of organomercury compounds in biological materials were performed by Westhoo. In view of the comparatively high mercury content of fish found in Swedish lakes and rivers, Westhoo *et al.* has embarked on an extensive survey of the nature and the concentration of mercury in fish from these waters (Westhoo, 1966, 1967, 1968).

He describes a combined gas chromatographic and thin-layer chromatographic method (Westhoo, 1966, 1967) for the identification and determination of methylmercury compounds in fish, in animal foodstuffs, egg yolk, meat and liver. He has also used a combination of gas chromatography and mass spectrometry to identify and determine methylmercury compounds in fish (Westhoo *et al.*, 1970).

To extract organically bound mercury from muscle tissue of fish, Westhoo homogenized the fish with water and acidified with concentrated hydrochloric acid (1/5 of the volume of the suspension). Organomercuric compounds were then extracted in one step with benzene using the method described by Gage (1961). Methylmercury either originally present or added to the fish, could be extracted only with difficulty, when only a small amount of acid was added (e.g., at pH 1). From an aliquot of the benzene solution organomercury could be extracted with ammonium or sodium hydroxide solution, saturated with sodium sulphate for elimination of lipids. The yields were low and variable, but could be improved as described below.

Several workers have found that a clean-up procedure is necessary to remove fatty acid and amino acids, which could otherwise poison the gas chromatography column. The clean up is achieved by adding to the organic phase a reagent, such as sodium sulphide (Gage, 1961), cysteine (Westhoo, 1966, 1967, 1968), sodium thiosulphate or glutathione which forms a strong water soluble alkylmercury complex to extract the mercury complex into the aqueous phase. A halide is added to the aqueous phase, and the alkylmercury halides formed are re-extracted into an organic phase. Aliquots of this phase are finally injected into the gas chromatograph.

The mercury compound in the shellfish that caused the Kinimata disease (Japan) was methyl(methylthio)mercury. Westhoo concluded that it is reasonable to assume that methylmercury, if present in Swedish fish, should at least to some extent be a methylthio derivative. The Hg-S bond is stronger than Hg-NH or Hg-OH bonds. Accordingly, it prevents the formation of these bonds, which should be produced by the ammonium hydroxide solution and increase the solubility in water. Any methylthio group present should therefore be removed before the extraction with alkali.

Distillation of the benzene extract at reduced pressure at room temperature or at ordinary pressure at 80 °C to 1/10 of the original volume removed the factor that prevented an acceptable extraction by ammonium or sodium hydroxide solution (probably methanethiol and perhaps hydrogen sulphide). After the distillation and subsequent extraction with ammonium hydroxide solution the extract was acidified with hydrochloric acid and the organomercury compound was extracted once with benzene. After drying with anhydrous sodium sulphate, the benzene solution was ready for gas chromatography and, after concentration, also for thin-layer chromatography.

In the above procedure about 30% of the methylmercury was lost, mainly by unfavourable partition coefficients. In a model experiment of the benzene extraction of methylmercury from a hydrochloric acid solution, for instance 14% of the methylmercury was left in the water layer. The losses by partition are, however, characteristic of the compounds involved and reproducible. Consequently, they can be included in the calibration curve, thus disturbing the results only slightly. The yields can be increased by repeated extractions but good results are obtained with the above simple procedure. The calibration curve is based on the partition laws for methylmercury chloride, though some methylmercaptide and perhaps sulphide are probably present in fish. However, when hydrogen sulphide or methanethiol was added (30 μg per 5 μg mercury as methylmercury) to the aqueous phase before the first extraction, the 5 μg point was unaltered on the calibration curve. Large amounts of these sulphur compounds disturbed the analysis because they were not completely removed by the distillation.

When known amounts of methylmercury dicyandiamide were added to salt-water fish (frozen cod, Gadus morrhua, or haddock, Gadus aeglefinus), 82–95% of the additions were recovered.

Westhoo (1966, 1968, 1970) used an electron capture detector and 150 cm × 3 mm (60 in × $\frac{1}{8}$ in) stainless steel columns fitted with Carbowax 1500 (10%) on Teflon 6, and washed DMCS. Nitrogen was used as carrier gas and column temperatures were 130–145 °C. He identified methylmercury chloride in pike caught in the Baltic Ocean at concentrations between 0.07 and 4.4 mg kg^{-1} of fish.

Westhoo (1966) pointed out that if methylmercury attached itself to a sulphur atom by reaction with a thiol or hydrogen sulphide then the nonvolatile HgS compound produced would not be included in the determination. He has developed a modification to this method, to render it applicable to a wider range of foodstuffs (egg yolk and white, meat, liver, or fish), by binding interfering thiols in the benzene extract of the sample to mercuric ions added in excess or by extracting the benzene extract with aqueous cysteine to form the cysteine methylmercury complex.

Westhoo *et al.* (1970) reported results obtained by gas chromatography with electron capture and with mass spectrometric detection on a range of samples of fish (Table 7). Total mercury was also determined on these samples by neutron activation analysis (Sjosfraud, 1964). Results obtained by the three methods agree within ± 10% of the average value.

It was mentioned above that in the Westhoo method (1966) for organomercury compounds in fish low recoveries are obtained unless the benzene extract of the fish homogenate is boiled to remove volatile mercaptans prior to extraction with ammonia. This distillation procedure was assumed to remove volatile thio compounds binding part of the methylmercury and preventing its uptake into ammonia.

When, however, small amounts of methylmercury dicyanidiamide (less than 0.05 mg kg^{-1}) are added to meat, liver or egg yolk and analysed according to the above method, the methylmercury was completely lost in liver and egg yolk, and only partly recovered from meat. After addition of 10 mg kg^{-1} of methylmercury to meat or liver, most of it was recovered from meat, but only 5% from liver. Such a failure of the procedure can be expected; if the methylmercury in the neutralized extracts from these food-stuffs is firmly attached, exclusively or to a considerable extent, to thiol groups of nonvolatile compounds, but only if the methylmercury salts formed are insoluble in alkali solutions. Model experiments showed, in fact, that after the addition of excess of methanethiol or thiophenol to methylmercury chloride in benzene, an extraction with 2N aqueous ammonia or with sodium hydroxide did not extract the mercury compound from the benzene layer.

Westhoo (1968) examined problems associated with the determination of methylmercury salts in egg yolk and white with low methylmercury content, liver, aquaria sediments and sludge, also bile, kidney, blood, meat

Table 7. Comparison between results for mercury levels in fish flesh, determined by combination gas chromatograph-mass spectrometer, gas chromatograph with electron capture detector, and activation analysis.

	Methylmercury; mg Hg, kg^{-1} fish flesh		Total Hg, mg kg^{-1}
	GLC-mass spectrometric measurement of ^{202}Hg^{+}	Gas chromatography with electron capture detector	fish flesh Activation analysis
Pike 1	0.14	0.17	Not determined
Pike 2	0.55	0.54	0.59
Pike 3	2.53	2.57	2.70
Pike 4	0.43	0.41	0.39
Pike 5	0.49	5	0.54
Pike 6	0.75	0.66	0.63
Pike 7	0.72	0.70	0.66
Perch 8	3.19	3.29	3.12

and moss, in many of which mercury could not be accurately determined by the mercuric chloride method or the cysteine method. By combining these two methods, however, he was able to obtain good results with these various types of samples.

Excess mercuric ions were added to an aqueous liver suspension containing known amounts of a methylmercury salt. The analysis was performed according to the cysteine acetate modification. More than 100% of the methylmercury was recovered. When the acidified liver suspension containing mercuric ions was kept at room temperature overnight, the recovery increased, indicating a synthesis of methylmercury ions from mercuric ions by the liver under the conditions used.

For egg yolk with a low content of methylmercury the cysteine acetate procedure gave less than 90% recovery. With the combined method using cysteine and mercuric ions the recovery of methylmercury salt decreased almost to zero. But for sediments in aquaria and sludge, which similarly could not be analysed by the original cysteine acetate modification, the combined method gave good results.

A further attempt to improve the recovery in the cysteine acetate method involved a precipitation of the proteins in liver by molybdic acid. This increased the recovery of added methylmercury salt to about 90%. In egg yolk with a low content of methylmercury compounds, however, neither molybdic acid nor phosphomolybdic acid improved the results.

In a further attempt to overcome interference by organic sulphur, acidic sodium bromide has been used to extract organomercury as the bromide. Cuprous chloride was added to mask the sulphur compounds and displace any mercury bound to sulphur. In the presence of divalent sulphide ion, methylmercury compounds form bis (dimethylmercury) sulphide. This is insoluble in aqueous cysteine acetate which in the Westhoo procedure is added to extract the organomercury compounds from benzene solution in order to free them from interfering thiols. By the addition of cuprous chloride, the bis (dimethylmercury) compounds are converted into methylmercury chloride; this is extracted into benzene and then into aqueous glutathione. After acidification of the aqueous phase with hydrochloric acid, methylmercury chloride is re-extracted into benzene and determined by gas chromatography on a column (40 cm × 4 mm) packed with 25% of poly (diethylene glycol succinate) on Celite (60–80 mesh) or 10% of poly (butanediol succinate) on Chromosorb W (60–80 mesh) with nitrogen as carrier gas and electron-capture detection.

Following the classic work on fish analysis of Westhoo other workers (Cappon and Crispin-Smith, 1977; Bache and Lisk, 1971; Longbottom, 1972; Bye and Paus, 1979; Society for Analytical Chemistry, 1977; National Institute for Drug Abuse, 1978; Callum *et al.* 1981) developed gas chromatographic methods for the analysis of biological materials including fish, blood (Van Burg *et al.* 1974; Cappon and Crispin-Smith, 1977), urine (Cappon and Crispin-Smith, 1977), hair (Odanaka *et al.* 1983; Cappon and Crispin Smith, 1977), sediments (Cappon and Crispin-Smith, 1977), seeds (Van Burg *et al.*, 1974), grain (Cappon and Crispin-Smith, 1977), faeces (Cappon and Crispin-Smith, 1977), milk (Cappon and Crispin-Smith, 1977) and tissue (Callum *et al.*, 1981). Callum *et al.* (1981) have described the use of the proteolytic enzyme subtilisin Carlsberg Type A for the breakdown of human and animal tissues prior to the release of methylmercury. This enzyme has a high, nonspecific proteolytic activity, which gives excellent breakdown of protein. The yields obtained are greater than those found using the more conventional acid hydrolysis. Cysteine hydrochloride and cupric bromide were also incorporated into the separation scheme. The benzene extract was analyzed by gas chromatography with electron capture detection on a column comprising 5% ethylendigycol adipate on Gas Chrom Q at 155 °C.

Below is given a comparison of results obtained by this procedure compared with the lower values obtained by a method involving extraction with acidic sodium bromide alone.

Analysis of Tuna and Dry Fish:

		Methylmercury mg/kg		Coefficient of variation
	Method	—	Range	%
Tuna	Enzyme	0.693	0.661–0.734	3.7
	Sodium bromide	0.912	0.812–1.006	5.5
Fish homogenate	Enzyme	0.057	0.043–0.069	15.4
	Sodium bromide	0.346	0.329–0.362	3.6

Ealy *et al.* (1973) described a gas chromatographic method for the gas chromatographic determination of methyl, ethyl, and methoxyethyl mercury halides as their iodides in inorganic sediments, aquatic systems, seeds and fish.

Newsome (1971) has described a method for the determination of methylmercury in fish and cereal grain products in which the sample (10 g) is homogenised for 10 min with N hydrobromic acid — 2 N potassium bromide (60 mL) and filtered through glass wool. The combined filtrate is extracted twice with benzene. The combined benzene layers are extracted with a cysteine acetate solution, an aliquot of which is acidified with 48% hydrobromic acid and extracted with benzene. The benzene extracts are submitted to gas chromatography on a glass column (40 cm × 4 mm) packed with 2% of butanediol succinate on Chromosorb W (AW-DCMS) (100–120 mesh) operated at 120 °C with nitrogen as carrier gas (80–100 mL per min) and ^{3}H foil electron capture detector. The sensitivity of the method is in the range 0.01–0.90 mg Hg kg^{-1}. Mean recovery generally exceeds 95%. When direct gas chromatographic methods are used in the determination of alkylmercury compounds, interferences are often a problem, especially with the electron-capture detector, which is sensitive to other halogen compounds.

Longbottom (1972) cooled the gases from the flame ionization detector and led the gases through an atomic absorption spectrometer, but reported that it was less sensitive than the electron-capture detector for dialkyl mercury compounds. Bye and Paus (1979) solved this problem by leading the effluent from the gas chromatographic column through a steel tube in a furnace at a temperature at which the organic mercury molecules are cracked. The products are then led through a 10 cm quartz cuvette placed in the beam from a hollow-cathode lamp in an atomic absorption spectrometer. These workers state that for many of the earlier methods, the calibration curves are obtained from measurements of peaks from pure standard solutions of organic mercury compounds. They doubt the correctness of such a procedure, because it does not take into account the fact that appreciable amounts of mercury may be lost during the many extraction steps used in the analysis, especially in work with small samples and small volumes and state that a standard addition procedure should be used for calibration, and the standard organic mercury solution should be added as early as possible in the procedure.

A Perkin-Elmer model 800 gas chromatograph was used. The following operating conditions were satisfactory: column, 10% SP2300 on Chromosorb W 80–100 mesh; oven temperature 145 °C; inlet temperature 200 °C; carrier gas, nitrogen at a pressure of 3.5 kPa cm^{-2} measured at the g.c. inlet; flow rate, 90 ml min^{-1}.

The Perkin-Elmer model 303 atomic absorption spectrometer was run at the 254 nm mercury line. Deuterium background correction was essential. 0.5 g portions of frozen fish were transferred to a tissue grinder, 0.5 μL of IM copper sulphate solution was added to each, and 50–100 L of the standard mercury solution were added to two of the samples. Following a fairly detailed work-up procedure in which the sample is treated successively with bromine, sodium thiosulphate and potassium iodide a final benzene extract is obtained for gas chromatography.

Bye and Paus (1979) detected methylmercury (not ethyl or phenylmercury) in fish samples. Ranges up to 10 mg kg^{-1} Hg for methylmercury and ethylmercury chloride in mixtures were measured. Fish samples were found to contain 2.2 mg kg^{-1} of mercury as methylmercury.

Bache and Lisk (1971) determined methylmercury compounds in fish by chromatography on a 60 cm glass column of Chromosorb 101 or 20% 1:1 OV-17/QF-1. Detection of the separated organomercury compounds was achieved by measurement of the emission spectrum of the 253.7 nm atomic mercury line which gave a linear response over the range of 0.1–100 mg of injected methylmercury chloride. Average recoveries of methylmercury chloride in fish were 62% at the 0.3 mg kg^{-1} level.

Cappon and Crispin-Smith (1977) have described a method for the extraction, clean-up and gas chromatographic determination of alkyl- and arylmercury compounds and inorganic mercury in blood, grain, faeces, fish, hair, milk, sediment, soft tissue and urine. Methyl-, ethyl-, and phenylmercury are first extracted as the chloride derivatives. Inorganic mercury is then isolated as methylmercury upon reaction with tetramethyltin. The initial extracts are subjected to thiosulfate clean-up and the organomercury species are isolated as the bromide derivatives. Total mercury recovery ranges between 75 and 90% for both forms of mercury, as assessed by using appropriate ^{203}Hg labeled compounds for liquid scintillation spectrometric assay. Specific gas chromatographic conditions allow detection of mercury concentrations of 1 ng kg^{-1}. Mean deviation and relative accuracy average 3.2 and 2.2%, respectively. The accuracy and precision of this procedure was evaluated by analysing different sample types fortified with mercuric chloride and methylmercuric chloride. Results were cross checked by an atomic absorption procedure. Results obtained on samples by both methods are given in Table 8. There is good agreement between the two methods for samples containing methyl-, ethyl-, and inorganic mercury and this is expressed in terms of gas chromatographic/atomic absorption ratios.

Table 8. GC-AA intercomparison study.

	mg L^{-1} Hg		
Sample	GC	AA as MeHg	GC/AA
Fish	1.10	1.06	1.04
Hair	266.2	272.9	0.98
Muscle	0.27	0.70	1.03
		as EtHg	
Blood	0.72	0.77	0.94
Kidney	0.66	0.68	0.97
		as inorganic	
Blood	0.59	0.57	1.47
Fish	0.08	0.07	1.14
Sediment	0.17	0.19	0.89

Column chromatography

Liquid chromatography using differential pulse electrochemical detection has been used to determine organomercury cations in tuna fish and shark meat (MacCrehan and Durst (1978). The differential pulse mode of detection offers a substantial increase in selectivity over amperometry.

Following alkaline hydrolysis the sample (1 g) is acidified with hydrochloric acid.

The organomercury cations can then be extracted from the aqueous solution with toluene as the neutral chloride complexes. The aqueous back-extraction solution used was 0.01 mol L^{-1} disodium thiosulfate buffered to pH 5.5 with 0.05 mol L^{-1} ammonium acetate. This extraction solution was compatible with the column chromatographic separation, and the determination was performed directly on this aqueous extract after filtering through a 0.2 μm syringe filter. In all cases, a standard additions procedure was used for the determination with known amounts of diluted CH_3Hg^+ solution added to the solid material before the hydrolysis step. The recovery was checked by comparison to a standard curve and found to be about 95%.

Various interference effects on the determination of organomercury compounds and how they are overcome are discussed by these workers.

Table 9 shows the results obtained when the method was applied to standard NBS fish samples. The sample chromatograms were characterised by a single response for methylmercury with a high signal-to-noise ratio. Ethyl and phenylmercury were not detected in these samples.

The results obtained (see Table 9) for the methylmercury content of the fish samples were in fairly close agreement to the total mercury (as measured by alternate technique such as atomic absorption and neutron activation analysis).

Thin layer chromatography

Thin layer chromatography was carried out by Westhoo (1966) either on the original methylmercury chloride containing fish extract or on derivatives prepared from this extract, such as the dithizonate, bromide, iodide or cyanide. Light petroleum:diethylether (70:330) was used as developing solvent, using aluminium oxide or silica gel plates. Separated organomercury compounds were detected with a saturated ethanolic solution of Michler's thioketone in ethanol.

Table 9. Methylmercury content of fish samples.

		Mercury species in ng kg^{-1}		
Sample	$MeHg^+$	$EtHg^+$	$PhHg^+$	Total Hg
RM 50 Albacore Tuna	0.93 ± 0.1	nd[a]	nd	0.95 ± 0.1
Japanese shark paste	8.41 ± 0.1	nd	nd	7.4

[a]nd = not detected.

Methylmercury dithizonate and phenylmercury dithizonate could be separated from each other in the fish extracts by thin-layer chromatography on aluminium oxide (limit of detection: 0.2 μg). Methylmercury cyanide, chloride, bromide and iodide were separated by thin-layer chromatography on silica gel (limit of detection of the chloride and bromide: 0.02 μg).

Substoichiometric analysis

Substiochiometric analysis is based on isotope dilution analysis. This method offers an accurate and precise determination of trace amounts of elements by measurement of radioactivity alone without corrections for chemical yield.

This technique has been applied to the determination of organomercury compounds in environmental samples. Kauda and Suzuki (1980) have applied substiochiometric isotope dilution analysis to the determination of inorganic mercury and organically bound mercury in hair. Thionalide (thioglycolic-B-amino-naphthalide) was used as the extracting agent.

To determine total mercury the sample plus ^{203}Hg was refluxed with sulphuric acid and 30% hydrogen peroxide and gently heated until pale yellow. Mercury was extracted with methyl isobutyl ketone. This phase was adjusted to PH 6.5 and was extracted with EDTA solution to recover mercury in an aqueous phase. The acidity of the aqueous solution was adjusted to 0.1 M in sulphuric acid and then the substoichiometric extraction of Hg (II) was carried out with 5 mL of 1 μM thionalide in chloroform. The organic phase was washed with 0.1 M sulphuric acid solution. To determine methylmercury the sample plus ^{203}Hg methylmercury was treated with 3 M hydrochloric acid. The extract was shaken for 5 min with two 10 mL portions of benzene to extract the methylmercury. Methylmercury in the combined benzene extract was back-extracted into 5 ml of 0.02 M sodium sulphate solution of pH 6.5 and then the substiochiometric extraction was carried out with 5 ml of 0.5 μM thionalide in chloroform. The radioactivity of the two extracts was measured as only a small proportion of the mercury is extracted in substoichiometry, the extractions can be carried out repeatedly from the same solution. From the amounts of radioactivity added to the original sample and that found in the final extracts and from the concentration of total mercury found in the final extract, it is possible to obtain the mercury content of the original samples. Down to approximately 1 μg of mercury can be determined by this procedure.

Organomercury in Air

Classical procedure

Christie *et al.* (1967) describe procedures capable of determining mercury at levels down to 10 mg m^{-3} in air. In one method the air sample (500 mL) is passed at 50 L min^{-1} through a column containing active carbon, and the carbon, freed from moisture by a stream of dry air, is then removed for determination of mercury. In a second method air (500 L) is drawn at 33.3 L min^{-1} through a glass-fiber pad treated with cadmium acetate and sodium sulphide. The pad is then removed for determination of mercury. The active carbon or the cadmium sulphide pad is ignited. The colour produced on selenium sulphide test paper is compared with a colour chart. Both methods are applicable to the determination of ethylmercury (chloride and phosphate), diphenylmercury and methylmercury dicyandiamide. The first method only is applicable to diethylmercury.

Polley and Miller (1955) have described a method for the determination in air samples of amounts of methyl- and ethylmercury chlorides down to 1–5 μg in 50–100 mL of sample. An alternate method developed by these workers (Miller and Polley, 1954) is best used for the determination of amounts above 10 μg of methyl- and ethylmercury chloride in 25 mL of the carbonate phosphate absorber solution previously mentioned by these workers (Kimura and Miller, 1960). Large aqueous sample volumes are not deleterious in this method as they are in the direct method of analysis mentioned above. This is because of a favourable distribution coefficient of p-tolyl mercury chloride between the chloroform and water phases. The Miller and Swanberg (1957) method is suitable for the determination of below 30 μg of alkylmercury compounds in sample sizes of up to 100 mL of carbonate-phosphate absorber solution.

Atomic absorption spectrometry

In earlier atomic absorption methods the air sample is passed through an absorber containing a liquid such as acidified potassium permanganate (Kimura and Miller, 1962) or a solid such as activated charcoal (Christie *et al.* 1967), silver or gold (Long *et al.* 1973), which collect not only elemental mercury but also alkyl or arylmercury halides and dialkyl or dialkyl mercury compounds. After desorption from one trap released mercury is determined by atomic absorption spectrometry at 257.3 nm. These methods do not have the required sensitivity for environmental air samples.

Dumareov *et al.* (1979) have described a method which operates down to the 5 μg Hg m^{-3} air level. In this method mercury is trapped on gold coated sand and the desorbed volatile mercury compounds determined by atomic absorption spectrophotometry.

Field samples were collected by drawing air through the absorber with a small pump (KNF, No. 5 ANE membrane pump) at flow rates of 2.5–3.5 L min^{-1}. A prefilter (Whatman GF/A, 13 mm diameter) is used to retain particulated and solid mercury compounds. The volume of air is measured by a calibrated dry gas meter. The volume sampled depends on the expected mercury concentrations. The loaded samplers can be stored for several days without change in mercury content. The mercury was desorbed by heating the absorber to 800 °C and sweeping the products by a carrier gas stream into an atomic absorption spectrophotometer.

Schroeder and Jackson (1983) determined mercury in the atmosphere using a method of selective preconcentration followed by pyrolysis and cold vapor atomic fluorescence detection to determine different mercury species collected from the atmosphere. Other studies have been performed by using sequential specific absorption tubes which separate different chemical forms of mercury by selective collection. In these later studies, mercury compounds were thermally desorbed and recollected on gold surfaces prior to elution into an emission detector. While these methods represented a significant advance in atmospheric mercury sampling by achieving the separation of volatile species of mercury, the analytical methods prevented positive identifications of the compounds by converting all forms to elemental mercury prior to detection. Chromatographic substrates have been used successfully for the collection of organics and of organic mercury (Aue and Tell, 1971). By logical extension, a chromatographic method of analysis would permit the positive identification of organic mercury compounds by comparison of sample elution times/volumes with standard compounds.

The electrostatic accumulation furnace for electrothermal atomic spectrometry technique (Torsi *et al.*, 1981, 1982) has been successfully used for the precise, simple and fast determination of mercury in air samples. It has also been shown that the electrostatic accumulation furnace can be easily operated with a collection efficiency of approximately 100% with particulate matter as well as with mercury vapour.

Gas chromatography

Ballantine and Zoller (1984) developed a mercury collection method that is compatible with a chromatographic method of analysis and is capable of detecting levels of organic mercury in the atmosphere as low as 0.1 ng m^{-3}.

Total volatile mercury air samples were passed through a column of gold coated glass heads. The mercury on the glass heads is directly eluted by heating at 500 °C on to a column packed with Chromosorb 101 maintained at a temperature of 20 °C to collect methylmercury chloride and 80 °C to collect dimethylmercury. Collection efficiencies on these columns under these conditions are about 95%. The organomercury compounds were then released from the columns by heating, respectively, to 200 and 90 °C and analysed under the conditions given in Table 10, detection being achieved by a microwave plasma detector operated at 257.3 nm.

Major disadvantages of this technique are the necessity of long collection times (3–12 h) when studying background levels, and relatively long analyses (approximately 1 h) for methylmercuric samples. The significant advantages over previous methods are the simplification of sample elution directly into the gas chromatographic column which minimises the possibilities of contamination and the ability to positively identify two of the most important organic forms of mercury present in the atmosphere.

Table 10. Analytical system parameters for the analysis of MMC, DMM, and total volatile mercury.

	System		
Parameter	MMC	DMM	Total Volatile Hg
flow rate, mL/min	85 ± 5	75 ± 5	60 ± 5
oven temp, °C	165 ± 5	same	same
column (1 (1 m × 6 mm o.d.)	5% FFAP on Gas Chrom Q (80/100 mesh)	Chromosorb 101 (60/80 mesh)	empty glass column
collection tube (TI)	Chromosorb 101 (60–80) (2–4 cm) Tenax GC(60/ 80 mesh)(5 cm)	Chromosorb 101 (5 cm cm)	gold coated glass beads
desorption temp °C	200	90	350
	Detector		
microwave power	26W (forward), 1W (refected)	slit width carrier gas pressure	110 um argon 7.55 = 5
monochromator setting	253.7 nm	at outlet	mmHg
quartz capillary	1 mm i.d. 6 mm o.d.		

Organotin compounds:
Organotin in water — Atomic absorption spectrometry

Chau *et al.* (1982) described an extraction procedure for the polar methyltin compounds and the use of the gas chromatography atomic absorption spectroscopy system for the determination of their butylated derivatives including inorganic tetravalent tin. Butulation of the organotin compounds was carried out with butyl magnesium chloride reagent. This procedure meets even the most searching present day requirements as regards to speciation and sensitivity in the determination of organotin compounds.

Large volumes of water sample can be handled. Under normal laboratory conditions, detection limit of 0.04 μg L^{-1} can be achieved with 5 L of water sample. The absolute detection limit of the GC-AAS for tin is 0.1 ng. Volatile organotin compounds such as tetramethyltin and methyltin hydrides can also be analyzed by this method.

In this method, the highly polar and solvated methyltin, dimethyltin, trimethyltin, and Sn(IV) species were extracted into benzene containing tropolone from water saturated with sodium chloride.

After the mixture was shaken for 0.5 h the benzene layers were separated and butylated with 1 mL of butyl magnesium chloride reagent in 10 mL glass stoppered micro Erlenmeyer flasks with stirring for ca. 10 min. The mixture was washed with 5 mL of 1 N sulphuric acid or hydrochloric acid to destroy the excess Grignard reagent. The organic phase was separated and dried with anhydrous sodium sulphate. The mixture now contained the butyl-derivatized methyltins, $MeSnBu_3$, Me_2SnBu_2, Me_3SnBu and Bu_4Sn ready for analysis by the gas chromatography-atomic absorption technique. The addition of solid sodium chloride to the original matter sample improved recoveries of organotin compounds.

The absolute recovery was found satisfactory for Me_2Sn^{2+}, and $MeSn^{3+}$ and Sn(IV), but was only 75% for the Me_3Sn^+ species even with 40 g of sodium chloride used to achieve a saturated salt solution. The Me_2Sn^+ species was only extracted in the presence of sodium chloride. The recovery, although not quantitative, was consistent.

Chau *et al.* (1982) found that the introduction of hydrogen to the quartz furnace was necessary to elevate the furnace temperature to ca. 900 °C and to enhance atomization of the methylbutylin derivatives. It was also found that introduction of air further enhanced the sensitivity. Heating the transfer line to 165 °C was necessary to give sharp peaks. Although this temperature was well above the boiling points of the tin derivatives no decomposition of the alkyltin compounds was noted at the transfer line. Precision at the 250 μg L^{-1} level of Me_3Sn^+, Me_2Sn^{2+}, $MeSn^{3+}$ and Sn(IV) in lake water was acceptable as reflected in standard deviations of 5.4, 8.6, 7.3 and 11%, respectively and recoveries of all species were in the range 91–117%.

The only tetravalent elements that were coextracted by tropolone and similarly butylated to the tetraalkyl derivatives are the Ge(IV) and Pb(IV) species. Tetraalkyllead compounds however, do not give any signals in the atomic absorption detection system for tin analysis at the 224.6 nm spectral line. There should not be any worry of interference from Ge(IV) in natural waters nor is its spectral interference expected.

Tetramethyltin and organotin hydrides can be analysed by direct gas chromatography-atomic absorption spectrophotometry without derivatization. As these compounds are volatile it is necessary to purge them from the water sample and the headspace of the sample vessel with nitrogen into U-trap packed with 3% OV-1 on Chromosorb W at 160 °C and subsequently mounting this trap onto the inlet of the gas chromatographic column.

Between 0.1 and 0.5 μg L^{-1}, Me_2Sn^{2+}, $MeSn^{3+}$ and Sn(IV) were found in harbours, or industrialised areas by this method (M_3Sn^+ net detected).

Gas chromatography

Methods have been described for the conversion of these compounds to their volatile hydrides which can then be separated and detected in an element specific detector (Braman and Tomkins, 1979; Hodge *et al.*, 1979).

Butyltin(IV) compounds have been determined by gas chromatography — mass spectrometry after methylation and by gas chromatography after pentylation (Maguire and Huneault, 1981).

Mueller (1984) detected tributyl tin compounds at trace levels in water and sediments using gas chromatography with flame photometric detection and gas chromatography — mass spectrometry. The tributyltin compounds are first converted to tributylmethyltin and then analysed using capillary gas chromatography with flame photometric detection and gas chromatography — mass spectrometry. Tributyltin was found in samples of river and lake water, and sediment and these results demonstrated the technique has detection limits of less than 1 pg L^{-1} for water and 0.5 pg L^{-1} for sediment.

Jackson *et al.* (1982) carried out gas chromatographic speciation studies of methyl stannanes in the Chesapeake Bay area using trap sampling with a tin selective detector. The sampler is coupled automatically to a gas chromatograph equipped with a commercial flame photometric detector, modified for tin-specific detection by use of an interference filter. The method allows non-destructive speciation and detection of both hydrophillic and hydrophobic organotin species in aqueous systems.

Maguire and Huneault (1981) described a method for the determination of butyltin species including bis (tri-n-butyltin) oxide and some of its dealkylation products in lake and river waters by gas chromatography with flame photometric detection. Mass spectra could be obtained with about 25 μg of the derivatives. Gas chromatographic-atomic absorption spectrometric methods for the determination of nanogram amounts of methyltin compounds and inorganic tin in natural waters and human urine have been described by Braman and Tomkins (1979). In this method the tin compounds in aqueous solution at pH 6.5 are converted by sodium borohydride to the corresponding volatile hydride, SnH_4, CH_3SnH_3, (CH_3)-SnH_2 and $(CH_3)_3SnH$ by reaction with sodium borohydride. These are helium scrubbed from solution, cryogenically trapped on a U-tube and separated upon warming. Detection limits are approximately 0.01 ng as tin when using a hydrogen-rich, hydrogen-air flame emission type detector (ShH band) of a type having considerably very low detection limits. Average tin recoveries ranged from 96–109% for sea-water and from 83–108% for human urine samples for six samples analysed to which were added 0.4 to 1.6 ng of methyltin compounds and 3 ng inorganic tin. Reanalysis of analyzed sampled shows that all methyltin and inorganic is removed in one analysis procedure.

Braman and Tomkins (1979) used a gas chromatographic column consisting of fully packed 30 cm U-tubes of silicone oil type OV-3, on Chromosorb W to separate the stannanes. They noted a resolution of two peaks within the dimethylstannane signal. Similar results were observed during the analysis of natural waters containing dimethyltin compounds. This may be due to the formation of stable bipyramidal geometric isomers of dimethylstannane but this was not verified. While the reasons for the observed effect are not known, the split signal is quantitative for dimethyltin dichloride and produced no problems during analysis. Detection limits are in the range 0.07 to 0.2 ng L^{-1} depending on the compound detected. The precision of the method averaged ±5% relative over the range of the response curve.

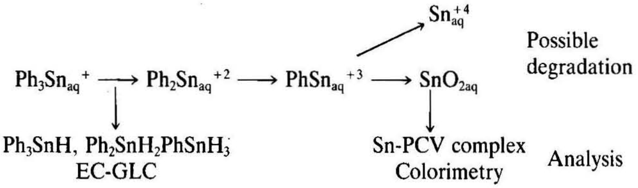
Braman and Tomkins (1979) did not observe any interference by organics in this method in the determination of organotin compounds in water samples. They did, however, observe that organic arsenic(III) compounds in sea water caused a positive interference effect due to the emission of the As 2^+ molecular band at 611.5 nm. Inorganic arsenic(III) is reduced to arsine at pH 6.5. It is, nevertheless, separated from stannane on the OV-3 column and is not an interference. The arsenic(III) peak can be eliminated by oxidation of arsenic(III) to arsenic(V) by the addition of a few drops of sodium thiosulphate solution to dispel excess iodine. Neither arsenic(V) nor the methylarsenic acids are reduced to corresponding arsines at pH 6.5.

Certain metal ions, Ag^+, Cu^{2+}, Hg^{2+}, Ni^{2+}, MoO_4^{2-} and Pb^{2+} at 2 μg L^{-1} in analyzed solutions were found to reduce the complete removal of stannane. Sea water did not inhibit recovery of stannane or methylstannanes. The ions Al^{3+}, CrO_4^{2-}, F^-, I^-, Mn^{2+}, PO_4^{3-} and Sb^{3+} did not interfere at 20 μg L^{-1} while Fe^{3+}, BiO_3^-, Cd^{2+}, S^{2-}, VO_3^{2-} and Zn^{2+} did not interfere at 2 μg L^{-1}.

Braman and Tomkins (1979) present extensive analytical data for the four methyltin species in saline, and estuarine waters, surface waters and rain waters obtained at a variety of locations in the United States.

Soderquist and Crosby (1978) have developed a method for the simultaneous determination of triphenyltin hydroxide and its possible degradation products tetraphenyltin, diphenyltin oxide, benzenestannoic acid (and inorganic tin) in water. The method is rapid (one sample set per hour), sensitive to less than 10 μg L^{-1} for most of the tin species and exhibits no cross-interferences between the phenyltins. The phenyltins are detected by electron capture gas-liquid chromatography after conversion to their hydride derivatives, using lithium aluminium hydride, while inorganic tin is determined by a procedure which responds to tin(IV) oxide as well as aqueous tin(IV).

Soderquist and Crosby (1978) found that nonvolatile hydroxyoxphenyl stannane ($PhSnO_2H$), oxodiphenyl stannane (PhSnO) and hydroxy-triphenyl stannane (Ph_3SnOH) upon conversion to their hydrides by lithium aluminium hydride produced derivatives with excellent gas chromatographic properties, high response to electron-capture detection and none of the attendant column stability problems encountered with other derivatives.



The basis for this method involves extraction of the phenyltin species from water followed by their quantification as phenyltin hydrides by electron capture gas chromatography and analysis of the remaining aqueous phase for inorganic tin (Sn^{4+} plus SnO_2) by colorimetry.

Soderquist and Crosby (1978) used a dual column/dual detector Varian model 2400 gas chromatograph equipped on one side with a flame-ionization detector and a 0.7 m by 2 mm (i.d.) glass column containing 3% OV-17 on 60/80 mesh gas Chrom Q. Column, injector and detector temperatures were 265, 275 and 300 °C, respectively, carrier gas (nitrogen) flow rate was 25 mL min^{-1}. Tetraphenyltin eluted within 8 min under those conditions. The second side of the chromatograph was equipped with a tritium EC detector and a 1.1 m by 2 mm (i.d.) glass column containing 4% SE-30 on 60/80 mesh Gas Chrom Q. The injector and detector temperatures were 210 °C and the carrier gas (nitrogen) flow rate was 20 mL min^{-1}. Column temperatures which eluted the following compounds within 6 min were: Triphenylstannane (PnSnH) (190 °C), diphenylstannane (Ph_2SnH_2) (135 °C), phenylstannane ($PhSnH_3$) (45 °C).

Whilst recoveries of tri and diphenyltin compounds were good, those of monophenyltin compounds were in the range 11 to 81%. Minimum detectable amounts (200 mL sample) ranged from 15 μgL^{-1} (Ph_4Sn) to 30 μgL^{-1} (Ph_3Sn^+ PH_2Sn^{2+} and $PhSn^{3+}$).

Valkirs *et al.* (1987) compared two methods for the determination of μgL^{-1} levels of dialkyltin and tributyltin species in marine and estuarine waters. The two methods studied were hydride generation followed by atomic absorption spectrometry and gas chromatography with flame photometric detection. Good agreement was obtained between the results of the two methods. Studies on the effect of storing frozen samples prior to analysis showed that samples could be stored in polycarbonate containers at minus 20 °C for 2–3 months without significant loss of tributyltin.

Unger *et al.* (1986) determined butyltin compounds in estuarine waters as their hexyl derivatives using gas chromatography with flame photometric detection. Traces of organotin compounds were analysed by solvent extraction with tropalone in n-hexane and derivitization with n-hexyl magnesium bromide to form tetra-alkyltins which were then determined by gas chromatography with flame photometric detection and confirmation by mass spectrometry. The n-hexyl derivatives of methyltin and butyltin species were easily separated and quantified relative to an internal standard (tripentyltin chloride) which was not found in environmental samples and did not interfere in the method.

Müller (1987) used high resolution gas chromatography with flame photometric detection to determine trace levels of organotin compounds in environmental water samples. Butyltin and other organotin compounds were determined via extraction, ethylation and capillary column gas chromatography. Identities were confirmed by mass spectrometry.

Hattori *et al.* (1984) determined trialkyltin dialkyltin and triphenyltin compounds in environmental water samples. The water samples were mixed with hydrochloric acid and sodium chloride and extracted into benzene. Following dehydration and concentration, the compounds were cleaned up, using glass columns packed with silica gel impregnated with hydrochloric acid and their hydrides generated using an ethanol solution of sodium borohydride. Sediment samples were extracted into methanolic hydrochloric acid and then, following mixing with water and sodium chloride, the mixture was extracted with benzene and treated identically to the water samples. The organotin hydrides were determined using gas chromatography with electron-capture detection. Recoveries were 70–95% from river water and sediment samples and detection limits 0.8 μgL^{-1} and 0.02–0.04 $\mu g\ g^{-1}$, respectively.

Matthias *et al.* (1986) described a comprehensive method for the determination of aquatic, butyltin and butylmethyltin species at ultratrace levels, using simultaneous sodium borohydride hydridization/dichloromethane extraction with gas chromatographic flame detection and gas chromatographic — mass spectrometric detection. The detection limits for a 100 mL sample were 7 ng of tin L^{-1} for tetrabutyltin and tributyltin, 3 ng of tin L^{-1} for dibutyltin and 22 ng tin L^{-1} for monobutyltin. For 800 ml samples detection limits were 1–2 ng tin L^{-1} for tri- and tetrabutyltin and below 1 ng tin L^{-1} for dibutyltin. The technique was applied to the detection of biodegradation products of tributyltin in natural waters. It was a rapid and simple analysis suitable for large scale environmental monitoring programs.

High performance liquid chromatography

High performance liquid chromatography coupled with hydride generation — direct current plasma emission spectrometry has been used for trace analysis and speciation studies of methylated organotin compounds in water (Krull and Panaro, 1985).

Total tin was determined by continuous online hydride generation followed by direct current plasma emission spectroscopy. Interfacing the hydride generation — DC plasma emission spectrometric system with high performance liquid chromatography allowed the determination of tin species. Detection limits, sensitivities, calibration plots were determined.

Organotins in sediments

Mueller (1984) has described a gas chromatographic method for the determination of tributyltin compounds in sediments. The tributyltin compounds are first converted to tributylmethyltin and then analysed using capillary gas chromatography with flame photometric detection and gas chromatography — mass spectrometry. Tributyltin was found in samples of river and lake water and sediment and these results demonstrated that the technique has detection limits of less than 1 pgL^{-1} for water and 0.5 pgL^{-1} for sediment.

Organotin in crops and plants

Chromopotentiometry (Nangniot and Martens, 1961) has also been applied to the determination of triphenyltin acetate at very low concentrations in plant material. In this method a hanging-drop electrode is used at which the ions are reduced in a pre-electrolysis step at -0.7 V or a silver-silver chloride saturated potassium chloride electrode for 5 min, the potential is then increased gradually to -0.1 V, and the anodic diffusion current is registered at about -0.45 V. The sample for analysis is obtained by extraction of plant material with chloroform, the extract is washed with 0.1 N potassium hydroxide and 0.5 N potassium tartrate, then mineralised with sulphuric acid — nitric acid and the residue is dissolved in 5 N — hydrochloric acid. A peak height of about one uA is obtained for a concentration of about 0.8 μgL^{-1} tin.

Gauer *et al.* (1974) have described a gas chromatographic method for the determination of the residues of tricyclohexylhydroxystannane and its dicyclohexyl metabolite on strawberries, apples and grapes that have been treated with Pictran miticide. Crop samples were treated with aqueous hydrobromic acid to form bromoderivatives of the organotin compounds and these derivatives were extracted into benzene. When the residue levels were less than that 1 μgL^{-1} the derivative solution was cleaned up on a column of silica gel. The derivatives were determined by gas chromatography at 200 °C on a column packed with 2% of OV-225 on Chromosorb G AW-DMCS or at 100 ° on a column packed with 0.5% of OV-225 on glass beads with helium as carrier gas. Background interference was minimised by use of a halide-sensitive Coulson detector. Recovery of 1 mgL^{-1} of added tricyclohexydroxystannane was 80 to 95%; that of 0.1 mgL^{-1} was 78 to 89%. Conditions are also described for the gas chromatographic determination of cyclohexylstannane acid, another possible degradation product of pictran.

Organotin in biological materials

Gas chromatography. A variety of seashells have been analysed for organotin compounds using the gas chromatographic procedure described by Braman and Tomkins (1979), (see section on organotin compounds in water). The average total tin content of seashell and egg samples was between 0.001–002 mg kg^{-1} and methylated tin compounds were detected (Me_4Sn^{3+} and Me_2Sn^{2+}). Less than 0.01 μg kg^{-1} Me_3Sn^+ was present.

The higher concentration of tin in the seashells relative to the water in which they were found would indicate the presence of bioaccumulation process.

Gas chromatographic methods have been described for the determination of tetraalkyl and trialkyl tins (Arakawa *et al.*, 1981) in biological materials. Unfortunately, these methods were not easily applicable to the determination of the dialkyl homologues because of their absorption and decomposition during chromatography.

Spectrofluorimetric methods

Spectrofluorometry has been applied to the determination of triphenyltin compounds. Coyle and White (1957) showed that 3-hydroxylflavone could be used to determine submicrogram amounts of inorganic tin and then Vernon (1974) used the reagent to determine triphenyltin compounds in potatoes. On the basis of this procedure Blunden and Chapman (1978), spectrofluorometrically determined triphenyltin compounds in water. Further, they showed that chloride ions quenched the fluorescence but that on shaking with aqueous sodium acetate solution a stable complex was formed, although the instability to light of the triphenyltin chloride-3-hydroxyflavone complex had been initially pointed out by Aldridge and Cremer (1957).

Arakawa *et al.* (1983) have shown that Morin (2′, 3, 4′, 5,7-pentahydroxyflavone) can be used as a fluorescence reagent for organotin, especially dialkyltin compounds. Although quercetin and 3-hydroxyflavone are similar to Morin in structure, they are unsuitable because of their sensitivity and instability. Morin produces a green fluorescence with various organotin compounds in organic solvent. The reagent is especially sensitive to dialkyltin compounds. The excitation and emission spectra show peaks at ca. 415 nm and ca. 495 nm, respectively, for each alkyltin-Morin complex and at ca. 405 nm and ca. 520 for the triphenyltin-Morin complex. The maximum fluorescence requires a ratio of 3 to 9 mol of Morin for 1 mol of dialkyl- and triphenyltin and 6–12 to 1 molar ratio for trialkyltin. Detection limits are 1×10^{-9}M for dialkyltin, 1×10^{-7}M for monoalkyltin, 5×10^{-7}M for trialkyltin and 1×10^{-7}M for triphenyltin. The fluorometric procedure can be used for the determination of individual organotin compounds especially in biological samples such as animal organs and urine following their prior separation by a suitable chromtographic technique. Recoveries of organotins added to various tissues at the 1.0–100 nmol level ranged from 91.0 to 99.7% depending upon the organotin species.

In this procedure, a n-hexane or ethyl acetate extract of a hydrochloric and homogentate of the biological sample was mixed with ethanolic Morin solution and examined fluorimetrically. The formation of the organotin-Morin complexes progressed very rapidly at room temperature and the fluorescence intensities remained constant for hours. Particularly, the dialkyltin complexes were stable over a number of hours. Dialklytin compounds produced a much stronger fluorescence than other organotin compounds with Morin. For 1 μM of each organotin compound the relative fluorescence intensity was 10.2 for $BuSnCl_3$, 42.5 for Me_2SnCl_2 99.2 for Et_2SnCl_2, 99.4 for Pr_2SnCl_2, 51.7 for Bu_2SnCl_2, 2.2 for Et_3SnCl, 2.8 for Pr_3SnCl, 1.6 for BuSnCl, and 12.7 for Ph_3SnCl at the same instrument setting. The concentration detection limits for dialkyltin compounds were in the 1–10 nM range, at which other organotin compounds could not be detected. This large difference in fluorescent intensities among different organotin-Morin complexes appears to be dependent on the valence state of the metal.

Organolead compounds such as di- and triethyllead and organosilane compounds such as di- and monomethylsilane did not interfere at 1 mM under the condition used for the determination of organotin. Other organometallic compounds such as dimethyl arsenide and methyl- and ethylmercury chlorides did not fluoresce at all. Although aluminium(III), zinc(II), tin(IV), magnesium(II) and cadmium(II) produced a strong fluorescence, and manganese(II), selenium(IV), and mercury(II) produced a very weak fluorescence with Morin in water solutions, these organometallic compounds did not interfere at 1×10^{-3} M under the condition of the organotin determination. Arsenic(III) or arsenic(V), lead(II), chromium(III) or chromium(VI), copper(II) and iron(II or III) did not fluoresence even in water solutions.

High Performance Liquid Chromatography

The high performance liquid chromatography — hydride generation direct current plasma emission spectrometric technique referred to previously (Krull and Panaro, 1985) for the determination of organotin compounds in water has also been applied to the analysis of clams and tuna fish.

Organolead Compounds

Organolead in water

Classical procedures. Direct polarography has been used to determine trialkyllead compounds in water (Hodges and Naden, 1979).

Bond *et al.* (1984) examined the interferences occurring in the stripping voltametric determination of trimethyllead in sea water by polarography and mercury -199 and lead-207 nuclear magnetic resource spectrometry. NMR and electrochemical data show that Hg (II) reacts with $(CH_3)_3Pb^+$ in seawater. Consequently, anodic stripping voltametric methods for determining $(CH_3)_3Pb)+$ and inorganic Pb(II) may be unreliable. Solvent extraction followed by spectrophotometry have been used to determine trialkyllead compounds in water (Aldridge and Street, 1981; Henderson and Snyder, 1961).

Atomic absorption spectrometry

De Jonghe *et al.* (1983) have developed a method for the determination in water of traces of triethyllead compounds without interference from mono-, di- and tetraalkyllead compounds and inorganic lead.

After enrichment of the sample by a fast vacuum distillation technique and saturation of the residual volume with sodium chloride, the analytes are extracted in chloroform. By incorporation of specific purification steps, interference from other forms of organic and inorganic lead is completely eliminated. The final chloroform extract is treated with sulfuric acid solution in order to transfer the trialkyllead compounds present back into an aqueous solution. The analysis is completed by graphite furnace atomic absorption spectrometry. A detection limit of 0.02 μg can be achieved with 1 L samples. In contrast to earlier approaches where other forms of organic and inorganic lead may give rise to serious interferences, the determination is highly specific for trialkyllead compounds, even in the presence of up to 100 μg L^{-1} of inorganic lead salts. For environmental applications a 1 L volume is advised. After shaking for 1 min with hexane (1 mL per 100 mL of water) the sample is filtered on a Type RA Milliprefilter of 1.2 μm pore size. The water is brought into a rotary evaporator and evaporated under vacuum at 60 °C until a residual volume of ca. 15 mL remains. The sample is then quantitatively transferred to a 100 mL separating funnel and the volume is adjusted to 25 mL with distilled water. After this, the sample is extracted twice with 25 mL portions of chloroform. The extracts are combined and 1 mL of a 1 mM dithizone in chloroform solution is added. Next, this organic phase is shaken for about 2 min with an aqueous solution consisting of 15 mL of an ammonium citrate/ammonia buffer and 35 mL of 0.1 M EDTA. The chloroform layer is separated off, shaken first with distilled water to remove traces of EDTA and buffer and then for 1 min with 5 mL of 0.1 N sulfuric acid solution. Analysis of this sulfuric acid extract by means of graphite furnace atomic absorption spectrometry allows the quantitation of the trialkyllead initially present.

The overall accuracy obtained in this procedure was 87 ± 4% for trimethyllead and 92 ± 5% for triethyllead.

It was found that in this method up to 1000 μg of inorganic lead and up to 100 μg of dialkyllead and tetraalkyllead compounds (in the sample portion taken) can be analysed without exceeding the limit of detection.

Aneva (1985) used graphite furnace atomic absorption spectrometry to determine 4–100 μg L^{-1} of tetraalkyllead compounds in waste waters. Tetraalkyllead compounds were extracted from the water with hexane, converted into water soluble iodides by reaction with iodine in the extract and re-extracted into dilute nitric acid. The mean recovery was 95% and no interference was experienced from other metallic or nonmetallic ions.

Gas chromatography

Several methods for the determination of tetraalkyllead compounds in water have been proposed which depend on a combination of gas chromatography with selective detectors. There have been few reports on the direct gas chromatographic determination of trialkyllead salts (Estes *et al.*, 1981) and none for dialkyllead salts. Forsythe and Marshall (1983) approach to the determination of these salts was to further alkylate them with a Grignard reagent to convert them to their tetraalkyl analogues prior to capillary column gas chromatography using electron capture detection. Ammoniacal buffer (pH 8.5 10 mL) was added to the sample which was then extracted three times with 0.5 mg/L dithizone in 50% benzene/hexane. The organic extracts were combined, reduced in volume to 0.5 mL and derivatized directly by reaction with phenyl magnesium bromide in tetrahydrofuran medium. Following the addition of water, organolead compounds were extracted with a small volume of hexane.

A feature of the gas chromatographic apparatus to avoid sample decomposition was the provision of an all-glass insert and modified injector, which increased internal volume and decreased metal surface area.

Chakraborti *et al.* (1984) determined ionic alkyllead compounds in water using a combination of gas chromatography with atomic absorption detection. Analysis of 500 mL samples enabled the determination of 1.25 ngL^{-1} for $PbMe_3^+$ and 2.5 ng L^{-1} for $PbEt_2^+$. Extraction recoveries were in excess of 90%.

Forsythe and Marshall (1983) used a 30 m fused silica DB-1 column as this gave a superior separation of alkylleads from coextractives. Helium was used as carrier gas and nitrogen was used as make-up gas relative to 5% argon methane because it resulted in more stable detector operation. Nitrogen doped with 10 μL/L oxygen caused increased detector response time.

A linear increase in detector response was observed with increasing analyte concentration (range 4–500 pg for $EtMe_2PbPh$, $Et_2MePbPh$ and $EtMePhPh_2$). Recoveries of dialkyl and trialkyllead compounds obtained from water by this procedure was consistently high in the 0–20 μgL^{-1} lead range.

Gas chromatography/mass spectrometry identified the following mixed alkylphenylleads, $EtMe_2PbPh$, $Et_2MePhPh$ and $EtMePbPh_2$ as well as biphenyl and terphenyls in the crude re-equilibration reaction mixtures. Forsythe and Marshall (1983) were not able to detect any of those "mixed" alkylleads during recovery trials of alkylphenyllead standards or during recovery trials using trialkyllead chlorides or dialkyllead chlorides.

Rapsomankis *et al.* (1986) studied the speciation of lead and methyllead ions in water using gas chromatography with atomic absorption detection. Methyllead compounds were first ethylated using sodium tetraethylborate. Using the purge and trap technique with an atomic absorption detector a detection limit of 0.2 pg L^1 was achieved for $PbMe_3^+$ and $PbMe_2^{2+}$, when 50 mL water samples were used.

Various workers (Chau *et al.*, 1976, 1979; Estes *et al.*, 1981) have discussed the application of gas chromatography combined with an atomic absorption detector for the determination of organolead compounds in water.

Chau *et al.* (1976, 1979) have described a simple and rapid extraction procedure to extract the five tetraalkyllead compounds (Me_4Pb, Me_3EtPb, $MeEt_2Pb$, $MeEt_3Pb$ and Et_4Pb) in hexane extracts of water samples. The extracted compounds are analyzed in their authentic forms by a gas chromatographic-atomic absorption spectrometry system. Other forms of inorganic and organic lead do not interfere. The detection limit for water (200 mL) is 0.50 μg L^{-1}. An average recovery of 89% was obtained by this procedure for the aforementioned alkyllead compounds.

These workers described a technique in which dialkyllead and trialkyllead are quantitatively extracted into benzene from aqueous solution, following their chelation with dithiocarbanate. Using a Grignard reagent they are then converted to their butyl derivatives for gas chromatography — atomic absorption spectrometry. A detection limit of 0.1 $\mu g L^{-1}$ can be achieved with one litre of water. Other metals coextracted with the chelating agent do not interfere. Molecular covalent tetraalkyllead species, if present in the sample, are also extracted and quantified simultaneously.

Estes *et al.* (1981) described a method for the measurement of triethyl- and trimethyllead chloride in tap water, using fused silica capillary column gas chromatography with microwave excited helium plasma lead specific detection. Element specific detection verified the elution of lead species, a definite advantage to the packed column method. The method involved the initial extraction of trialkyllead ions from water into benzene, which was then vacuum reduced to further concentrate the compounds. Direct injection of the vacuum concentrated solutions into the gas chromatography—microwave excited helium plasma system gave detectability of triethyllead chloride at the 30 mgL^{-1} level and trimethyllead chloride at the mgL^{-1} level, but the method was time consuming and only semiquantitative.

The equipment used by Estes *et al.* (1981) featured a gas chromatograph interfaced with a microwave induced and sustained atmospheric pressure helium plasma (9C − MEF) for element selective and sensitive detection. It incorporates a chemically deactivated, low-volume, valveless fluidic logic gas switching interface, to vent large quantities of eluent solvent which would disrupt the helium discharge as sustained by the TM_{010} cylindrical response cavity. The neatness and venting characteristics of the interface are outstanding. The detection system features a low resolution scanning monochromator with a quartz retractor place background corrector directly after the entrance slit to improve selectivity ratios of elements whose emission wavelengths occur in the cyanogen background region. Use of the plasma can be used as a nonselective universal organic compound detector.

The gas chromatographic-microwave excited helium plasma detection system operating perameters are presented in Table 11. In order to avoid thermal decomposition of trialkyllead compounds at active sites on the apparatus the quartz injection port liner, quartz discharge tube and the quartz interface tubing were removed and silanized by passing 100% dichlorodimethylsilane through the tubing. The tubing was placed in an airtight container flushed with nitrogen and allowed to react for 30 min. The tubes were washed with a large quantity of "spectrograde" methanol in order to quench any remaining chlorosilane bonds and dried at 250°C for 1 h while being flushed with helium. This was followed by helium flushing at room temperature overnight. It is quite evident from examination of the gas chromatograms that the differences in triethyllead chloride response from the "at plasma" and "venting" column positions was negligible. Thus, the loss of triethyllead chloride when utilising the nonsilanised quartz interface tubing was due to the chemically active quartz surface.

Table 11. GC-MED operating parameters for lead and carbon.

Parameters	For Lead
column	
packing material	sp-2100 WCOT fused silica Carbowax pretreated
dimensions	12.5m, × 300 μm o.d. × 200 μm i.d.
injection split	100 to 1
carrier gas flow rate (helium)	1 mL/min
temperatures	
column or program	140–185 °C
injector	180 °C
transfer block	180 °C
interface oven	180 °C.
total plasma flow rate	125 mL/min
PMT tube and voltage	RCA 1P28 700V.
entrance and exit slit	
widths	25 μm
height	12 mm
microwave input power	54W
wavelength	405.8 nm
picoammeter time constant	0.10s

Estes *et al.* (1982) and Chau *et al.* (1984) have also reported the *n*-butyl Grignard derivatization of the trialkyllead ions extracted into benzene as the chlorides from spiked tap water which has been saturated with sodium chloride. A precolumn trap enrichment technique is substituted to replace solvent extract vacuum reduction. Final measurement of the lead compounds, now as *n*-butyltrialkylleads, is undertaken with the gas chromatograph-microwave emission detector system. Precolumn Tenax trap enrichment of the derived trialkylbutylleads enables determination to low μgL^{-1} levels to be carried out. In this procedure the water sample (100 mL) is adjusted to pH7, saturated with sodium chloride and extracted with a small volume of Specpure benzene.

A 5 mL portion of the benzene extract was placed in a centrifuge test tube and 1 mL of 2.0 M *n*-butylmagnesium bromide Grignard reagent in tetrahydrofuran was added. The test tube was tightly stoppered and the solution was mixed throughly and was allowed to stand for 1 h. After *n*-butylation, 250 μL of a tetra-*n*-butyllead in benzene-internal-reference solution (0.316 mg mL^{-1}) was added. Excess Grignard remained in the mixture which could be stored at 0°C lower without decomposition for at least 1 day if the subsequent analysis could not be performed immediately. A 95 ± 8% derivativization *n*-butylation recovery was obtained.

The direct quantitative gas chromatographic measurement of trimethyllead chloride or triethyllead chloride suffers from two major difficulties: (a) Both compounds are thermally unstable and tend to decompose even at the lowest possible injection port temperatures (ca. 160–170°C) required to give complete and rapid volatilization, and (b) both compounds are very chemically reactive giving some tailing of chromatographic peaks even with the most inert chromatographic column available. Thus, direct quantitative gas chromatographic measurement of trialkyllead compounds is difficult.

If the trialkyllead compounds can be converted to tetraakylleads, quantitative determination is feasible. The use of *n*-butylmagnesium bromide Grignard reaction for trimethyl- and triethyllead chlorides appeared to be promising. Tetra-*n*-butyllead can be used as an internal reference which will not interfere with speciation of methyl or ethyl tetra- or trialkyllead compounds and should mark the termination of the lead specific analysis, since it should be the last tetraalkyllead compound to elute.

Over the spiked tap water concentration range investigated and extraction efficiency of trimethyllead chloride was 5.7 ± 0.6% and of triethyllead chloride was 93 ± 12%, a not unexpected result in view of the more ionic nature of the former compound. Detection limits were 35.0 $\mu g\ L^{-1}$ based on a 2 × noise signal for triethyllead chloride and 5.6 μgL^{-1} for trimethyllead chloride. In addition, the detectability of both compounds could be improved by the use of a larger precolumn Tenax trap.

Other organolead compounds elute at detectable levels after the compounds of interest but before the internal reference. These compounds could result from decomposition impurities in the trimethyl- or triethyllead chloride, thermal redistribution products occurring from reaction in the injection port, impurities in the internal reference, or organoleads in the tap water. A tap water blank was carried through the analysis procedure and to ensure detection of organoleads other than the internal reference, three 30 μL samples were placed on the same trap before desorption. The additional organolead compounds were not seen in these experiments. Injection port thermal redistribution of alkyllead compounds is unlikely to occur; hence it seems likely that the unidentified lead peaks are derivatized species perhaps of decomposition impurities (i.e., di- and monoethyl and methylleads in the trialkyllead chloride standards).

This procedure offers several advantages for the simultaneous determination of trimethyllead and triethyllead ions in aqueous media. It is rapid and reproducible; it does not require the most strictly deactivated fused silica columns, since the chemically active trialkyllead chlorides are quantitatively converted to relatively chemically inert *n*-butyltrialkylleads. Thus, other capillary columns can be utilised with little effect on the quantitation, because the tetraalkylleads are so amenable to gas chromatography. The precolumn trap enrichment procedure eliminates the need to destroy excess Grignard reagent (to prevent column degradation) and the need for solvent extract vacuum reduction. Elimination of the vacuum reduction step solves the problems of trialkyllead chloride decomposition on the walls of the vacuum vessel and the loss of analyte compound due to volatilization at reduced pressure. The use of an *n*-butyl Grignard reagent allows the simultaneous speciation of all organoleads of the methyl and ethyl alkyls (i.e., tetraalkyltrialkyl, dialkyl and monoalkyl) which might be extracted and derivatised.

Organolead in sediments

Chau *et al.* (1984) have described the optimum conditions for extraction of these compounds from sediment samples for alkyllead speciation analyses. Analyses of some environmental samples revealed for the first time the occurrence of dialkyl- and trialkyllead in sediments in areas of lead contamination.

The various alkyllead species and lead(II) are isolated quantitatively by chelation extraction with sodium diethyldithiocarbamate, followed by n-butylation to their corresponding tetraalkyl forms, $R_nPbBu_{(4-n)}$, and BuPb, respectively (R = Me, Et) all of which can be determined by a gas chromatograph using an atomic absorption detector. The method determines simultaneously the following species in one sample: tetraalkyllead (Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$, Et_4Pb); ionic alkyllead (Me_2Pb^{2+}, Et_2Pb^{2+}; Me_3Pb^+, Et_3Pb^+); Pb^{2+}. Detection limits expressed for Pb were 15 $\mu g\ kg^{-1}$ for sediment samples.

In this method, the sediment (1–2 g) sample was extracted for two h in a capped vial with 3 mL of benzene after addition of 10 mL of water, 6 g of sodium chloride, 1 g of potassium iodide, 2 g of sodium benzoate, 3 mL of sodium diethyldithiocarbamate and 2 g of course glass beads (20–40 mesh). After centrifugation of the mixture, a measured aliquot (1 mL) of the benzene was butylated using 0.2 mL n-butyl magnesium chloride with occasional mixing for 10 m. The mixture was washed with 2 mL sulphuric acid (1 N) to destroy excess Grignard reagent. The organic layer was separated in a capped vial and dried with anhydrous sodium sulphate. Suitable aliquots were injected into the gas chromatograph.

Chau *et al.* (1984) found that in spiking experiments on sediments both the diethyl and triethyl species were recovered at satisfactory levels (Table 12).

Chau *et al.* (1979) has described a simple and rapid extraction procedure to extract the five tetraalkyllead compounds (Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$, Et_4Pb) from sediment. The extracted compounds are analysed in their authentic forms by a gas chromatographic-atomic absorption spectrometry system. Other forms of inorganic and organic lead do not interfere. The detection limits for sediment (5 g) is 0.01 mg kg^{-1}. In this method 5 g wet sediment and 5 mL of EDTA reagent, (0.1 M, 37 g $Na_2EDTA\ 2H_2O/1$), and 5 mL of hexane are placed in a 25 mL test tube with a Teflon-lined screw cap and shaken for 2 h then centrifuged. The extract was analysed by gas chromatography using an atomic absorption spectrometer set at the 217 μm lead line and with a silica furnace as a detector (Chau

Table 12. Recovery and reproducibility of alkyllead and lead (II) compounds from sediment.

amt of Pb added, µg	Recovery,[b]%				
	Me_3Pb	Et_3Pb	Me_2Pb	Et_2Pb	Pb(II)
1	113 (9)	73 (14)	103 (6)	104 (15)	
5	111 (3)	86 (2)	116 (2)	94 (5)	
10	122 (4)	106 (1)	114 (3)	85 (1)	
20	99 (1)	111 (4)	118 (2)	89 (3)	
av	111	94	113	93	
% rel std dev (n = 6) at 5 mg kg^{-1} level	4	4	14	15	9[c]

[a]Sediment 1 g; spiked compounds expressed as Pb.

[b]Average of two results with average deviation in parentheses.

[c]The sediment contained 71 mg kg^{-1} of Pb(II) which was used to evaluate the reproducibility. No Pb(II) was added to sample.

et al., 1976). This combination has a detection limit of about 1 µg lead, about three orders of magnitude better than can be achieved using a flame ionization detector.

The system used by these workers consisted of a Microtek 220 gas chromatograph and a Perkin-Elmer 403 atomic absorption spectrophotometer. These instruments were connected by means of a stainless steel tubing (2 mm o.d.) connected from the column outlet of the gas chromatograph to the silica furnace of the atomic absorption spectrometer. The silica furnace was set at 1000 °C. The gas chromatographic column was packed with 3% OV-1 supported on Chromosorb W. The column was temperature programmed at 15 °C hr to 150 °C.

The furnace was constructed from silica tubing (7 mm i.d., 6 cm long) with open ends. The lead compounds separated by gas chromatography were introduced to the centre of the furnace through a side-arm. Hydrogen gas was introduced at the same point at a flow rate of 1.35 mL min^{-1}, the burning of the hydrogen improved the sensitivity. The silica furnace was mounted on top of the atomic absorption spectrometer burner and aligned to the light path. When the absorbances were plotted against lead concentrations, each of the five tetraalkyl compounds gave similar calibration curves; the response was linear up to at least 200 ng Pb, above which over-lapping of the peaks occurred.

Organolead in biological materials

In the determination of these ionic alkyllead compounds in biological tissues, difficulties are further compounded by their strong affinity with protein and lipid matrices. There has been a dearth of information on the occurrence of these compounds in biological samples mainly because of the lack of suitable methodology. Up to the present time there have been only relatively few methods (Chau *et al.*, 1983; Chau *et al.*, 1976; Sirota and Uthe, 1977; Estes *et al.*, 1981; Harrison and Laxen, 1978; Andreae, 1977; Chau *et al.*, 1984), dealing with the ionic alkyllead compounds in biological samples.

Several analytical methods for the determination of trialkyllead compounds have been reported: (a) the separation of triethyllead ion as the benzoate from liver and identification by infrared spectrometry; (b) the separation of trialkyllead compounds from rat blood, urine, brain, liver and kidney via a laborious multiple extraction separation procedure with final dithizone complexation of the decomposed organoleads and colorimetric determination of the lead dithizone complex (Esters *et al.*, 1981; Harrison and Laxen, 1978).

Atomic absorption spectrometry

Chau *et al.* (1976) applied gas chromatography atomic absorption to the determination of tetraalkyllead compounds in fish samples in high lead areas. Of some 50 fish samples analysed, only one sample was found to contain detectable amounts (0.26 mg kg^{-1}) of tetramethyllead in the fillet. Since there is no known tetraalkyllead industry and tetramethyllead is not used in gasoline in this area, the source of tetramethyllead is not yet known. The possibility that it comes from *in-vivo* lead methylation in the sediment or in the fish cannot be totally disregarded.

Sirota and Uthe (1977) have described a fast, sensitive atomic absorption procedure for determining tetraalkyllead compounds in biological materials such as fish tissue. Tissue homogenates were extracted by shaking with a benzene/aqueous EDTA solution, a measured portion of the benzene was removed and after digestion, the residue was defatted if necessary. The resultant Pb^{2+} was determined by flameless atomic absorption spectroscopy using a heated graphite atomizer. Using a sample weight of 5 g, 10 µg kg^{-1} of lead as PbR_4, can be determined with a relative standard deviation of 5%. No other forms of lead that were tested (e.g., PbR_3X, PbR_2X_2), were found to partition into the benzene layer under these conditions.

The recovery and selectivity of the method was evaluated by adding known amounts of different lead compounds to previously analyzed tissue samples. The results obtained are summarized in Table 13 and indicate a satisfactory recovery and selectivity for tetraalkyllead compounds. Various marine tissues were sampled for total lead and tetraalkyllead. Results are summarized in Table 14. Di- and tri-substituted alkylleads were also evaluated in this system and the results were satisfactory.

Gas chromatography

Chau *et al.* (1979, 1984) have described a gas chromatographic method for the determination of the nanogram level of trialkyllead ions as the chloride in biological materials.

Chau *et al.* (1979) have described a simple and rapid method for the determination of Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$ and Et_4Pb in fish samples. This procedure, discussed in more detail in the section on water analysis above, involves homogenisation of the

Table 13. Recovery of tetraalkyllead compounds from cod liver homogenate.

Compound	Amount added, µg Pb	Amount added, ng/g	Total Pb present prior to spike µg	Total Pb found after spike, µg	Amount of spike found µg	Recovery %
Tetramethyllead	0.10	20	0.25	0.38	0.13	130
	0.10	20	0.27	0.40	0.13	130
	0.50	100	0.06	0.575	0.515	103
	0.50	100	0.06	0.625	0.565	113
Tetraethyllead	0.10	20	0.14	0.21	0.07	70
	0.10	20	0.16	0.26	0.10	100
	0.50	100	1.056	1.548	0.492	98
	0.50	100	0.053	0.65	0.542	119
	0.50	100	0.045	0.42	0.375	75

sample with EDTA and extraction with a small volume of hexane prior to analysis by gas chromatography utilizing an atomic absorption detector. Using this method it was demonstrated that trout after exposure to water containing 3.5 µg L^{-1} tetramethyllead concentrated this substance in its tissues, mainly in lipid layers with concentration factors between 124 and 934.

Chau *et al.* (1984) have also described a method for the determination of dialkyllead and triaalkyllead compounds in fish. This method involves use of a tissue solubilizer to digest the sample followed by chelation extraction with sodium diethyldithiocarbamate, followed by n-butylation using butyl magnesium chloride to their corresponding tetraalkyl forms, RnPb Bu(4-n) and R_4Pb, respectively (R = methyl and ethyl). The method determines simultaneously in one sample; tetraalkyllead, ionic alkyllead (R_2Pb^{2+} and R_3Pb^+), and divalent inorganic lead, all of which are determined by gas chromatography using an atomic absorption detector.

In this method, the fish samples were homogenized a minimum of five times. About 2 g of the homogenized paste was digested in 5 ml of tetramethylammonium hydroxide solution in a water bath at 60 °C for 1–2 h until the tissue had completely dissolved to a pale yellow solution. After cooling, the solution was neutralized with 50% hydrochloric acid to pH 6–8. The mixture was extracted with 3 mL of benzene for 2 h in a mechanical shaker after addition of 2 g sodium chloride and 3 mL of sodium diethyldithiocarbamate. After centrifugation of the mixture, a measured amount (1 mL) of the benzene was transferred to a glass-stoppered vial and butylated with 0.2 mL of butyl magnesium chloride with occasional mixing for ca. 10 min. The mixture was washed with dilute sulphuric acid to destroy the excess Grignard reagent. The organic layer was separated in a cupped vial and dried with anhydrous sodium sulphate. Suitable aliquots (10–20 µL) were injected to the gas chromatographic atomic absorption system for analysis.

The recoveries of trialkyllead and dialkyllead species at different levels obtained by this procedure are shown in Table 15. The relative low recovery of dimethyllead is in agreement with the results of other investigators, Chau *et al.* (1984) noticed that there was a large Pb(II) peak in the fish sample containing spiked dimethyllead, but such was not found in the standard which was run in parallel but without the sample. They attributed such low recovery to the decomposition of dialkyllead in the fish matrix. Diethyllead, however,

Table 14. Concentrations of total lead and tetraalkyllead in various marine tissues.

Tissue	Concentration total Pb, mg kg^{-1}	Concentration PbR_4, mg kg^{-1}	% Tetraalkyllead of total lead
Frozen Cod (liver homogenate)	0.39 ± 0.04	0.037 ± 0.003 0.010 ± 0.001	9.5
Large, freshly killed cod (liver homogenate)	0.52 ± 0.05	0.125 ± 0.005	24
Small, freshly killed cod, (2 separate lobes analyzed).	A. 0.21 ± 0.04[a]	0.028	13.3
	B.	0.044	20.9
Lobster digestive gland (homogenate)	0.20 ± 0.02	0.162 ± 0.004	81
Frozen mackerel muscle (homogenate)	0.14 ± 0.02	0.054 ± 0.005	38.6
Flounder meal	5.34 ± 1.02	4.79 ± 0.32	89.7

[a] For total lead determinations both lobes.

Table 15. Recovery and reproducibility of alkyllead and lead (II) compounds from fish[a].

Amount of Pb added μg	Recovery[b]%				
	Me_3Pb	Et_3Pb	Me_2Pb	Et_2Pb	Pb (II)
1	72 (5)	102 (5)	79 (4)	93 (0)	
5	88 (4)	88 (3)	89 (5)	103 (2)	
10	93 (2)	88 (2)	56 (10)	92 (2)	
20	91 (2)	81 (2)	62 (6)	114 (2)	
av	86	92	71	101	
% rel std dev (n = 6) a^+ 5 mg kg^{+1} level	15	7	18	20	14[c]

[a] Fillet, 2 g; spiked compounds expressed as Pb.

[b] Average of two results with average deviation in parentheses.

[c] The fish fillet contained 142 mg kg^{-1} of Pb(II) which was used to evaluate the reproducibility. No. Pb(II) was added to sample.

did not decompose significantly and was recovered near quantitative levels. For the first time, the occurrence of triethyl and diethyllead compounds was detected in fish samples and in other environmental materials (Table 16).

Chau *et al.* (1984) have also applied derivitization with butylmagnesium halides, followed by gas chromatography to the determination of mono, di, tri and tetraalkyllead compounds in biological samples. Detection was achieved by an atomic absorption detector.

The capillary column gas chromatographic method developed by Forsythe and Marshall (1983) for the determination of di and trialkyllead compounds in water, described earlier, has also been applied to the determination of these compounds in whole egg samples. Alkyllead salts (R_3Pb^+ and R_2Pb^{2+}, R + Me or Et) are recovered from water or whole eggs by complexometric extraction with dithizone. The dithizonates are phenylated and speciated by capillary column gas chromatography on a 30 m fused silica DB-1 column with electron capture detection. The method is sensitive to low μg kg^{-1} levels of lead salts in 2.5 g egg homogenate. At these levels methyllead salts (but not ethyllead salts) interact strongly with the sample matrix. Treatment of the matrix with lipids and proteases releases them.

Whole egg hydrolysis procedure

Whole egg homogenate was incubated at 37 °C for 24 h in 60 mL of 5% ethanol/0.1 M phosphate buffer (Ph 7.5) containing 30 mg of Lipase Type(III) and 30 mg of Protease Type(XIV). This technique was found to be 72 ± 9% effective after 24 h relative to classical acid hydrolysis.

Absolute ethanol (15–22 mL) and ammoniacal buffer (pH 9.5 10 mL) were added to the sample. The mixture was extracted three times with 0.5 g/L dithizone (10 mL) in 50% benzene/hexane. The organic extracts were combined, centrifuged and back-extracted three times with 10 mL of nitric acid, (0.15 M). The aqueous washes were combined neutralized with sodium hydroxide and further basified with 5 mL ammoniacal buffer (pH 9.5). The alkyllead salts were recovered by extracting the aqueous phase three times with 0.1 g/L dithizone (10 mL) in 50% benzene/hexane. These washes were combined and centrifuged and the organic layer was reduced in volume to 0.5 mL.

Organolead in Air

Classical methods

Earlier methods were based on polarography, spectrophotometry of lead dithizonate and reaction with iodine monochloride (Moss and Browett, 1966). None of these methods are of adequate sensitivity to be applicable to environmental air analysis. Methods based on gas chromatography combined with atomic absorption spectrometry operated with lead specific detectors are more appropriate to such measurements as discussed below.

Atomic absorption spectrometry

Various workers (Hancock and Slater, 1975; De Jonghe and Adams, 1979; Thilliez, 1967) have applied

Table 16. Analysis of environmental samples (St. Lawrence River Near Maitland Ontario.)[a]

Sample	Me_4Pb	Me_3EtPb	Me_2Et_2Pb	$MeEt_3Pb$	Et_4Pb	Me_3Pb^+	Me^2Pb^{2+}	Et_3Pb^+	Et_2Pb^{2+}	Pb^{2+}
Carp	137	—[b]	—	—	780	2735	362	906	707	1282
	—	—	96	142	7475	162	—	1215	1310	4133
Pike	—	—	—	169	1018	215	—	—	—	1040
	—	—	—	146	1125	205	—	53	—	1187
White sucker	—	—	—	—	4384	196	—	3433	4268	3477
	—	—	—	293	2948	95	—	2171	2196	3610
Small mouth bass	—	—	57	187	1204	—	—	223	92	254
	—	—	71	252	1834	—	—	660	275	305
Sediment	—	—	—	142	1152	—	—	187	22	10000
	—	—	—	—	309	—	—	—	—	5582
Macrophytes, mixed										
surface	—	—	—	—	68	—	—	132	—	4327
4 m deep	—	38	1501	3613	16515	—	—	558	113	59282

[a] Data expressed in μg kg^{-1} as Pb, wet weight; whole fish for fish samples.

[b] Not detectable.

this technique to the determination of organolead compounds in air.

Methods such as direct atomic absorption spectrometry and flame photometry (Thilliez, 1967) are unsuitable for the determination of tetraalkyllead in environmental samplés because of the lack of specificity and ion sensitivity or because of the long time required to analyse a single air sample.

Torsi and Palmisano (1983) have described a procedure for sampling air using a battery powered field sampler and capturing organolead compounds by electrostatic attraction and subsequently determining them by electrothermal atomic absorption spectrometry. Down to 100 pg tetralkyllead (as lead) can be determined by this procedure.

Gas chromatography

Gas chromatography with electron capture detection and gas chromatography with catalytic hydrogenation prederivitivization and flame ionization detection (Soulages, 1966) and gas chromatography with microwave plasma detection (Reamer *et al.*, 1978) are unsuitable for tetralkyllead compounds in environmental samples because of the lack of specificity and/or sensitivity or because of the long time required for the analysis of a single air sample. Most of the available methods with high sensitivity and low detection limits are based on a sampling step, often performed by cryogenic trapping, followed by an analysis step by gas chromatography combined with atomic absorption spectrometric detection (both flame and electrothermal), (De Jongne *et al.*, 1980a,b; Chau *et al.*, 1976).

These methods determine the tetraalkyllead compounds present but are time-consuming and require a complex set up.

Boettner and Dallas (1965) have compared the sensitivities of the electron capture, thermal conductivity, argon ionization and flame ionization detectors to the chromatographic determination of organolead and aliphatic chloride compounds in the atmosphere. They used a Wilkins Hi-Fi Model 600 Chromatograph with both hydrogen flame and electron capture detectors, a Beckmann Model GC-2A Chromatograph with a thermal conductivity detector and a Research Specialities Model 600 Chromatograph with an argon ionization detector. All separations were made on 3 mm ($\frac{1}{8}$ in) or 6 mm × 2 mm ($\frac{1}{4}$ in × 6 ft) stainless steel columns. The compounds studied and the column coatings used are tabulated in Table 17.

The sensitivities of the thermal conductivity and the argon ionization detectors are independent of the molecular weight or the number of chlorine atoms in the chlorinated compounds, but the flame detector decreases slightly in sensitivity with increasing numbers of chlorine atoms. The electron capture detector was found to have its greatest response to the chlorinated compounds at 10 volts. With the electron capture detector the sensitivity was dependent in rather a complex manner on the molecular weight and the number of chlorine atoms in the chlorine compound.

The conclusions reached by Boettner and Dallas (1965) concerning the electron capture detector were as follows: that for analysis of volatile chlorinated aliphatic hydrocarbons this detector is no more sensitive than the ionization detectors for those compounds having one or two chlorine atoms. For those compounds having three or four chlorine atoms, the electron capture detector was from 100 to 1,000 times more sensitive than the ionization detectors. For the two alkyllead compounds tested, the electron capture detector gives little improvement in sensitivity but its discrimination toward the lead substituted compounds as compared with unsubstituted hydrocarbons makes it a preferable detector for analysing mixtures of these two types of compounds.

Gas chromatography using an atomic absorption spectrometer as detector has been used by several workers to determine tetraalkyllead compounds (Radzuik *et al.*, 1979; Robinson *et al.*, 1977; De Jonghe *et al.*, 1980a, 1980b).

Robinson *et al.* (1977) have carried out a detailed study of atomization processes in carbon furnace atomizers during the development of a gas chromatography-furnace atomic absorption combination for the determination of organolead compounds in gasoline and air. The carbon furnace atomizer is attached directly to the gas chromatograph column. The atomizer exhibits high sensitivity and eliminates many of the problems involved with interferences encountered with furnace atomization. Their study of the furnace atomization step revealed the problems involved in obtaining accurate quantitative data. Thus, it is vital to control all the variables which affect the rate and degree of atomization of lead and to use pyrolytic carbon sample boats.

A further problem relates to the variation of the electrical resistance of the carbon rod or tube with use. Thus, with a standardized atomization programme, the temperatures achieved will differ somewhat as the carbon ages, although the time and voltage remain the same, and this will affect the atomization rate.

These difficulties lead Robinson *et al.* (1977) to develop a new type of atomizer in which the effluent from the gas chromatograph enters the base of the atomizer where the gaseous sample is decomposed and the atomization takes place. The atoms flow into the cross-piece which is in the optical light path. The advantage of the process is that the peak of the solvent used is quite separate from the peak of the metal-bearing component on the gas chromatogram. The gas chromatograph separates the metal-bearing components from the rest of the material, which eliminates many of the problems encountered in the solvent evaporation step and other matrix effects. Decomposition is fairly rapid, although several seconds elapse from the time that the sample enters the carbon atomizer before the atoms reach the

Table 17. Column coatings and supports for the separation of chlorinated aliphatic and lead alkyl compounds using gas chromatographs with various detector.

	Thermal Conductivity	Argon Ionization	Flame Ionization	Electron Capture
Methyl Chloride	C	A	A	A
Dichloromethane	C	A	C	B
Chloroform	C	A	A	B
Carbon Tetrachloride	A	A	A	B
Ethyl Chloride	A	A	A	A
1,2 Dichloroethane	A	A	A	B
1,1,1 Trichloroethane	C	A	A	B
1,1,2 Trichloroethane	C	A	C	B
1,1,2,2 Tetrachloroethane	C	A	C	E
1,2 Dichloropropane	C	A	C	C
1,2,3 Trichloropropane	C	A	C	E
Chloroethylene	A	A	A	A
1,2 Dichloroethylene cis	A	A	A	A
1,2 Dichloroethylene trans	A	A	C	B
Trichloroethylene	C	A	A	B
Tetrachloroethylene	D	A	C	B
Lead Tetramethyl	D	G	D	F
Lead Tetraethyl	D	G	F	F

A - 20% Carbowax 600 on C-22 Firebrick
B - 5% Silicone 550 and 5% Ucon (Water insoluable) on Chromosorb P
C - 10% Silicone 550 on C-22 Firebrick
D - 20% Carbowax 20 M on C-22 Firebrick
E - 10% Silicone SE 30 on Chromosorb W
F - 5% Silicone SE 30 on Chromosorb W
G - 5% Silicone 550 on Anakrom ABS

optical light path. This permits chemical decomposition to take place and virtually eliminates chemical interference, which is usually caused by varying rates of atomization from different compounds rather than by prevention of decomposition. Even if the rate varies, decomposition is virtually complete before the free atoms enter the light path. The peak height is a product of the metal concentration and the resolution of the g.c. column. The definition of sensitivity as that concentration which results in 1% absorption is therefore unrealistic. Sensitivity measurements were based on peak area data.

The sensitivity of ths equipment was shown to be of the order 0.1 ng lead. Robinson *et al.* (1977) studied the applicability of their technique to the determination of organolead compounds in the atmosphere. In this work 1 m^3 of air was pulled through a cryogenic trap. The trapped material was then put into the gas chromatograph under conditions suitable for tetramethyllead or other organic lead compounds. The concentrations of tetraethyllead were so small that in many samples none was detected.

De Jonghe *et al.* (1980a, 1980b) have described a sampling system for the analysis by gas chromatography-atomic absorption spectrometry of alkyllead compounds in air. This method, when compared with many other published procedures is relatively rapid.

Sampling periods of 1 h or less proved to be sufficient, even for the determination of alkyllead species in relatively nonpolluted air. The major difficulty in collecting the compounds from air samples on gas chromatographic column packing material is the condensation of moisture from the air sample in the trap. Ice condensation on the column material leads to clogging of the pores and a sharp decrease in the air flow rate. The volume of air that can be sampled is therefore limited.

De Jonghe *et al.* (1980a, 1980b) used a large U-tube filled with glass beads at −80 °C to condense water from the sample before it entered the column.

In this way the predeposition of water was much improved as a result of a better cooling efficiency of the air. However, at −80 °C a substantial fraction of the tetraalkylleads is retained also, especially the less volatile species, whereas at higher temperatures also a rapid obstruction of the chromatographic adsorption tube occurs. Provided the trap is cooled down to sufficiently low temperatures to retain also the more volatile species, dimethyldiethyllead, trimethylethyllead and tetramethyllead it could therefore be used for the direct collection of the lead alkyl compounds. This would allow much higher air flow rates than is possible with chromatographic adsorption tubes.

The air to be analysed was passed at a flow rate of about 6 L min^{-1} for 1 h through a two-component collection system. The first stage was a 47 mm Nucleopore membrane filter (0.4 μm) to remove the lead-containing particulates. The second stage was a cryogenic sampling trap for the collection of the volatile tetraalkyllead compounds. It consists of a U-shaped Pyrex tube (50 cm long by 25 mm i.d.) filled with glass beads of 4 mm diameter and immersed in a liquid nitrogen-ethanol slush bath at −130 °C. After sampling is completed the U-tube remains in the slush bath until analysed.

After the sample was obtained the trapped alkyllead compounds were thermally desorbed from the large U-tube and transferred to a short adsorption tube by connecting the sampling tube, still immersed in the slush bath, with a short glass column (26 cm long by 6 mmo.d. and 2 mm i.d.) packed with 0.2 g of 3% OV — 101 on 100/120 mesh Gaschrom Q and kept in liquid nitrogen. While air was passed at a flow rate of 1 L min^{-1} the U-tube was removed from the slush bath and allowed to warm slowly in air and then in a water bath, at 60 °C. With this treatment a rather constant air flow through the desorption system can be maintained, but near the end of the operation, when appreciable amounts of water start to evaporate out of the trap and condense on top of the adsorption tube, the flow rate decreases and desorption stops.

The adsorption tube was then attached to the four-port valve installed between the carrier gas inlet and the injection port of the gas chromatograph. The tube was immersed in a hot water bath at ca. 90 °C, and the trapped sample was swept into the gas chromatograph by the carrier gas. Simultaneous with this injection, the gas chromatograph oven temperature program was initiated and the graphite furnace brought to 2000 °C.

The reproducibility of measurement achieved by this method are better than 2% at the nanogram level. A detection limit of below 100 pg lead m^{-3} air was achieved. Typical values of the five ethyl methyl lead compounds in suburban and residential air samples ranged between <0.02 and 30.3 μgm^{-3}.

Radzuick *et al.* (1979) have described a sensitive gas chromatographic graphite furnace atomic absorption method for the determination of individual alkyllead compounds in air. The atomic absorption instrument was operated at the 283.3 nm leadline. Gas chromatography — mass spectrometry was used to identify the separated organolead compounds.

A Perkin-Elmer 603 atomic absorption spectrophotometer was equipped with a deuterium background corrector, and a HGA 2100 graphite furnace. The radiation source was a Perkin-Elmer electrodeless discharge lamp operated at 10W. A Pye series 104 chromatograph was interfaced with the graphite furnace with a tantalum connector machined from a 6.4 mm diameter rod. The glass chromatographic column (150 cm long, 0.6 cm o.d.) was packed with 3% OV-101 on Chromosorb W operated at 150 °C. The effluent was transferred to the furnace by Teflon-lined aluminium tubing (3 mm o.d.) heated electrically to 80 °C. The adsorption tube for air samples were U-shaped Teflon-lined aluminium tubes (30 cm long, 3 mm o.d.) packed with 3% OV-101 on Chromosorb W (80–100 mesh). Moisture was condensed from air by using glass U-tubes at −15 °C.

The detection limit of this method was found to be about 40 pg of lead for each compound, based on peak-height measurements. For a 70 L air sample, 0.5 ng m^{-3} of each compound could be detected.

Radzuick *et al.* (1979) showed that total atmospheric alkyllead averaged 14 ng Pb m^{-3}.

Vehicular exhaust fumes are an insignificant contributor to this total. Tetraethyllead, the only alkyllead compound used in Southern Ontario gasoline, is unstable in air. Besides decomposing, it reacts to give other alkyllead compounds, which can also be determined.

Reamer *et al.* (1978) have discussed the applicability of a gas chromatograph coupled with a microwave plasma detector, for the determination of tetraalkyllead species in the atmosphere. The tetraalkyllead species are collected by a cold trap. The volatile lead species are concentrated within an organic solvent, separated by a gas chromatographic column and determined by measurement of emission intensity at the lead 405.78 nm line. A cold trap containing SE-52 on Chromosorb F at −80 °C was used to collect alkyllead compounds from the atmosphere. This trap had a collection efficiency for tetraalkyllead compounds of 84–100% at the 150 μg tetraethyllead level.

When using the wave-length modulation mode for background correction, the tetraalkylead calibration curves extended from the low pg range to the low ng range with the following detection limits: tetramethyllead, 6 pg; trimethylethyllead, 10 pg; dimethyldiethyllead, 23 pg; methyltriethyllead, 35 pg; and tetraethyllead, 40 pg.

The absorbent from the sampling tube was transferred to a 50 mL round-bottom flask which was attached to a miniature freeze-drying system. The sample was dried for 12 h, resulting in the quantitative removal of the tetraalkyllead compounds and water present in the sample. The gases were quantitatively trapped cryogenically at liquid nitrogen temperature. The trap was removed from the system and slowly warmed. The container walls were rinsed with distilled water to ensure quantitative retention of the analyte. The organic lead compounds were extracted with 200 μL of hexane by shaking for 10 min. Sample analysis involved injecting a 1 to 5 μL aliquot of the hexane layer into the gas chromatograph with a 10 μL microsyringe.

Individual concentrations of the five ethyl/methyl lead compounds found in vehicle exhausts ranged between 2 and 650 μg m^{-3} and total tetraalkyllead compounds ranged from 57 to 1030 μg m^{-3}.

High performance liquid chromatography

Koizumi *et al.* (1979) coupled a Zeeman graphite furnace atomic absorption detector to a high performance liquid chromatographic column to separate alkyllead compounds collected from air samples and automotive exhausts. One of the problems with conventional graphite furnace atomic absorption spectrometers is that, because the maximum attainable atomization temperature is too low different absorbance values are obtained for each of the five ethyl methyl lead compounds. One way of overcoming this difficulty is to atomize at a very high temperature. Koizumi *et al.* (1979) achieved this with a new detector design which is capable of achieving an atomization temperature of 2800 °C. This furnace consists of several separate parts; the sample cup, the thermal converter and reactor of porous graphite, a narrow hole (which at high temperatures also acts as a thermal converter), and the absorption cell. The sample vapor flows through the thermal converter and its temperature is raised sufficiently to decompose the compound and to atomize the metal. After that, the sample vapor is carried to the absorption cell for Zeeman atomic absorption spectrometry measurement.

The centre portion of the cuvette is heated to a high temperature first because of the small heat capacity and the large electrical resistance. Conductive heating causes the porous graphite to be heated next and, finally, the tantalum cup is heated. A few seconds after the current is turned on, the temperature difference between the three sections begins to decrease. Vaporized sample in the cup follows the flowing argon gas through the porous graphite which its temperature is raised by coming into intimate contact. It then passes through a small hole, the walls of which have the highest temperature. Because of the intimate contact with these surfaces, the gas temperature becomes equal to the wall temperature before passing into the absorption cell.

The system used to separate alkyllead compounds is described in Table 18. Methyl alcohol was used as the eluent. The pressure was about 30 kg/cm^2, and the flow rate was 0.67 mL min^{-1}. A sample of 10 mL was injected into the high performance liquid chromatograph while the flow was stopped. A 10 μL aliquot from each 250 μL portion of column effluent was intermittently introduced into the furnace.

Table 18. Instrumentation for HPLC-ZAA system.

- HPLC
  - high performance liquid chromatograph Hitachi M633, 0.350 kg/cm^2, 0.36 3.6 mL/min
  - column. Hitachi, 2.5 × 500 mm
  - resin, Hitachi Gel No. 3010
- Furnace
  - graphite. Ultra Carbon 0.5 - in. diameter,
  - porous graphite, RVC 100 PPI porosity grade
  - furnace power supply, reactor controlled, 20 V. 700 A
- ZAA spectrophotometer.
  - light source, magnetically confined lamp (dc +rf (50 Mhz)).
  - magnet, permanent 12 kg
  - variable retardation plate, 0 /2, 30 Hz
  - polarizer, Rochon prism (quartz optical contact)
  - monochromator, Hitachi M100 spectrophotometer
  - photomultiplier, Hamamatsu T.V. YA 7122
  - chopper, Bulova L2C, 1.0 KHz
- electronics.
  - lock-in amplifier, (including log convertor, AGC)
  - recorder, Honeywell Electronik 17.

To determine organolead compounds in automotive exhaust gases, the gas was collected in a polythene bag and was forced to flow through the furnace carrier gas inlet port at a flow rate of 0.09 L min^{-1}. The lead concentration in the exhaust gas was determined from the area under the absorption signal.

Organoarsenic Compounds

Organoarsenic in water

Classical methods. Most of the classical procedures for decomposing any organoarsenic compounds present in samples prior to the determination of total inorganic arsenic incorporate some mode of wet or dry digestion to destroy any organically bound arsenic, in addition to any other organic constituents present in the sample.

Probably the most frequently used method of digestion incorporates the use of nitric and sulfuric acids. Kopp (1973) used this digestion method and experienced 91 to 114% recovery of arsenic trioxide added to deionized water and 86 to 100% recovery of the compound added to river water. The uncertaintities seem to arise when reviewing digestive methods using nitric and sulfuric acid. First, the addition of inorganic arsenic to an organic matrix and subsequent recovery of all the inorganic arsenic added is not definite proof of total recovery of any organoarsenicals present. Secondly, the choice of o-nitrobenzene arsenic acid and o-arsanilic acid by Kopp (1973) in his recovery studies seems unfortunate since both compounds present arsenic attached to an aromatic ring which is a typical of cacodylic acid and disodium methyl arsonate, two widely used organoarsenicals.

Aside from nitric and sulfuric acid, a relatively simple digestive method employing 30% hydrogen peroxide in the presence of sulfuric acid was reported by Kolthoff and Belcher (1957) and subsequently used by Dean and Rues (1978) to determine arsenic in triphenylarsine.

Armstrong *et al.* (1966) observed that organic matter in sea water could be oxidized to carbon dioxide on exposure to sufficient ultraviolet radiation from a medium pressure mercury arc vapor lamp. This approach has also been used to decompose organoarsenicals giving 111% recovery for o-arsenilic acid, 97% for sodium cacodylate and 108% for arsenazo.

Stringer and Attrap (1979) applied the Dean and Rues (1978) sulphuric acid-hydrogen peroxide and the Armstrong *et al.* (1966) ultraviolet decomposition methods to the determination of organoarsenic compounds in waste water.

Arsenic determinations were performed by either the silver diethyldithiocarbamate colormetric procedure (Kopp, 1973) or the arsine-atomic absorption method (Manning, 1971).

The organoarsenicals investigated were disodium methanearsonate, dimethylarsinic acid, and triphenylarsine oxide. All the digestive methods gave quantitative arsenic recoveries for the three organoarsenic compounds when added to wastewater samples. The ultraviolet photodecomposition proved to be an effective digestive technique, requiring a 4 h irradation to decompose a primary settled raw wastewater sample containing spiked quantities of the three organoarsenicals.

Between 96 and 105% recovery of triphenyl arsine oxide, disodium methanearsonate and dimethylarsinic acid at the 5 μg arsenic level were obtained by this procedure in water samples.

Atomic absorption spectroscopy

Various workers have used volatile hydride generation (arsine) with sodium borohydride followed by various separation and detection systems for the determination of organoarsenic species.

Separation of volatile arsines is achieved by gas chromatography (Andreae, 1977) or sequential volatilization (Braman *et al.*, 1977; Crecelius, 1978). The detection systems are microwave emission spectrometry (Talmi and Bostick, 1975), electron capture and flame ionization detection (Andreae, 1977), dc discharge emission (Talmi and Bostick, 1975), atomic absorption spectrometry and neutron activation analysis (Andreae, 1977; Shalk and Tallman, 1978).

Gifford and Bruckenstein (1980) generated the gas hydrides As^{III}, Sn^{II} and Sb^{III} by sodium borohydride reduction and separated them on a column of Poropak Q. Detection was at a gold gas porous electrode by measurement of the respective electro-oxidation potentials. Detection limits were (5 mL samples) As^{III} 0.21 μgL^{-1}, Sn^{II} 0.8 μgL^{-1} and Sb^{III} 0.2 μgL^{-1}.

Persson and Ingram (1982) have described a method for the determination of dimethylarsinic acid in sea water in the sub mgL^{-1} range by electrothermal atomic absorption spectrometry after preconcentration of a strong cation exchange and elution with ammonia.

Edmond and Francesconi (1976) have reported that the alkylated arsesicals methylarsonic acid and dimethylarinic acid occurring in the environment may be estimated directly by vapour generation atomic absorption spectrometry at 193.7 μm without prior digestion. Sodium borohydride treatment produces methylarsine, and dimethylarsine, respectively, which are swept directly into a hydrogen-nitrogen entrained air flame by the excess hydrogen generated by hydrolysis of the sodium borohydride. These methylated arsines are estimated in a manner identical to the arsine produced following acid digestion or dry ashing. The calibration curves and instrument responses are directly comparable and are dependent only on the quantity of arsenic entering the flame.

The sample containing sodium arsenate, methylarsonic acid, and dimethylarsinic acid was treated with sodium borohydride and the mixed arsines generated trapped in a glass bead packed tube (200 mm × 25 mm) at −180 °C. The cooling agent was removed and the trap allowed to warm slowly in the laboratory atmosphere. A valve assembly kept the trap sealed and was released periodically with a simultaneous flow of nitrogen through the trap into the flame. The valve was opened for 5 s each min. The instrument responses was recorded on a chart moving at 2 mm min and reassembled, in outline, a gas chromatographic trace with arsine peaking at 3 min methylarsine at 8 min and dimethylarsine at 13 min.

Detection limits were 500 ng for inorganic arsenic and 1 μg for monomethylarsonic acid and dimethylarsinic acid. Aqueous solutions of methylarsonic acid and dimethylarsinic acid were adjusted to 2% in hydrochloric acid before addition of the sodium borohydride solution.

Arsenic itself, originating by the reduction of inorganic arsenic and methyl arsines, originating by the reduction of organoarsenic compounds, have different responses in colorimetric versus atomic absorption methods of analysis. The colorimetric diethyl-dithicarbamate method is much more responsive to arsine than to methyl arsines, whilst vapour generation atomic absorption spectrometry is equally responsive to both forms of arsenic, depending only on the weight of arsenic entering the flame.

Gas chromatography

Lussi-Schlatter and Brandenberger (1976) have reported a method for inorganic arsenic and phenylarsenic compounds based upon gas chromatography with mass specific detection after hydride generation with head space sampling. However, methylarsenic species were not examined.

Odanaka *et al.* (1983) have reported that the combination of gas chromatography with multiple ion detection system and a hydride generation heptane cold trap technique is useful for the quantitative determination of arsine, monomethyl-, dimethyl-, and trimethylarsenic compounds and this approach is applicable to the analysis of environmental and biological samples.

In this method, arsine and methylarsines produced by sodium borohydride reduction are collected in n-heptane (−80 °C) and then determined. The limit of detection for a 50 mL sample was 0.2–0.4 μgL^{-1} of arsenic for arsenic compounds. Relative standard deviations ranged from 2% to 5% for distilled water replicates spiked at the 10 μgL^{-1} level. Recoveries of all four arsenic species from river water ranged from 85% to 100%.

Dimethyl arsinic acid yields predominantly dimethylarsine, whilst methylarsonic acid yields predominently methylarsine and trimethylarsine oxide yields predominently trimethylarsine. In this method aqueous samples (1–50 mL) that had been previously neutralized with hydrochloric acid and/or sodium bicarbonate were placed in the reaction vessel and were diluted to 60 mL with water. Then 6 mL of 4 N hydrochloric acid and 2 mL of methanol were added. The cold trapping system was then connected and the carrier gas (helium) was allowed to pass through the system at 100–150 mL min^{-1} for 1 min to flush out any air. The reduction was initiated by injecting 3 mL of 10% sodium borohydride solution through the rubber septum into the aqueous sample. The volatile arsines were collected in a n-heptane (3–5 mL) cold trap for 2 min. The low temperature was maintained by submerging the trap in a dry ice-acetone (−80 °C) bath. The helium flow was contained for 1 min to ensure complete generation and trapping of the arsines. After the collection of the arsines, n-heptane (5 mL) was injected into the gas chromatograph/mass spectrometer.

The following ions were characteristic and intense ions in the mass spectra of arsines, arsine m/z 78 M^+, 76 $(M - 2)^+$, methylarsine; m/z 92 $M^{+.}$, 90 $(M - 2)^{+.}$, 76 $((M - CH_3) - 1)^{+.}$, dimethylarsine m/z 106 $M^{+.}$, 90 $((M - CH_3) - 1)^{+.}$, trimethylarsine, m/z 120 $M^{+.}$, 105 $((M - CH_3) - 1)^{+.}$, 103 $((M - CH_3)^+ - 2)^+$. To achieve simultaneous measurement and to assess the specificity of the analysis, for instance the m/z 76, 78, 89 and 90 were monitored for arsine, methylarsine, and dimethylarsine and/or m/z 90, 103, 105 and 106 for alkylarsines as methylarsine, dimethylarsine and trimethylarsine. However, simultaneous determination of all four arsenicals could not be done at one injection because of a limited range of detectable mass spectra in the system used.

Andreae (1977) described a method for the sequential determination of arsenate, arsenite, mono-, di, di- and trimethylarsine, monomethylarsonic and dimethylarsinic acid, and trimethylarsine oxide in natural waters with detection limits of several ngL^{-1}. The arsines are volatilized from the sample by gas stripping; the other species are then selectively reduced to the corresponding arsines and volatilized. The arsines are collected in a cold trap cooled with liquid nitrogen. They are then separated by slow warming of the trap or by gas chromatography and measured with atomic absorption, electron capture and/or flame ionization detectors. He found that these four arsenic species all occurred in natural water samples.

The apparatus for the volatilization and trapping of the arsines is constructed from Pyrex glass, with Teflon stopcocks and tubing and with Nylon Swagelok connectors. The sample trap consists of a 6 mm o.d. Pyrex U-tube of ca. 15 cm length, filled with silane treated glass wool. The interior parts of the six-way valve which interfaces the volatilization system with the gas chromatograph are made of Teflon and stainless steel.

The gas chromatograph is equipped with a ^{63}Ni electron capture detector mounted in parallel with a flame ionization detector and an auxilliary vent by the use of a column effluent splitter. The separation is performed on a 4.8 mm o.d., 6 m long stainless steel column packed with 16.5% silicone oil DC-550 on Chromosorb W AW DMCS. The helium carrier gas flow rate is 80 mL min^{-1}.

The electron capture detector (Hewlett-Packard 2-6195 with a ^{63}Ni source) is operated in the constant pulse mode with a pulse interval of 50 μs. The atomic absorption detection system consists of a Varian AA5 with a hollow cathode arsenic lamp; the standard burner head is replaced by a 9 mm i.d. quartz burner cuvette.

To isolate the arsine species the sample 1–50 mL is introduced into the gas stripper with a hypodermic syringe through the injection port.

Any volatile arsines in the sample are stripped out by bubbling a helium stream through the sample. Then 1 mL of the Tris buffer solution for each 50 mL sample is added, giving an initial pH of about 6. Into this solution 1.2 mL of 4% sodium borohydride solution is injected while continuously stripping with helium. After about 6–10 min the As(III) is converted to arsine and stripped from the solution. The pH at the end of this period is about 8. Then 2 mL of 6 N hydrochloric acid is added, which brings the pH to about 1. The addition of three aliquots of 2 mL of 4% sodium borohydride solution during 10 min reduces As(IV) monomethylarsonic acid, dimethylarsinic acid, and trimethylarsine oxide to the corresponding arsines, which are swept out of the solution by the helium stream coming from the reaction vessel stream and the evolved hydrogen.

In Table 19 are reported some values obtained for inorganic arsenic, monomethylarsonic and (MMAA) and dimethylarsinic and (DMAA) in natural water samples.

Andreae (1977) commented that if stored in airtight containers, the free arsines are stable in solutions for a few days. They are slowly oxidized by traces of air to the corresponding acids. From untreated samples, the methylated acids, are lost measureably after a period of about three days, depending on the initial concentrations. They are stable indefinitely if the sample is made 0.05 N in hydrochloric acid. Arsenite is slowly oxidized to arsenate in samples below 0.05 μgL^{-1} As(III), a loss of arsenite becomes detectable after about one week. Acidification of the sample increases the oxidation rate and arsenite loss can be detected after one day. If the samples are stored in a freezer below −15 °C or under dry ice, an initial loss of arsenite corresponding to about 0.02 μgL^{-1} is experienced. The sample then remains unchanged with prolonged storage.

Parris *et al.* (1977) have studied in detail the chemical and physical considerations that apply in the determination of trimethylarsine using an atomic absorption spectrophotometer with a heated graphite tube furnace as a detector for a gas chromatograph. 5 μg arsenic could be detected by this technique.

Ion-exchange chromatography

Ion-exchange chromatography has been used to achieve separations of monomethylarsonate, dimethylarsenite and tri- and pentavalent arsenic. Dietz and Perez (1976) have described methods which separated the inorganic arsenic from each of the organic species

Table 19. Arsenic species concentrations in natural waters, μgL^{-1} As.

Locality and Sample Type	As(III)	As(V)	MMAA	DMAA
Seawater, Scripps Pier, La Jolla, CA				
5 Nov. 1976	0.019	1.75	0.017	0.12
11 Nov. 1976	0.034	1.70	0.019	0.12
Seawater, San Diego Trough Surface	0.017	1.49	0.005	0.21
25 m below surface	0.016	1.32	0.003	0.14
50 m below surface	0.016	1.67	0.003	0.004
75 m below surface	0.021	1.52	0.004	0.002
100 m below surface	0.060	1.59	0.003	0.002
Sacramento River, Red Bluff, CA	0.040	1.08	0.021	0.004
Owens River, Bishop, CA	0.085	42.5	0.062	0.22
Colorado River, Parker, AZ	0.114	1.95	0.063	0.051
Colorado River, Slough Near Topcock CA	0.085	2.25	0.13	0.31
Saddleback Lake, CA	0.053	0.020	0.002	0.006
Rain, La Jolla, CA				
10 Sept. 1976	0.002	0.180	0.002	0.024
11 Sept. 1976	0.002	0.094	0.002	0.002

using ion-exchange chromatography. Here, further inorganic speciation relies on redox-based colorimetry (Johnson and Pilson, 1972). Both the accuracy and precision suffer from the low As(III),/As(IV) and As (total)/P ratios normally encountered in the environment. Henry and Thorpe determined these four arsenicals by coupling a digestion and reduction scheme with ion-exchange chromatography (Henry and Thorpe, 1980). However, the utility of this technique for routine environmental analysis is limited, since the implementation time is substantial. This method also relies on estimating As(V) by difference.

Grabinski (1981) has described an ion-exchange method for the complete separation of the above four arsenic species, on a single column containing both cation and anion exchange resins. Flameless atomic absorption spectrometry with a deuterium arc background correction is used as a detection system for this procedure. This detection system was chosen because of its linear response and lack of specifity for these compounds combined with its resistance to matrix bias in this type of analysis.

The elution sequence was as follows: 0.006 M trichloroacetic acid (pH 2.5), yielding first As(III) and then monomethylarsonate; 0.2M trichloroacetic acid yielding As(V): 1.5 M NH_4OH followed by 0.2M trichloroacetic acid yielding dimethylarsinite. Detection was by flameless atomic absorption spectrometry. Arsenic recoveries (full-procedure) ranged from 97% to 104% for typical lake water samples; more erratic but still acceptable recoveries (98% to 107%) were obtained from arsenic contaminated sediment interstitial water. The overall analytical detection limit was 10 μgL^{-1} (original sample mixture) for each individual arsenic species. Relative standard deviations ranged from 0.7% to 1.3% for lake water and distilled deionized water replicates spiked at the 500 μgL^{-1} level.

Grabinski (1981) spiked 0.500 μg of each arsenic species into filtered (0.45 μM) lake water and distilled and deionized water. Arsenic recoveries for the entire procedure averaged 104%, 100% and 97% and 99% for As(III), monomethylarsonate, As(IV) and dimethylarsinite, respectively. Relative standard deviations for replicate determinations ranged from 0.7% for As(III) and dimethylarsinite to 1.3% for As(V).

Aggett and Kadwani (1983) report the development and application of a relatively simple anion-exchange method for the speciation of arsenate, arsenite, monomethylarsonic acid and dimethylarsinic acid. As these four arsenic species are weak acids the dissociation constants of which are quite different it seemed that separation by anion-exchange chromatography was both logical and possible.

Aggett and Kadwani (1983) employed a two stage single column anion-exchange method using hydrogen carbonate and chloride as eluate anions. These species appear to have no adverse effects in subsequent analytical procedures. Its successful application is dependent on careful control of pH. Analyses were performed by hydride generation atomic absorption spectroscopy.

Separation of arsenic(III) and dimethylarsinic acid by elution with carbon dioxide-hydrogen carbonate was satisfactory in the pH range 5.2–6.0. Elution of monomethylarsonic acid was accelerated and satisfactory separation from arsenic(V) achieved using saturated aqueous carbon dioxide (pH 4.0–4.2) containing 10 gL^{-1} of ammonium chloride. In order to avoid oxidation of trivalent to pentavalent arsenic on the column, it was necessary to pretreat the resin with 1 M nitric acid and 0.1 M EDTA before use.

The application of these methods to interstitial waters of lake sediment and also species of lakeweek revealed no methylated arsenic species, only As(III) and As(IV) in the 0.5 μgL^{-1} range were found.

Organoarsenic in Sediments

Gas chromatography

Odanaka *et al.* (1983) have reported the application of gas chromatography with multiple ion detection after hydride generation with sodium borohydride to the determination of mono, di-, methyl arsenic compounds, trimethylarsenic oxide and inorganic arsenic in soil and sediments; this work is discussed more fully in the section of organoarsenic compounds in water. Recoveries in spiking experiments were 100 to 102% (mono and dimethylarsenic compounds and inorganic arsenic) and 72% (trimethyl arsenic oxide).

Organoarsenic in crops/plants

Odanaka *et al.* (1983) have reported the applications of gas chromatography with multiple ion detection after hydride generation with sodium borohydride to the determination of mono, di methylarsenic compounds, trimethylarsenic oxide and inorganic arsenic in plant materials; this work is discussed more fully in the section of organoarsenic compounds in water. Recoveries in spiking experiments were 92–103%.

Organoarsenic in Biological Materials

Gas chromatography

Odanaka *et al.* (1983) have reported the application of gas chromatography with multiple ion detection after hydride generation with sodium borohydride to the determination of mono, di-methyl arsenic compounds, trimethylarsenic oxide and inorganic arsenic in animal tissues; this work is discussed more fully in the section of organoarsenic compounds in water. Recoveries in spiking experiments were 87–103%.

This work showed that in living animal tissue administered inorganic arsenic may be biomethylated to monomethylated, dimethylated and even trimethylated compounds.

Schwedt and Russel (1972) have described a method for the gas chromatographic determination of arsenic (as triphenylarsine) in biological material. In this method, the dry sample is burnt in a Schoniger flask containing 3 N hydrochloric acid, the products are washed out with 3 N hydrochloric acid and aqueous potassium iodide and aqueous sodium bisulphite are added to the solution which is then extracted with diethyldithiocarbamate solution in dichloromethane. The extract is evaporated and the residue is stirred for 30 min with diphenylmagnesium solution in ethyl ether. After addition of dilute sulphuric acid the separated ether phase is evaporated and the residue is treated with mercaptoacetic acid solution. After being set aside for 20 min, the solution is chromatographed on a glass column (2 metres × 3 mm) packed with 5% of teraphthalic acid-treated Carbowax 20 M on Gas-Chrom Q (80 to 100 mesh) and operated at 220 °C with nitrogen, helium or argon as carrier gas and flame ionization detection. Down to 2 $\mathrm{mgL^{-1}}$ of arsenic in the sample could be determined by this procedure.

High performance liquid chromatography

High performance liquid chromatography with inductively coupled argon plasma-atomic emission spectrometric detection, has been used to separate mixtures of arsenic compounds on anion and cation exchange columns using phosphate buffer (Norita *et al.*, 1981). The inductively coupled argon plasma-atomic emission spectrometric detection is used as a selective detector by observing arsenic emissions at 193.6 nm. The detection limit was at the nanogram level. With anion exchange chromatography, the best separation was achieved with Nagel-N-$(CH_3)_3$ column packing and with 0.05 M phosphate buffer. A slight tailing is seen at the As(III) and dimethylarsinic and (DMAA) peaks.

With a cation exchange chromatography (Nagel-SO_3H-10), these arsenicals were separated. Since arsenate is a stronger acid than arsenite, As(V) is more negatively charged than As(III) at the neutral region employed. Arsenobetaine may be neutral or weakly positive. These ionic characteristics may explain the elution sequence of arsenobetaine, arsenite, and arsenate: AB $\rightarrow$ As(III) $\rightarrow$ As(V) in anion exchange chromatography and As(III), As(V) $\rightarrow$ arsenobetaine in cation exchange chromatography. Dimethylarsinic acid eluted later than monomethylarsonic acid on both columns, indicating the affinity of methyl groups of arsenic to alkyl groups of the column packing. In ion-suppression reversed-phase chromatography dimethylarsinic acid was eluted later than monomethylarsonic acid.

Morita *et al.* (1981) pointed out that with the argon/hydrogen flame and 193.7 nm line, the sensitivity of atomic absorption spectrometry was about 1/20th of that obtained using inductively coupled argon plasma-atomic emission spectrometry as the detector in conjunction with high performance liquid chromatography detector. Therefore, atomic absorption spectrometry can be applied only for relatively concentrated samples. Arsenic was also monitored with dc plasma atomic emission spectrometry. The sensitivity of this technique was about one-fifth of that obtained using the inductively coupled plasma technique.

Ion-exchange chromatography

Ion chromatography can separate these arsenicals in the liquid phase. Ion-exchange resins have been employed for the separation of As(III), As(V), methylarsonic acid and dimethylarsinic acid in biological samples. Stockton and Irgolic (1979) separated As(III), As(V) arsenobetaine, and arsenocholine by high-performance liquid chromatography using a reversed-phase ion suppression technique. Ion-exchange high performance liquid chromatography seemed applicable to the separation of these arsenicals with better resolution than the conventional ion-exchange chromatography using resin.

Because a selective and sensitive detection is necessary after the separation, atomic absorption spectrometry has been used for this purpose (Edmond and Francesconi, 1976). DC plasma and microwave helium plasma atomic emission spectrometry have been employed for gas-phase detection (Andreae, 1977; Dietz and Perez, 1976). For the liquid phase, a graphite furnace Zeeman effect atomic absorption method has been used with the automated sampler. Inductively coupled argon plasma emission spectrometry seems another choice as a high performance liquid chromatography detector because it has high sensitivity for arsenic, low chemical interference and wide dynamic range.

Maher (1981) used ion-exchange chromatography to separate inorganic arsenic and methylated arsenic species in marine organisms and sediments. The method determines monomethylarsenic, and dimethylarsenic. The procedure involves the use of solvent extraction to isolate the arsenic species which are then separated by ion-exchange chromatography and determined by arsine generation.

Morita *et al.* (1981) have described a method of speciation and quantitative analysis of organoarsenic compounds in biological samples.

Hanumura *et al.* (1983) applied thermal vapourization and plasma emission spectrometry to the determination of organoarsenic compounds in fish.

Organoantimony Compounds

Organoantimony in water

Andreae *et al.* (1981) have described a method for the determination of methylantimony species, Sb(III) and Sb(V) in natural waters by atomic absorption spectrometry with hydride generation. Some results are also reported for estuary and sea waters.

Talmi and Norwell (1975) have studied the application of the gas chromatography-microwave plasma detector technique to the analysis of organoantimony compounds in environmental samples (Odanaka *et al.*, 1983).

Organogermanium compounds

Hambrick *et al.* (1984) observed germanium compounds in some natural waters which are reduced and trapped similarly to $Ge(OH)_4$, but which elute from chromatographic packings after GeH_4. They suggested that these peaks are unidentified methylgermanium species by analogy with previous observations for arsenic, antimony and tin. Further work confirmed the presence of methylgermanium in natural waters and led them to modify their technique in order to optimize the recovery of the methylgermanium species. The technique used by Hambrick *et al.* (1984) was a modification of the method developed earlier for inorganic germanium by Andreae and Froelich (1981).

Inorganic and methylgermanium species were determined in aqueous matrix at the parts-per-trillion level by a combination of hydride generation, graphite furnace atomization, and atomic absorption spectrometry. The germanium species were reduced by sodium borohydride to the corresponding gaseous germanes and methylgermanium hydrides, stripped from solution by a helium gas stream, and collected in a liquid nitrogen-cooled trap. The germanes were released by rapid heating of the trap and enter a modified graphite furnace at 2700 °C. The atomic absorption peak was recorded and electronically integrated. The absolute detection limits are 155 pg of Ge for inorganic germanium 120 pg of Ge for monomethylgermanium, 175 pg of Ge for dimethylgermanium and 75 pg of Ge for trimethylgermanium. The precision of the determination ranges from 6% to 16%. The method was applied to marine, freshwater and rain water samples. The major germanium species in sea water is monomethylgermanium. Trimethylgermanium is not found in sea water. Total germanium values for sea water are slightly lower than those of Braman and Tompkins (1979) (79 ng l^{-1}).

Organomanganese in air

Coe *et al.* (1980) have described a gas chromatographic-graphite furnace — atomic absorption technique for the determination of methylcyclopentadienylmanganese at the $\mu g\ m^{-3}$ level in air samples.

The method involves trapping of methylmanganese in a small segment of gas chromatographic column and then determination by gas chromatography with an electrothermal atomic absorption detector. The detection limit of the procedure is 0.05 ng m^{-3}.

A Pye gas chromatograph was interfaced to the graphite furnace using a tantalum connector. A glass chromatographic column (2.3 m long, 6 mm o.d.) was packed with 3% OV-1 on high performance Chromosorb W (80/100 mesh). The gas from the chromatograph was transferred to the furnace through Teflon-lined aluminium tubing.

Samples of air were collected in Teflon-lined aluminium U-tubes (30 cm long, 3 mm o.d.) packed with 3% OV-1 on Chromosorb W (80–100 mesh). These tubes were placed in a water-ice cooling bath. Air entered through an air filter and was pumped through the U-tube at about 70 mL min^{-1} using a vacuum pump. The length of sampling time and the average flow rate, checked frequently during sampling, were used to compute sample volume.

Organosilicon Compounds

Organosilicon in water

Mahone *et al.* (1983) have described a method for the quantitative characterization of water born organosilicon compounds. Substances such as silanol or silanol-functional materials are converted to trimethylsilylated derivatives which can be determined by gas-liquid chromatography. The method gives good accuracy and precision in the ppm range and with suitable precautions, can be extended to the low μgL^{-1} range.

Organosilicon in biological materials

Horner *et al.* (1960) describe two methods for the visible and infrared spectroscopic determination of trace amounts of silicones in biological materials. In one method the sample is decomposed by wet oxidation and the residues are fused with sodium carbonate. The metals are dissolved in hydrochloric acid and the silicon is determined by the molybdenum blue procedure. In cases where it is desired to identify the type of silicone present, an infrared technique is used. Preliminary separation of the silicone from the sample by solvent extraction may or may not be necessary, depending on its concentration and on the degree of interference by other sample constituents. Recoveries ranged from 86–98% for the colorimetric method on a groundbeef sample and from 79–89% for the technique when applied to pineapple juice.

Organonickel Compounds

Organonickel in air

Nickel tetracarbonyl is one of the most dangerous chemicals known. It exhibits acute toxicity carcinogenicity, tetraogenicity and can be produced spontaneously in unsuspecting environments whenever carbon monoxide contacts an active form of nickel.

Infrared spectrometry, Fourier transform IR (FTIR) chromatography and chemiluminescence have all been used to analyse for nickel carbonyl. All of these methods have the advantage of direct measurement with detection limits of about 1 μgL^{-1} and are also adaptable to process stream monitoring. The methods based on the FTIR and the plasma chromatography methods have been compared in real sample analyses and agree within a few percent. The chemiluminescent analysis for nickel carbonyl demonstrates a detection limit of 0.01 μgL^{-1} with a linearity over four orders of magnitude.

Campana and Risby (1980) have studied the possibility of the formation of nickel carbonyl by the reaction of carbon monoxide (present in exhaust gases in the range 1–15%) with nickel containing catalysts (Monel) under typical automotive operating conditions.

Chemical ionization mass spectrometry was used to determine trace levels of nickel carbonyl in a typical exhaust gas mixture. Also a catalytic flow reactor system was designed to study the formation of nickel carbonyl where the reacted gas was analyzed for nickel carbonyl. This reactor approximated the conditions found in an automotive exhaust catalytic converter system. These workers found various positive ions which can be attributed to nickel carbonyl and its fragments in this mass spectrum. The effect of pressure on the intensity of both the reactant gas ions and the nickel carbonyl was studied in an attempt to find the optimum condition for the quantification of nickel carbonyl. Using these data, the minimum detectable limit was found to be 10 μgL^{-1} for nickel carbonyl. This methodology was used to monitor nickel carbonyl in the effluent from a model reactor for a catalytic controlled automobile.

Organocopper Compounds

Organocopper in water

Brown *et al.* (1983) have studied the application of reversed phase high performance liquid chromatography with molecular and atomic absorption to the separation and quantification of organocopper speciation in soil-pore waters. Polar dissolved organic compounds and associated copper complexes are separated using either a single Hypersil GDS column or two Hypersil ODS columns and a Hamilton PRP 1 column in series. Quantifications was achieved using ultraviolet detectors for the organic molecular species and graphite furnace atomic-absorption spectrometry for the copper. As well as the high relative molecular mass compounds, such as polysaccharides, peptides, lipids and humic substances, there is a wide range of low relative molecular mass metabolites produced in soils by micro-organisms and plant roots. Reversed phase columns will retain polar compounds most effectively when their ionization is suppressed. As many of the polar organic ligands present in pore waters are acidic (e.g., citric acid), the eluent system chosen to suppress ionisation was also acidic (0.02% V/V orthophosphoric acid, pH 2.6). A less acidic eluent was utilised for less polar compounds. Ammonium formate solution (0.01 M, pH 6.1) was found to be suitable because it gave a low signal to noise ratio for graphite furnace a.a.s. analysis. This eluent was used for substances with higher retention values than the citric acid-copper complex.

One soil-pore water examined contained five recognisable polar dissolved organocopper compounds as revealed by absorbance measurement at 215 nm on the eluate. Analysis of soil-pore waters using the single-column high performance liquid chromatographic system interfaced with graphite furnace atomic-absorption spectroscopic system showed that the copper was not always associated with the polar dissolved organic compounds in the same proportions. In the majority of pore waters association of the copper with citric acid and neighboring eluting compounds was found.

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Ionizing Radiation Exposure of the Population of the United States, NCRP Report No. 93. National Council on Radiation Protection and Measurements, Bethesda, Maryland, 1987. 87 pp., paper $15.00.

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Building on Success: The Age of Energy Efficiency. Christopher Flavin and Alan Durning. Worldwatch Paper 82. Worldwatch Institute, Washington, D.C., 1988. 74 pp., paper $4.00.

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Protecting Life on Earth: Steps to Save the Ozone Layer. Cynthia Pollock Shea. Worldwatch Paper 87. Worldwatch Institute, Washington, D.C., 1988. 46 pp., paper $4.00.

Ill Winds. Airborne Pollution's Toll on Trees and Crops. James MacKenzie and Mohamed El-Ashry, World Resources Institute, Washington, D.C., 1988. 74 pp., paper $10.00.

Pesticides. Research and Monitoring. Environment Canada. Beauregard Press Limited, Canada, 1988. 63 pp.

WaBoLu. 85 Jahre Umweltschutz 1901–1986. Institut Für Wasser-, Bodenund Lufthygiene, Berlin, 1986. 178 pp. The report contains an historic overview of the activities of the Institute for Water, Soil and Air Hygiene, a component of Public Health Service of the Federal Republic of Germany.

Probleme der Ökologie. (*Problems of Ecology*), Heinz Kutzleben, Ed. Akademie-Verlag Berlin, DDR, 1987. 109 pp. This 13th volume of publications of the Akademie der Wissenschaften der DDR (Academy of Sciences of the German Democratic Republic) consists of papers presented at a meeting dealing with geo and cosmo sciences on 17 May 1985. The volume contains eight papers.

Health Impact of Different Energy Sources. World Health Organization, Copenhagen, Denmark, 1986. 71 pp., paper, Sw.fr. 13. The findings of an expert group are reported in this volume. The group developed a matrix for evaluating health risks of various energy options, including energy conservation. According to this group, the number and severity of problems of the various energy sources increases from water, gas and the sun to oil, nuclear energy and coal. The Working Group recommended actions and research needed to safeguard health and meet energy needs.

The Biological Alkylation of Heavy Elements. P. J. Craig and F. Glockling, Ed. Royal Society of Chemistry, London, United Kingdom, 1988. 298 pp., paper £42.50 ($89.00).

Hazard Assessment of Chemicals. Volume 5. Jitendra Saxena, Ed. Hemisphere Publishing Corporation, Washington, D.C., 1987. 436 pp., cloth $69.95. Nine chapters are included in this multi-author volume. The emphasis of the book is hazard rather than quantitative risk assessment. A review of the pesticide ratings system contains one chapter. Other chapters deal with subjects ranging from biotechnology to electrode systems.

The Greening of Aid. Sustainable Livelihoods in Practice. Czech Conroy and Miles Litvinoff, Eds. Earthscan, London, United Kingdom, 1988. 302 pp., paper £8.95.

Energy Efficiency: Perspectives on Individual Behavior. Willett Kempton and Max Neiman Eds. American Council for an Energy-Efficient Economy, Washington, D.C., 1987. 333 pp., paper $19.50. This five-chapter book is primarily written by social scientists. Included are sections dealing with the economics of energy and energy conservation. The chapters are intended as self-contained contributions, and deal with specific aspects of energy conservation. The book is an advocacy document for energy conservation.

Manual of Pesticide Residue Analysis: Volume I. VCH Publishers, Inc., New York, 1987. 432 pp., cloth $95.00. The book is a compilation of manuals prepared by working groups of the Deutsche Forschungsgemeinschaft, a West German research support organization. These manuals were initially published in German. The detailed analytical methods have been checked for accuracy and their applicability of environmental samples. The manuals are widely used in many countries, and their English translation will provide them to a wider audience.

Acid Rain. Rhetoric and Reality. Chris C. Park. Routledge, Chapman & Hall, New York, 1988. 272 pp., cloth $42.50. The author, a lecturer in geography, attempts to write a book combining the science, technology, policy and politics of acid rain. He uses data primarily from the U.S. and Britain to draw his conclusions. The author describes his belief that acid rain is caused by the emission of SO_2, and the damage seen in lakes and forests is attributable to acid rain.

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This Section contains abstracts and, where appropriate, illustrations of recently issued United States patents and published patent applications filed from over 30 countries under the Patent Cooperation Treaty. This information was obtained from recent additions to the Pergamon PATSEARCH® online database in accordance with interest profiles developed by the Editors. Further information about Pergamon PATSEARCH® can be obtained from Pergamon Orbit InfoLine Inc., 8000 Westpark Drive, McLean, Virginia 22102 U.S.A.

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4724778

AIR CONTROL FOR COMBUSTOR

John T Healy assigned to Westinghouse Electric Corp

A rotary combustor, in which material is burned in a gas porous cylinder, having a sectioned and compartmented wind box permitting selective delivery of air through the burning material, above the burning material, at the start of the burning process, and after burning has been well initiated.

4724780

PRESSURIZED CYCLONIC COMBUSTION METHOD AND BURNER FOR PARTICULATE SOLID FUELS

Franklin D Hoffert, J Davi Milligan, James Morrison assigned to Power Generating Inc

A pressurized cyclonic combustion method and a cylindrical burner apparatus for pressurized combustion of particulate solid fuels to produce a pressurized clean effluent gas. In the burner, the particulate solids such as wood chips are fed tangentially into a primary combustion chamber at its inlet end and flow at high tangential velocity in a helical path through the burner. Oxygen-containing combustion gas such as air is supplied tangentially at high velocity through multiple ports spaced along the burner length to maintain and/or increase the high tangential velocity and produce high centrifugal forces on the particulate solids and provide for prolonged combustion and produce high burner volumetric heat release rates exceeding about 400,000 Btu/hr ft3. A choke opening is provided centrally located at the combustion chamber outlet end for promoting prolonged combustion of solid fuel particles upstream of a quench zone. A secondary combustion chamber is provided downstream of the choke opening. Also, a quench gas stream is introduced into the choke zone preferably in a tangential flow direction opposite to the helical flow in the burner primary combustion chamber, so as to effectively mix the quench gas with the hot effluent gas and reduce its temperature, usually to about 1400 degrees-2000 degrees F. as determined by downstream metallurgy considerations. The resulting pressurized effluent gas can be further processed to remove any existing fine solids, and the clean pressurized gas can then be expanded in a gas turbine to produce useful power.

4726301

SYSTEM FOR EXTRACTING CONTAMINANTS AND HYDROCARBONS FROM CUTTINGS WASTE IN OIL WELL DRILLING

Ormeaux Farrell Des, Ormeaux Thomas Des, Ormeaux Mark R Des

A system wherein the contaminated cuttings are fed into the system for eventual incineration. The principal apparatus of the system comprises a plurality, preferrably three, of horizontally disposed cylindrical drying chambers mounted onto a skid for receiving contaminated cuttings into each separate chamber. There is provided on the first end of the chambers a receiving bin or hopper, wherein the cuttings are received from the shakers or the like into the bin, and dropped into an opening in the first end of the three chambers. Each chamber is provided with a seperate variable motor controlled auger disposed substantially throughout the length of the chamber wherein rotation of the auger would move the cuttings along the length of the interior of the chamber. The second end of each chamber is provided with a lower exit chute for removal of the cuttings from the chamber as the auger has moved into position. There is further provided a heat exchange means for drawing the hot exhaust gases from each chamber and reducing their temperature significantly, while also drawing oxygen into the heating chambers for providing the necessary oxygen for the incineration process.

4726681

MONITORING DEFLOCCULATED PARTICLES IN A SUSPENSION

Terence Webb, Cornwall, United Kingdom assigned to E C C International Limited

A method of monitoring the deflocculation of particles in a suspension, which particles, when deflocculated, are such that they can become aligned in an applied field, comprises applying a beam of radiation to a region of the suspension, applying a field to the region and detecting a change, if any, in radiation scattering properties of said region due to the aligning of deflocculated particles if any, of the suspension in the field, the method comprising applying such a field to such a region of a first sample of suspension whose degree of deflocculatin is desired to be monitored and applying such a field to such a region of a second sample of suspension, whose particles are known to be substantially fully deflocculated, detecting the change in radiation scattering properties of each region due to the field to produce a respective output indication, and comparing the indications to produce an indication related to the degree of deflocculation of the particles in the first suspension.

4726688

MONITORED BACKGROUND RADIOMETER

Christian Ruel, Dollard des Ormeaux, Canada assigned to Spar Aerospace Limited

This radiometer accurately measures IR and solar spectrum radiation in a vacuum, and accounts for radiation loss from its sensing plate by measuring the housing temperature. Calibration is performed by measuring the temperature of the sensing plate and housing while power to a heater attached to the sensing plate is varied. The square of the difference between the measured power dissipation of the heater and the heat absorbed by the sensing plate as determined from the heat balance equation of the sensing plate is minimized to obtain calibration factors for the heat balance equation.

4726710

CO-DISPOSAL POLLUTION CONTROL METHOD

Edward Rosar, Maurice G Pattengill assigned to Industrial Resources Inc

Process for disposal of fossil fuel ash by addition thereto of sodium salts, preferably sodium sulfur oxide salt Na2SOx where x is 3 and/or 4, in an amount ranging from 5-85 weight percent (dry basis) and adjusting the water percentage to within the range of 6-35%, preferably 15-28%. The coefficient of permeability of the ash and sodium salt is reduced from 102 cm/sec to the impermeable standard of 10-6 and below. The preferred mixes also call for a smectite clay additive present in the range of from 0.1% to 5%. A flocculant in amounts of 0.01% to 1% can be substituted for about 3-5% of the water content. A principal source of the Na2SOx is sodium FGD waste, preferably from the use of Nahcolite (a natural mineral form of sodium bicarbonate) as an SOx sorbent in the Nahcolite FGD process. The resulting co-disposal process simultaneously renders the highly soluble Na2SOx (102 g/L) and ash impermeable, and suitable for geomorphologically stable landfill disposal by known techniques to heights in excess of 200'.

4726824

AIR PURIFICATION SYSTEM

Michael D Staten

A complete system for indoor air pollution control and its components is disclosed herein, incorporating a furnace, heat pump or the like for supplying conditioned air to a room or zone via a duct network. Air filters are removably disposed at exhaust vents leading into the room or zone and intake vents are included for drawing air away from the room or zone for re-circulation. Ambient air intake vents are included in the duct network and the network is suitable for multiple level buildings. The system further includes sensing circuits within the duct work or zone which tests or senses the air for multiple characteristics of air quality and a panel having a variety of displays portrays the results of the individual characteristics being monitored. Such characteristics of air quality include ozone, carbon monoxide, nitrogen dioxide, etc.

4727489

APPARATUS FOR ANALYZING THE ANNULUS EFFLUENT OF A WELL

Terry Frazier, Henry J Grimm, John F Rooney, Richard Allen, Alfre Brown, Donald S Mims assigned to Texaco Inc

The disclosed invention is an apparatus for analyzing the annulus effluent of a producing well. The apparatus is designed to measure the flow rate of the annulus effluent, sample the annulus effluent and determine the quantities of each of the various phases of the annulus effluent. The apparatus is preferably mounted on a mobile vehicle and comprises a means for measuring the flow rate of the annulus effluent, a liquid vapor separator to split the annulus effluent into streams of entrained liquid and vapor, a separator to split the entrained liquid into the phases of oil and water, a sampling loop for extracting a sample of annulus effluent vapor which contains a condensor and a separator for splitting the fluid into its various phases, a means for measuring the amounts of all of the phases of the annulus effluent, and a means to record the data gathered. The apparatus is very useful in determining whether a producing well should be shut-in, worked over or left to produce as is .

4727936

RECOVERY AND CONTROL SYSTEM FOR LEACHATE COLLECTION

David Mioduszewski, David A Fischer, David H Edwards assigned to Q E D Environmental Systems Inc

A fluid sampling apparatus is disclosed for withdrawing samples of groundwater or other fluids from a well or other monitoring site. The apparatus preferably includes pump means, conduit means and a wellhead assembly that are substantially permanently installed at such well or monitoring site and are thereby dedicated thereto in order to avoid or minimize cross-contamination of samples from site to site. The apparatus preferably also includes a removable and portable controller means adapted for easy and convenient transportation and connection to such dedicated fluid sampling components at various wells or monitoring sites. A recovery, collection and control system for cleanup of leachate or other liquid material or contaminated groundwater from a landsite is also disclosed. Such system preferably includes fluid-operated pump means, each with associated preferably pneumatic controller apparatus, as well as a collection system for collecting, monitoring and controlling the collection and disposal of hazardous or other material withdrawn from in-ground wells at the landsite.

4728082

APPARATUS FOR BIOLOGICAL PROCESSING OF METAL CONTAINING ORES

Robert C Emmett, Lawrence T O'Connor assigned to Envirotech Corporation

A method and attendant apparatus for use in bioleach processing of metal-bearing solids is disclosed. The method includes the placement into a tank of metal-bearing solids, a predetermined quantity of water, oxygen, carbon dioxide, nutrients and a species of microorganisms capable of oxidizing some portion of the metal-bearing solids and obtaining energy for growth from that oxidation. The slurry formed by this placement is continuously filtered to remove process delimiting metabolic end products produced by the oxidation reaction. The ratios of the various slurry components are monitored and controlled to effectuate an optimized environment for oxidation to occur. The attendant apparatus includes a means of introducing oxygen into the bottom of the reactor vessel in the form of small widely dispersed bubbles.

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SOFTWARE SURVEY SECTION

Editor's Note: The following Software Descriptions have been submitted by our readers in response to our call for an open exchange of information on software programs. They are offered without review or comment to provide a rapidly published, easily accessible avenue of communication. Other readers with relevant software packages are invited to complete and submit a Software Description Form (found at the end of this section).

Software package EI-050-S87 A25-BI, SCINPLEX^{TM} Gamma-Ray Analysis Software for Multiple NaI Detectors

Contributor: Dr. T.T. Twomey, EC&G ORTEC, 100 Midland Road, Oak Ridge, TN 37831

Brief description: SCINPLEX^{TM} is designed for use with EC&G ORTEC ADCAM^{R} and ACE^{TM} MCA hardware, and MAESTRO^{TM} MCA software to provide an integrated solution to multiple detector gamma spectroscopy application involving scintillation detectors such as NaI, CsI, etc. SCINPLEX can accommodate 1-64 detectors operating simultaneously on a single system, providing quantitative results/automation of the acquire/store/analyze/report sequence. FMPC calculations can be performed and alarms sounded in response to out-of-limits samples.

Potential users: Gamma spectroscopists in environmental and health physics.
Fields of interest: Gamma spectroscopy with scintillators.

§ This application program in the area of gamma spectroscopy has been developed for IBM PC and compatibles, including Model 30, in FORTRAN to run under DOS 2.1 and higher. It is available on 5-1/4" and 3-1/2", dual-sided, double-density floppy diskette. Required memory is 512K.
§ Distributed by EC&G ORTEC.
§ The minimum hardware configuration required is 1.5MB disk storage. No user training is required. There is extensive external documentation. Source code is available.
§ The package is fully operational. It is in use at 10 sites. The contributor is available for user inquiries.

Software package EI-051-S87 SPECTRAN-AT V4.0

Contributor: Canberra Industries, Inc., One State Street, Meriden, CT 06450

Brief description: SPECTRAN-AT is an application software package that performs rapid and accurate analysis of gamma ray spectra obtained with high resolution germanium detectors. Routine operations include system calibration, automatic peak search, multiplet deconvolution, nuclide identification, specific activity and/or minimum detectable activity determination. Data may be analyzed directly from a Canberra multichannel analyzer (MCA) or from data files on disk. A built-in "batch mode" capability allows completely automatic data acquisition and analysis. Utility programs are included for nuclide library editing, listing spectra from disk or MCA and modification of analysis parameters. SPECTRAN-AT is an enhanced version of SPECTRAN-F, which was developed for DEC PDP-11 computers and has been in use in hundreds of facilities for over 8 years.

Potential users: Laboratories, utilities, universities.
Fields of interest: Gamma ray analysis.

§ This application program in the area of X-Ray Spectroscopy has been developed for IBM PC/AT and PS/2 in FORTRAN 77 to run under PC-DOS, MS-DOS v3.01 or later. It is available on 3-1/2" and 5-1/4", dual-sided floppy diskettes. Required memory is 256K.
§ Distributed by contributor.
§ The minimum hardware configuration required is clock, disk. No user training is required. There is extensive external documentation. Source code not available.
§ The package is fully operational. The contributor is available for user inquiries.

Software package EI-052-S87 Dynamic Code for Radioactivity Transfer Through the Food Chain (TRANFOOD)

Contributors: Ibrahim Uslu and M.G. Yalcintas, Oak Ridge National Laboratory, Health and Safety Research Division, Research Initiatives Group, P.O. Box X, Building 7509, MS 383, Oak Ridge, TN 37831

Brief description: Fallout deposition may result from routine or accidental releases from nuclear power plants and nuclear fuel cycle facilities or nuclear explosions. The steady-state approach is not suitable for description of acute releases. A dynamic, time-dependent model has been developed for simulation of an acute environmental transfer of radionuclides through agricultural systems. The model TRANFOOD estimates the integrated intake by ingestion of radionuclide in SI units per unit deposition in the local area. Resulting cumulative dose calculations are based on ICRP 30. The systems of linear first order ordinary differential equations describing the model are solved using first order (Simple Euler), second order or fourth order Runge Kutta method (user selection). Preliminary validation of the model was carried out by comparing the results with Chernobyl Nuclear Reactor accident data of Greece and Turkey.

Potential users: ORNL, HASRD, research initiatives.
Fields of interest: Long term environmental assessment, emergency planning, radiation protection.

§ This application program in the area of environmental assessments has been developed for IBM PC/XT/AT/compatibles and IBM System 136 to run under MS-DOS. It is available on 5-1/4", dual-sided, double-density floppy diskette. Required memory is 256K.
§ Distributed by contributors.
§ No user training is required. Source code is available.
§ Design is complete. It has been in use at 2 sites for approximately one month. The contributor is available for user inquiries.

Software package EI-053-S87 RADDOSE III

Contributor: Michael O'Hare, HMM Associates, Inc., 336 Baker Avenue, Concord, MA 01742

Brief description: RADDOSE-III is a radiological dose assessment computer model. The RADDOSE-III program uses a variable-trajectory, puff advection model of atmospheric dispersion to predict offsite radiological doses rates and cumulative doses resulting from a release of radioactive material from a nuclear power plant. The model calculates whole body gamma and thyroid doses, as well as deposition rates and cumulative deposition, at both pre-defined and user-defined locations, and meets the qualifications for both Class A and Class B dose assessment according to NUREG 0654, Appendix 2. The program can also calculate dose rate at any given distance from the plant. The model accommodates radioactive-isotope decay of both the source term and puff inventories, and includes routines to calculate puff depletion from both wet and dry deposition. The atmospheric dispersion routines used in the model allow for the thermal invasion boundary layer (sea breeze) effects. RADDOSE-III is completely menu-driven, offering users a series of informational screens directing them through the program. User "help" functions are available on command, and upon entry of invalid data. Meteorological and source-term data entry screens are modeled upon familiar spreadsheet formats, allowing both easy data entry and the ability to review inputs made for other time steps. The user interface design facilitates verification of model inputs and correction of entry errors. Program results are presented in graphical form, showing the current location of the plume on a map of the 10-mile Plume Exposure Pathway EPZ, and in tabular form with specific information (dose rates, accumulated dose, doses at user-defined receptors, etc.) selectable from an output menu. All information displayed on the computer screen can, at the user's option, be printed out for a permanent hard-copy record.

Potential users: Health physicists/radiological dose assessment personnel.
Fields of interest: Emergency preparedness.

§ This application program in the area of dose assessment has been developed for IBM PC/XT/AT and compatibles in Quick BASIC to run under MS-DOS version 3.1 or 3.2. It is available on 5-1/4", dual-sided, double-density floppy diskette. Required memory is 512K.
§ Distributed by HMM Associates, Inc.
§ The minimum hardware configuration required is 4 MB hard disk space, with or without a math coprocessor, monochrome or color CGA or EGA. No user training is required. There is extensive external documentation. Source code is available.
§ The package is fully operational. It has been in use at 1 sites for approximately 4 months. The contributor is available for user inquiries.

Software package EI-054-S88 Curve Fitting Package

Contributor: Dale G. Olson, U.S. Department of Energy, 785 DOE Place, Idaho Falls, ID 83402

Brief description: Two curve fitting subroutines are included in the package. The first contains least squares polynomial (LSP), exponential, algorithmic, power, linear regression and spline fitting routines. This routine is intended to determine the best type of fit to be used for any given set of data. The second routine is intended for use by gamma-ray spectrometrists in preparing calibration curves. The subroutine allows from

1-3 LSP fittings to be used to describe the major portion of the curve. The final fit is a spline which includes data from the lower, rapidly changing portion of the curve where an LSP is not used, plus the derived data from the LSP fits to draw a new curve. An accompanying article "Obtaining the Best Efficiency Curve by Curve Fitting Routines" describes the process.

Potential users: Gamma-ray spectroscopists.
Fields of interest: Chemistry, physics, health physics.

§ This application program has been developed for VAX 750 in BASIC to run under VMS. It is available on 5-1/4", dual-sided, double-density floppy diskette (copied onto by a PC). Required memory is 1MB.
§ Distributed by National Energy Software Center.
§ The minimum hardware configuration required is VAX 750. No user training is required. There is minimal self-documentation. Source code not available.
§ The package is fully operational. It has been in use at 1 site for approximately 2 years. The contributor is available for user inquiries.

Software package EI-055-S88 GRAPH

Contributor: Myles L. Lamson, Ph.D., MicroMath Scientific Software,
2034 East Fort Union Boulevard, Salt Lake City, UT 84121-3144

Brief description: GRAPH is a program that dramatically simplifies the preparation of publication-quality X-Y plots. Data may be plotted on the screen, edited, transformed, annotated, archived and reproduced at high resolution on common dot matrix printers. For very high quality output (figures for publication, or transparencies for lectures) plots from GRAPH may be sent directly to a PostScript printer such as the Apple LaserWriter. GRAPH allows simple transformations or sequences of transformations using In, log 10, exp, invert, square, sqrt, add, subtract, multiply and divide operators. The program keeps track of the current transformation and includes the transformed variable name in menus and along plot axes, e.g., if the X values are "time," applying the sqrt transform causes X-values to be referred to as "sqrt(time)." Empirical curves may be selected from among several interpolating functions, including polynomials, cubic splines, rational functions, or Stineman interpolation; least squares regression may be performed for straight lines, polynomials or cubic splines. Standard errors can be entered and plotted along with Y-data values, or data may simply be plotted with straight line segments connecting the points. Multiple data sets may be plotted on the same graph, with or without their associated empirical curves.

Potential users: Anyone who needs to plot or transform X-Y data along with model-independent curves.
Fields of interest: Research data presentation.

§ This program in the area of scientific plotting/data transformation has been developed for IBM PCs and compatibles to run under MS-DOS 2.0 or greater. It is available on 5-1/4" floppy diskette. Required memory is 512K.
§ Distributed by MicroMath Scientific Software.
§ The minimum hardware configuration required is two floppy disk drives (hard disk is recommended), graphics adapter, plotter. There is extensive external documentation.
§ The package is fully operational. The contributor is available for user inquiries.

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Title of software program: ____________________

____

Type of program: ☐ Application ☐ Utility ☐ Other__________

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Developed for (name of computer/s): ____________________

in (language/s):____________________

to run under (operating system): ____________________

available on: ☐ Floppy disk/diskette. Specify:

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☐ Magnetic tape. Specify:

Size ________ Density ________ Character set __________

Hardware required: ____________________

Memory required: ________ User training required: ☐ Yes ☐ No

Documentation: ☐ None ☐ Minimal ☐ Self-documenting
☐ Extensive external documentation

Source code available: ☐ Yes ☐ No

Stage of development: ☐ Design complete ☐ Coding complete
☐ Fully operational ☐ Collaboration welcomed

Is program in use? ☐ Yes How long? ________ How many sites? ________
☐ No

Is the contributor available for user inquiries: ☐ Yes ☐ No

Distributed by: ____________________

Cost of program: ______________

Demonstration disk available? ☐ Yes Cost: __________
☐ No

(continued)

RETURN COMPLETED FORM TO:

Ms. Barbara Moghissi
Environment International
P.O. Box 7166
Alexandria, VA 22307

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Description of what software does [maximum: 200 words]:

Potential users: ______________________________

Field/s of interest: ______________________________

# # # # # # #

Name of contributor: ______________________________

Institution: ______________________________

Address: ______________________________

____

Telephone number:______________________________

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Would you like to have your program:

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Aims and Scope

Environment International, published bimonthly, is a multidisciplinary forum for the publication of original environmental literature. Vital data, causes of pollution, and methods for protection are all featured. Covering the entire field of environmental protection, *Environment International* includes contributions from the following areas:

- Concentration of elements and compounds, notably pollutants
- Release rates of pollutants from various sources
- Transport of pollutants in the environmental media
- Health and ecological effects of pollutants
- Control technologies
- Description and interpretation of laws, regulations, and standards
- Information which will contribute to the understanding of environmental behavior of pollutants or will promote environmental protection
- Public policy alternatives including legislation
- National and international recommendations and practices to help bring about a lasting improvement in environmental protection

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Report Reference: Heit, M. and Burke, J.C. (1977) Sediment sampling in six western lakes. HASL-315, U.S. Engergy Research Development Administration, New York, NY.

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