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Development of sensitive GC-AAS instrumentation for analysis of organometallic species in the environment[†]

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Atomic absorption spectrometry provides a highly sensitive element-specific detection system for organometallic species pre-separated by gas chromatography. Both flame and flameless atomisation systems have been used and high sensitivity attained with elements such as Sn, Pb and As. Non-ionic alkyl or hydride species which are G.C.-volatile may be analysed directly, whilst ionic species generally require conversion to a hydride or a butylated form prior to analysis.

The development of a G.C.-A.A.S. interface will be described, together with the optimisation of an A.A.S. detector based upon a hydrogen diffusion flame, which is sensitive to picogram levels of organometallic compounds. The G.C.-A.A.S. equipment has been further interfaced with a two-stage thermal desorption system for analysis of vapours collected on polymeric absorbents. The application of the system to the analysis of organometallic species of Pb in a variety of environmental media will also be described.

KEY WORDS: Organometallics, gas chromatography-atomic absorption spectroscopy, butylation.

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INTRODUCTION

Many analytical methods are now available for the speciation of metals and metalloids in environmental media but when considering the organometallic and organometalloid compounds the use of sensitive and truly specific methods of detection is most important in order to avoid erroneous estimates of their environmental abundance. Although sensitive wet chemical methods are available for the determination of organometallic compounds, for example methods based upon collection in iodine monochloride solution for organolead compounds in air,¹ followed by an alkyllead-specific extraction procedure, their unequivocal specific measurement usually implies the use of a chromatographic separation technique and a metal-specific detector.

Several such methods have previously been described but most suffer from one or other of a number of limitations. For example a microwave plasma detector² or mass spectrometer,³ both of which have been successfully interfaced with a gas chromatograph for the analysis of tetraalkyllead compounds, are expensive instruments and not available in most laboratories for routine use. Similarly the dedication of a graphite-furnace atomic-absorption spectrophotometer may be beyond the resources of many laboratories.

In our laboratory we have sought to develop an analytical system for the determination of organometallic compounds in a wide variety of environmental media based upon relatively unsophisticated instrumentation. Although this is at present dedicated to the analysis of organolead compounds it can equally well be used for other groups of organometal or metalloid compounds, such as the alkyltins or alkylgermaniums.

In fact two classes of compounds amenable to analysis by gas chromatograph-atomic absorption spectroscopy may be identified. The first are those present in the environment as volatile species, usually fully-alkylated compounds such as the five tetraalkyllead species, dimethylmercury or tetramethyltin.⁵ Provided a suitable method of extracting and pre-concentrating these volatile species from the environmental medium under investigation can be found then direct chromatographic separation should be possible.

The second class of compounds comprise those which are present in the environment with low or negligible volatility and which are not

readily separable by chromatography, but which yield, after a chemical reaction, a volatile product. Two such methods of derivatisation are used at present, these being hydride generation and alkylation using a butyl Grignard reagent. Examples of compounds which may be analysed using the first method are the alkylarsenic⁶ and alkyltin^{7,8} salts which form volatile and relatively stable hydrides by reaction with sodium borohydride. The second method of derivatization may be used for the alkyltin salts, the methyltin, dimethyltin and trimethyltin species, which can all readily be butylated with a Grignard reagent to yield the volatile tetraalkyltin compounds.⁵ Similarly dialkyllead and trialkyllead compounds may be butylated to their tetraalkyllead derivatives.⁹⁻¹¹

This latter technique has greatly extended the scope of GC-AAS as an analytical tool for investigating the occurrence and fate of organolead and tin compounds in the environment but should also be applicable to other metals and metalloids. Detection limits obtained for different organometallic compounds by GC-AAS methods are shown in Table I.

TABLE I
Detection limits of organometallics by GC-AAS

Detector type	Reference	Compound	Detection limit pg
Graphite furnace	4	(CH ₃) ₄ Pb	40
		(C ₂ H ₅) ₄ Pb	90
Graphite furnace	18	(CH ₃) ₄ Pb	40
		(C ₂ H ₅) ₄ Pb	40
Quartz/silica furnace	12	(CH ₃) ₄ Pb	17
		(C ₂ H ₅) ₄ Pb	17
Quartz/silica furnace	15	(CH ₃) ₄ Pb	23
		(C ₂ H ₅) ₄ Pb	30
Silica tube	5	(CH ₃) ₃ Sn ⁺	100
		(CH ₃) ₂ Sn ²⁺	100
		(CH ₃)Sn ³⁺	100
Graphite furnace	23	(CH ₃) ₃ Ge ⁺	75
		(CH ₃) ₂ Ge ²⁺	175
		(CH ₃)Ge ³⁺	120

EXPERIMENTAL

Development of GC-AAS system

A Perkin-Elmer F17 gas chromatograph with a $2\text{ m} \times 1/8''$ o.d. stainless steel column packed with 1,2,3-tris (2-cyanoethoxy) propane on Chromosorb W or, more recently and with slightly better resolution, a $1\text{ m} \times 6\text{ mm o.d.} \times 2\text{ mm i.d.}$ glass column packed with 3% OV101 on Gaschrom Q (100–120 mesh) is used to separate the five environmentally-occurring tetraalkyllead compounds and the derived trialkylbutyl and dialkyldibutyllead compounds. The chromatography column is interfaced with an Evans Electroselenium 240 MK2 flame atomic absorption spectrophotometer by a $0.5\text{ m} \times 1/16''$ o.d. stainless steel transfer line. The eluate from the chromatograph is introduced into a ceramic tube of recrystallised alumina of length 150 mm and 14 mm o.d. via a 6 mm diameter hole in its side according to the method of Ebdon et al.¹² The ceramic tube is suspended in the air/acetylene flame and lies along the light beam path. Hydrogen is also introduced at the same point by mixing with the eluate and burns in the tube with a small diffusion flame which provides the reducing conditions necessary for lead atomisation and maximises the residence time within the optical path, thus providing high sensitivity.

Optimisation of GC-AAS

The variable parameters of the detector system were optimised with the gas chromatograph operated isothermally at 60°C using dilute solutions of tetramethyllead (TML) and tetraethyllead (TEL) in toluene and n-hexane. First the position of the ceramic tube within the acetylene flame relative to the light path was found which gave maximum light transmission and the position of the interface line from the g.c. relative to the entrance of the sampling port in the ceramic tube which gave maximum response was found. The influence of the carrier gas flow rate on absorbance signal was determined, the optimum being $30\text{ cm}^3\text{ min}^{-1}$ He for the 1,2,3-tris (2-cyanoethoxy) propane column and $165\text{ cm}^3\text{ min}^{-1}$ for the OV-101 column. The influence of the hydrogen flow rate on absorbance signal was also investigated, the optimum being $50\text{ cm}^3\text{ min}^{-1}$ for the propane column and $80\text{ cm}^3\text{ min}^{-1}$ for the OV-101 column.

Having optimized the atomic absorption detector to give maximum sensitivity for TML and TEL, different column temperatures were investigated to maximize peak separation and sharpness. Temperature ramping at $20^{\circ}\text{C min}^{-1}$ from 45° – 145° (propane column) and 35° – 135° (OV-101 column) was found to give good separation of all five tetraalkyllead peaks, plus separation of tetramethyllead from the hexane solvent flare, with minimal tailing of the less volatile species. A typical chromatogram of a standard solution of the five tetraalkyllead compounds is shown in Figure 1. Interference from non-lead compounds is largely eliminated by use of an element-specific detector. However relatively large quantities of hydrocarbons are found to give broad-band nonspecific absorption which could be eliminated by background correction. Thus n-hexane, which we routinely use for sample extraction and standard solution dilution purposes, gives a sharp flare eluting before the first lead compound. Toluene gives a rather broader flare which coincides with the three intermediate mixed methyl and ethyl tetraalkyllead compounds and is thus not suitable for use when these species may be present in a sample. Direct injection of the headspace gas above leaded gasoline gives two non-lead peaks (before TML and before TEL respectively) which are still present when an adjacent non-absorbing lamp wavelength (280.3 nm) is used. Non-lead peaks have not been found in air samples (except in a few samples taken at exhaust level in a street canyon) nor in sediment or water sample extracts, and we have not experienced any interference problems when analysing environmental samples. Use of deuterium background correction is a means of eliminating these types of interferences but is considered unnecessary in routine use.

Other potential problems which may occur are sample loss during transfer from the chromatograph column to the detector and peak tailing of the less volatile species. The loss of sample in the interface line was investigated by varying the length of tubing used from 0.5 m to 1.5 m. We have found no loss of sample using new high-quality stainless steel tubing and connectors although other workers have reported this to be a problem. Glass-lined stainless steel, nickel or Teflon tubing are all possible alternatives although the latter may lead to sample loss through the walls. Peak tailing has also been reported to be a problem, necessitating the heating of the transfer line to 150 or 165°C . We have not found this necessary, although it is necessary to heat the g.c. injector port to 150°C .

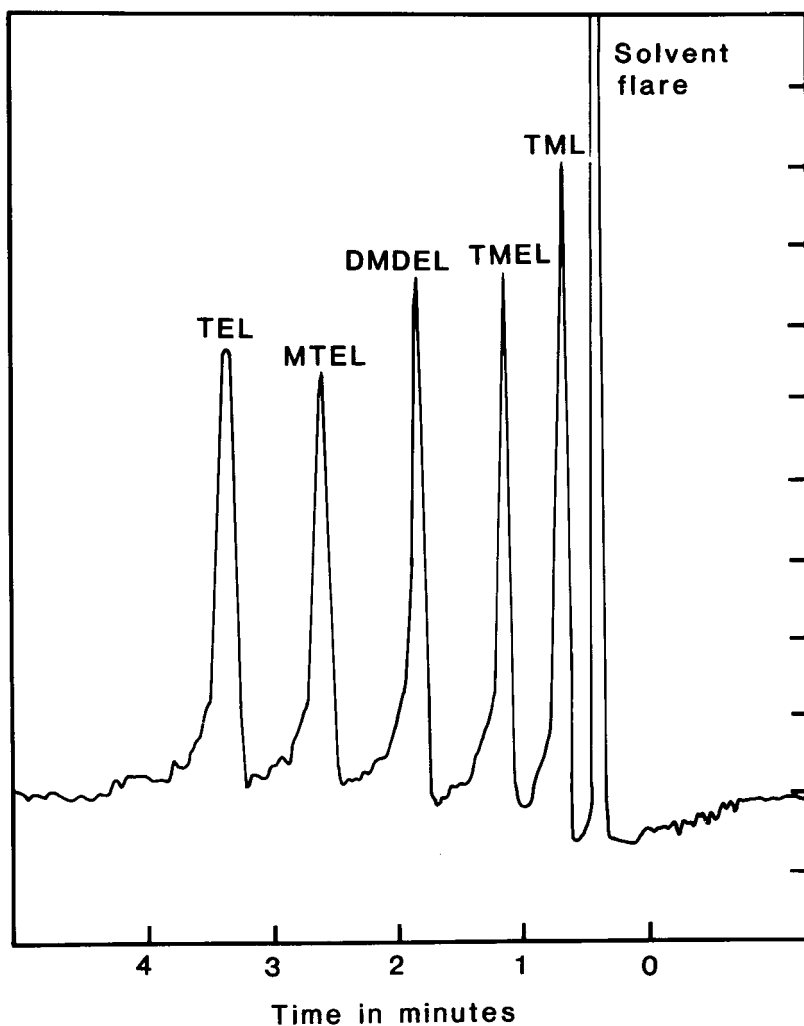


FIGURE 1 Typical chromatogram of standard TAL solution.

The detection limits of the five tetraalkyllead compounds as obtained with this system, defined as three times the standard deviation of the baseline noise, divided by the sensitivity are shown in Table I. They range from 23 pg (Pb) for tetramethyllead to

30 pg(Pb) for tetraethyllead. These are only typical values as there are day to day variations in the sensitivity of the system and it is usual therefore to bracket sample analyses with injections of standard solutions.

The precision of analysis for tetraalkyllead was found by injection of 15 replicates of a standard solution containing 1 ng (Pb) of each of the five compounds. The relative standard deviations of the peak heights varied from 9–14%. Precision could probably be improved by the use of peak area rather than peak height.

Providing the carrier gas pressure is maintained constant the retention times of the lead compounds are found to be highly repeatable, so allowing the unequivocal identification of sample peaks.

For analysis of samples containing the butylated derivatives of di- and tri-alkyllead compounds a higher carrier gas flow rate ($210 \text{ cm}^3 \text{ min}^{-1}$) and a column temperature programme of 30–160°C at $20^\circ \text{C min}^{-1}$ are found necessary.

Collection of air samples

The main application of our GC-AAS system is for the analysis of organic lead compounds in air samples but this requires some means of sample trapping and enrichment. Two methods are available for the collection and preconcentration of tetraalkyllead in air, either using a porous polymer adsorbent^{3, 13, 14, 15} or by cryogenic trapping at -80°C or lower.^{2, 16–19} Both these techniques suffer from limitation. The practical difficulties of cryogenic trapping methods in the field preclude their use in truly remote areas or for the semi-automated collection of sequential samples.¹⁵ Collection on a porous polymer is also problematic as tetraalkyllead, and particularly the more reactive tetraethyllead, is liable to decomposition on the absorption medium during sampling and storage. An upper-limit estimate of the sample loss can be obtained by the addition of known amounts of deuterated TML (d_{12} -TML) and TEL (d_{20} -TEL) to the sampling column in advance and analysis by isotope-dilution gas chromatography-mass spectroscopy.³ However a more satisfactory approach is to remove the most important oxidant, ozone, from the sampled air with a ferrous sulphate prefilter, so eliminating the possibility of sample decomposition during sampling and storage.¹⁵

Stainless steel tubes ($3\frac{1}{4}'' \times \frac{1}{4}''$ o.d.) packed with 0.5 g Porapak Q (Waters Associates) with silanised glass wool plugs were used for collection of the analytes. The breakthrough volume of tetramethyllead was determined experimentally at elevated temperatures by injection of TML onto tubes which were then heated continuously in an oven whilst being flushed with helium. Continuous detection of the eluate by GC-AAS allowed the time at which lead appeared from the tube to be measured and by extrapolation of the linear plot of log (retention volume) against the reciprocal of the temperature the breakthrough volume at ambient temperature was obtained. This was found to be 89 dm^3 for 0.45 g Porapak Q at 20°C .

Teflon tubing ($2'' \times \frac{1}{4}''$ o.d.) packed with 0.25 g ferrous sulphate crystals was found to remove ozone quantitatively, but not to remove more than 2% of the TML and TEL, from an air stream, and was thus used as a prefilter on the upstream end of the sampling tubes.

Thermal desorption

Two stage thermal desorption of the sample from the adsorption tube into the injector port of the gas chromatograph is achieved using a GN Concentrator (GN Instrumentation Consultancy Ltd.). This has a variable-temperature oven and a glass-lined stainless steel U-tube cryogenic trap ($6'' \times 1/8''$ o.d.) containing 0.1 g 4% Apiezon M on Chromosorb P, 60–80 mesh (Phase Separation Ltd.). The GN Concentrator is linked into the system's carrier gas supply such that the flow may be diverted to pass through the adsorption tube once this is loaded into the oven, through the U-trap which is cooled in a liquid nitrogen bath, and through a $1/16''$ o.d. glass-lined stainless steel interface line (heated to 150°) to the injector port of the gas chromatograph. Once the sample has desorbed from the tube (at 150°) and been collected in the U-tube trap the liquid nitrogen bath is removed and the trap flash heated to 90°C . The sample is then flushed into the G.C. column in a very small volume of carrier gas. Figure 2 shows the sample collection and desorption and analytical system. With an air sample volume of 80 dm^3 detection limits in the range 250 pg(Pb)m^{-3} for TML and 375 pg(Pb)m^{-3} for TEL may be expected.

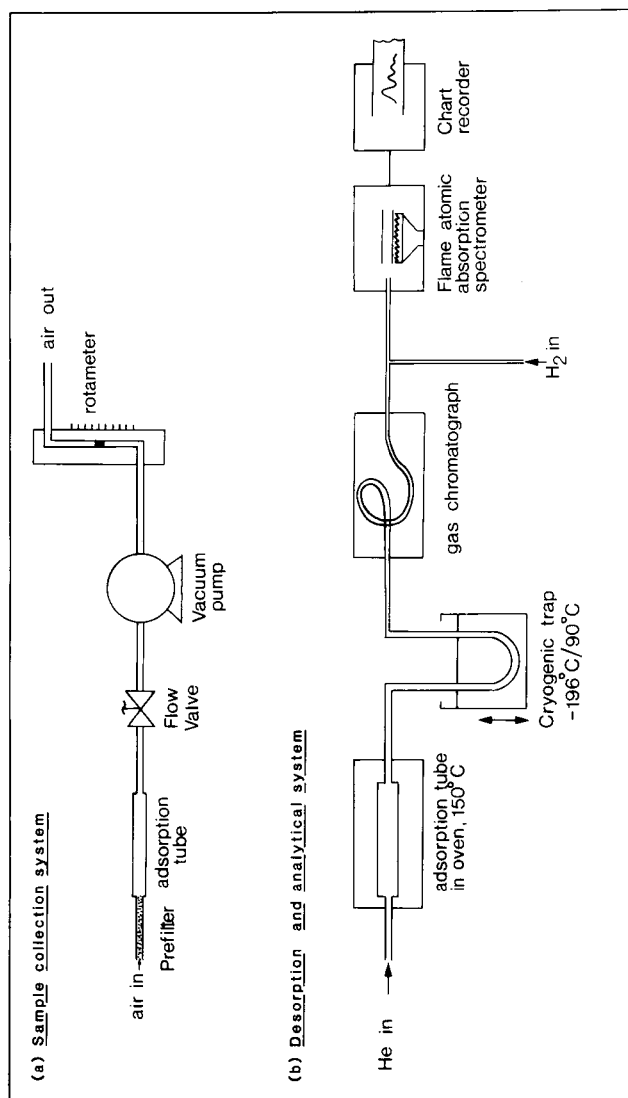


FIGURE 2 Schematic of sample collection, desorption and analysis system.

RESULTS AND DISCUSSION

Examples of applications to which our GC-AAS system has been put are numerous. Its versatility as an analytical tool is demonstrated by its use for the determination of tetraalkyllead in samples as diverse as rural air and leaded gasoline. Table II summarised some of the environmental media investigated by GC-AAS, the extraction methods used and the detection limits obtained.

TABLE II
Detection limits of organometallics in environmental samples by GC-AAS.

Sample type	Sample size	Reference	Compound	Detection limit ^a
Air	80 dm ³	15	(CH ₃) ₄ Pb	0.25 ng m ⁻³
Air	80 dm ³	15	(C ₂ H ₅) ₄ Pb	0.375 ng m ⁻³
Air	70 dm ³	18	R ₄ Pb	0.5 ng m ⁻³
Water	200 cm ³	24	R ₄ Pb	500 ng dm ⁻³
Sediment	5 g	24	R ₄ Pb	10 ng g ⁻¹
Fish	2 g	24	R ₄ Pb	25 ng g ⁻¹
Water	1 dm ³	25	R ₄ Pb	100 ng dm ⁻³
Water	1 dm ³	25	R ₃ Pb ⁺	100 ng dm ⁻³
Water	1 dm ³	25	R ₂ Pb ²⁺	100 ng dm ⁻³
Water	1 dm ³	26	R ₃ Pb ⁺	20 ng dm ⁻³
Water	0.5 dm ³	27	(CH ₃) ₃ Pb ⁺	1.25 ng dm ⁻³
Water	0.5 dm ³	27	(C ₂ H ₅) ₂ Pb ²⁺	2.5 ng dm ⁻³
Water	0.25 dm ³	23	(CH ₃) ₃ Ge ³⁺	0.3 ng dm ⁻³
			(CH ₃) ₂ Ge ²⁺	0.71 ng dm ⁻³
			(CH ₃)Ge ³⁺	0.48 ng dm ⁻³
			Ge	0.62 ng dm ⁻³
Water	5 dm ³	5	(CH ₃) ₃ Sn ⁺	40 ng dm ⁻³
			(CH ₃) ₂ Sn ²⁺	40 ng dm ⁻³
			(CH ₃)Sn ³⁺	40 ng dm ⁻³
			Sn	40 ng dm ⁻³

^aAs mass concentration of element where R=alkyl group.

Gasoline analysis

For analysis of gasoline a 1 cm³ aliquot of four-star (98 octane) fuel was diluted to 100 cm³ with n-hexane and 1 µl injected into the G.C. The total tetraalkyllead content of the gasoline was found to be

0.310 g(Pb) dm.⁻³ Of this 16% was as TML, 38% as TEL and 15%, 19% and 12% as TMEL, DMDEL and MTEL respectively. However when the headspace gas (1 cm³) from a closed container of the same gasoline was analysed it was found that the relative composition of the mixture of lead compounds was different. TML accounted for 62% of the total lead and TEL only 17%, showing the differences in volatility of these compounds. The results obtained are shown in Table III. It should also be noted that two extra peaks were observed when headspace gas was analysed, eluting just before TML and TEL. These peaks were not seen when liquid injections of the diluted gasoline were made and were confirmed to be broad-band non-atomic absorption, presumably due to volatile components of the gasoline, by analysis at a neighbouring non-absorbing lamp wavelength.

TABLE III
GC-AAS analysis of gasoline: relative composition

	Liquid gasoline	Headspace above gasoline
Total Pb	0.310 g dm ⁻³	2.55 × 10 ⁻⁹ g cm ⁻³
TML	16%	62%
TMEL	15%	16%
DMDEL	19%	4%
MTEL	12%	1%
TEL	38%	17%

Air sampling

In order to validate the Porapak Q—thermal desorption—GC-AAS method for the measurement of tetraalkyllead in air atmospheric sampling was carried out at a rural site by this method in parallel with the established iodine monochloride method. Fifty 24-hour air samples were collected using pairs of Porapak tubes with and without ferrous sulphate prefilters and also using pairs of iodine monochloride bubblers with and without the prefilters. The results of this study showed that the iodine monochloride method, which gives a measure of the total vapour-phase organic lead present in the

sample and is not entirely specific towards tetraalkyllead, consistently gave higher concentrations than the Porapak method, which gives a measure of tetraalkyllead only. It has previously been postulated that vapour-phase organic lead compounds other than tetraalkyllead may be present in the atmosphere,^{3, 20, 21} probably as the trialkyllead species, and the higher concentrations of vapour-phase organic lead than of tetraalkyllead suggest that this is indeed the case. Furthermore the prefiltered iodine monochloride samples were found to have lower organic lead contents than the non-filtered samples and laboratory experiments confirmed that the ferrous sulphate removes about half of the vapour-phase trialkyllead chloride from an artificially-generated air stream. These data suggest that a minimum of $\sim 1 \text{ ng m}^{-3}$ vapour-phase organic lead other than tetraalkyllead may be expected at this sampling site under the conditions prevailing during February/March 1984, but that the amount of excess (i.e. non-TAL) vapour-phase lead varies appreciably between samples.¹⁵

These data have prompted us to investigate possible methods of determining the vapour-phase trialkyllead content of air. Various collection and preconcentration methods have been evaluated but only limited success has been achieved to date. However one method has proved useful, which, although not applicable to the environmental analysis of trialkyllead, may have useful applications elsewhere for the determination of tetraalkyllead in polluted atmospheres. This uses GC-AAS as the analytical method and is described below.

Collection of tetraalkyllead in NaDDC

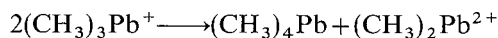
During the course of experiments to evaluate the aqueous solution of the complexing agent sodium diethyldithiocarbamate (NaDDC) as a collection medium for vapour-phase trimethyllead chloride it was found that both trialkyl and tetraalkyllead species are absorbed by the solution.

A 125 cm^3 gas bubbler, modified by extending the central tube to within 2–3 mm of the base of the bubbler with 0.5 mm capillary tube, and containing 80 cm^3 0.05M NaDDC solution adjusted to pH9 with aqueous ammonia solution was used to sample a known volume of the gaseous output from a trimethyllead chloride vapour generator.

The generator consists of a stainless steel tube containing ~ 1 g trimethyllead chloride held at a constant temperature of 0°C in an ice/water bath. Charcoal filtered air is pumped through the tube and the output filtered through a $0.45\ \mu\text{m}$ Millipore membrane to exclude any particulate lead. Diluent air (charcoal filtered) is added to the output and the resultant air stream sampled by drawing through the bubbler with a third pump.

After the required volume (as determined by the use of a GAP rotameter) has been sampled the NaDDC solution is transferred to a 125 cm^3 glass bottle and the organic lead extracted and butylated according to the method of Chau,¹⁰ as modified for water samples.²² To the solution 1 g sodium chloride, 1 cm^3 0.2M EDTA solution and 2 cm^3 n-hexane are added and the mixture shaken for 30 mins. After phase separation in a 125 cm^3 separating funnel the aqueous layer is discarded and the hexane layer butylated with 0.5 cm^3 1.9M n-butylmagnesium chloride in tetrahydrofuran. After shaking for 10 mins, excess Grignard reagent is removed by reaction with 5 cm^3 0.5M H_2SO_4 and the hexane layer then placed in a small capped tube. A small amount of anhydrous Na_2SO_4 is added to dry the hexane which is then ready for analysis by GC-AAS.

Calibration of the trimethyllead generator was carried out by bubbling the output through iodine monochloride solution and analysis by graphite furnace AAS.¹ The alkyllead produced by the generator was also collected in a cryogenic trap, a glass U-tube 20 cm in length and 1 cm diamter containing 2 mm glass beads and immersed in a liquid nitrogen/ethanol slush bath at -130°C . After sampling the trap was removed from the slush bath, 10 cm^3 water and 2.5 cm^3 n-hexane added and allowed to warm to room temperature. The beads and liquid were transferred to a glass tube and 1.5 g NaCl and 1.5 cm^3 0.1M NaDDC solution added and the tube shaken for 30 mins. The organic phase was removed after separation and butylated as described above.²² The total organic lead output of the generator as determined by this method was in close accord with that found by the iodine monochloride method, but it was found that 50% of the output was as tetramethyllead and 50% as the trimethyllead species. The presence of tetramethyllead may be explained by the disproportionation reaction



Having established the specific output of the trimethyllead generator it was possible to quantify the collection and recovery efficiency of the NaDDC solution. This was found to be 85% at a flow rate of $2\text{--}5\text{ dm}^3\text{ min}^{-1}$ and for tetramethyllead and trimethyllead concentrations of $5.0\text{ ng(Pb) dm}^{-3}$.

The output of a diffusion cell tetramethyllead vapour generator was similarly calibrated using iodine monochloride solution. This generator consists of a capillary tube containing liquid TML, the open end of which protrudes into an air stream. The whole system is held at constant temperature. Collection of the output in a cryogenic trap and extraction into hexane confirmed that 100% of the lead produced was as tetramethyllead.

When tetramethyllead was bubbled through NaDDC at pH 9 and extracted and butylated as described above it was found that about 70% was recoverable, but that it was present as trimethylbutyllead. It appears therefore that tetramethyllead is decomposed in NaDDC solution to yield the soluble trimethyllead species which in turn is recoverable by hexane extraction and butylation. These results are shown in Table IV.

By applying the recovery efficiency factor of 0.7 for TML to that found for TML and TriML together (0.85) from the trimethyllead generator it would appear that trimethyllead is collected by and recovered from NaDDC solution with approximately 100% efficiency. However this is obviously not suitable as a method of determining trimethyllead in air until the interference from tetramethyllead can be overcome.

TABLE IV
Analysis of alkyllead vapour generators.

Method of analysis	TriML generator	TML generator
Iodine monochloride ^a	10.0 ng dm^{-3}	210 ng dm^{-3}
Cryogenic trap—	5.0 ng dm^{-3} as TML	205 ng dm^{-3}
GC-AAS ^a	5.0 ng dm^{-3} as TriML	
NaDDC-GC-AAS ^a	8.5 ng dm^{-3}	141 ng dm^{-3b}

^aAll values mean of three determinations.

^bAnalysed as TriMBuL.

Applications

The NaDDC bubbler method appears to offer an alternative to the iodine monochloride method as a means of determining the total vapour-phase organic lead in air. Whilst it cannot be used to distinguish between the tetraalkyl and trialkyl species it does offer the possibility of distinguishing between the methyl and ethyl compounds with reasonable collection efficiency. Although no further detailed validation studies have been carried out on this method the preliminary findings outlined above indicate that it may be useful as an alternative or complementary method to the iodine monochloride method, especially in polluted air or in the workplace. It also has a distinct advantage over the iodine monochloride method in that it utilizes GC-AAS as the analytical method and so, subject to the limitation outlined above (i.e. its inability to differentiate between vapour-phase TriML and TML), is species-specific.

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