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Determination of Trimethyl-lead in Rainwater and Road Dust by Capillary GC MIP-AE Spectrometry after *in situ* Ethylation and Extraction

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A rapid and sensitive method for the determination of trimethyl-lead in water and road dust is described. It is based on *in situ* ethylation of ionic methyl-lead by sodium tetraethylborate and the extraction of the compound formed into hexane. The extract is gas-chromatographed and the lead species determined by microwave-induced plasma atomic emission spectrometry (MIP-AES). The reaction conditions are optimized and the method is applied to the analysis of artificial rainwater and road dust in the framework of an international round-robin exercise.

Keywords: Organolead, analysis, ethylation, atomic emission spectroscopy

INTRODUCTION

Despite stronger restrictions to the use of organolead compounds in petrol, their concentrations in the environment remain high, especially in urban areas.[1–4] Tetra-alkyl-lead compounds are primarily used and their ionic degradation products show increased toxicity compared with elemental lead because of their good solubility in lipids. Methyl-lead species are the dominating additive in Europe. Methyl-lead is more persistent than ethyl-lead and was recently found to contaminate some alimentary products via the atmosphere.[5] The interest in methyl-lead determination is also attributable to the still-controversial issue of its natural production via biomethylation.[6] Despite more than 200 papers published on organolead speciation, intermethod comparisons were not attempted until the EC European Community Bureau of Reference Materials (BCR) embarked on their last project to issue certified reference materials for rainwater and road dust.[7]

The state-of-the-art of the speciation analysis for organolead has been reviewed recently.[8] The most common approach is a multistep procedure involving extraction of ionic organolead as a chelate complex followed by its Grignard derivatization, and is often accompanied by off- or on-line evaporative preconcentration. The sample preparation can be simplified by combining extraction and derivatization steps, using ethylation by sodium tetraethylborate ($NaBEt_4$). This reagent, initially introduced for methyl-lead,[9] has recently been used for the volatilization of several elements such as tin[10–18] mercury,[10,19–21] selenium,[10,22] germanium[10] and cadmium.[23,24]

The derivatization of organolead species with $NaBEt_4$ was hitherto followed by either purge-and-trap processing prior to GC separation or was used for post-column volatilization of alkyl-leads in an HPLC effluent.[25] Purge-and-trap methods ensure efficient processing of the analyte but require an additional manifold and reduce sample throughput. In addition to that, analysis of real samples was not reported, probably because of a large excess of the concomitant lead(II) (Pb^{2+}). Extraction methods are faster and much simpler in terms of handling but require more sensitive detectors as only a tiny amount of sample is finally introduced to the detector.

This work has aimed at developing one-step sample preparation procedures based on combined *in situ* derivatization/extraction for the determination of trimethyl-lead in rainwater and road dust, to be carried out in one vessel and to be applicable to capillary GC MIP-AES. The methods were further applied to the artificial rainwater and the road dust samples issued in the

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Table 1 Dilution scheme, sample and extraction volumes for the artificial rainwater samples

	Solution	Sample volume (ml)	Hexane extraction volume (μl)	Vessel type
A	10-fold dilution of solution I	0.25	500	c
B	10-fold dilution of solution II	2	500	c
C	100-fold dilution of solution II	20	500	a
D	1000-fold dilution of solution II	50	250	b

framework of a BCR intercomparison study on analysis for trimethyl-lead.[26]

EXPERIMENTAL

Apparatus

An HP Model 5890 Series II gas chromatograph (Hewlett–Packard, Avondale, USA) fitted with an HP-1 capillary column (25 m × 0.32 mm × 0.17 μm) and coupled via a transfer line of the same column to an HP Model 5921 A atomic emission detector was used. The gas chromatograph was equipped with a model KAS 503 PTV cool on-column injection system (Gerstel, Mühlheim, Germany) and an HP 7673 A automatic sampler. Smooth finished glass vaporization tubes (liners) packed with a 2 cm plug of Tenax (Hewlett–Packard) were used during the injections.

Reagents

All reagents used were of analytical grade and obtained from Merck (Darmstadt, Germany) unless otherwise stated. Deionized water, further purified in a Millipore Milli-Q system, was used throughout.

The ammonia citrate/EDTA buffer solution was prepared by dissolving 21.01 g citric acid monohydrate and 3.72 g EDTA in 100 ml water and adjusting the pH to 8 with concentrated ammonia.

The integrated extraction reagent (IER) was prepared by dissolving 5.25 g citric acid monohydrate and 1.86 g EDTA in *ca* 40 ml water, adjusting the pH to 8 with concentrated ammonia and adding 2.25 g sodium diethyldithiocarbamate (NaDDTC). The solution was made up to 50 ml with water and the pH was controlled with an indicator paper. The reagent was extracted once with 2 ml of hexane to remove the impurities.

Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals (Bischheim, France). An 0.8% (w/v) aqueous solution was prepared daily.

Samples analysed

The samples were analysed in the framework of the second intercomparison study on trimethyl-lead of the European Community Bureau of Reference Materials in December 1993.[26] Two solutions of synthetic rainwater issued were numbered I, with a trimethyl-lead content of *ca* 50 $\mu g\ l^{-1}$ and II, with *ca* 5 μg^{-1} (as Pb). Both samples contained concentrations of 5–90 $\mu mol\ l^{-1}$ of ions usually present in rainwater (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, NO_3^-).

The road dust sample analysed was expected to contain *ca* 5 ng g^{-1} of trimethyl-lead (as Pb). The humidity was determined by drying three times 0.1 g sample at 105 °C until subsequent weighings did not differ by more than 1 mg

Procedures

Storage and dilutions

The concentrated standard solution, artificial rainwater and dust samples were stored at 4 °C in the dark. The working standard was diluted with water on a daily basis. Prior to each measurement the water samples were diluted with water, resulting in four solutions A–D with different concentrations. The dilution scheme, together with the sample and extraction volumes, is summarized in Table 1. The dilution factors were controlled gravimetrically.

Analysis of water samples

A sample aliquot was placed in a custom-designed extraction vessel, which allows easy separation of a very small volume of organic solvent. The different types of vessels used are displayed in Fig. 1. The pH was brought to 7–8 with 0.5 ml

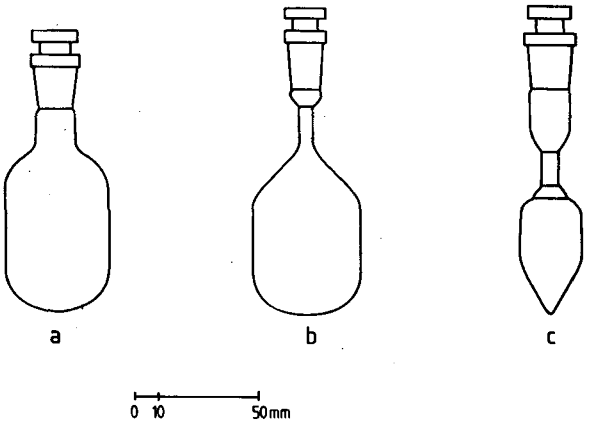

Figure 1 Types of vessels used in the analysis of water samples.

ammonia citrate–EDTA buffer; this was followed by the addition of 1 ml $NaBEt_4$ solution and an appropriate volume of hexane. The mixture was shaken for 2 min and set aside for another 2 min to enable phase separation. The hexane phase was collected with a micropipette, placed in an autosampler glass vial and analysed by GC MIP-AES.

Analysis of road dust

A sample (0.1–0.2 g) was weighed into a 8 ml glass centrifuge tube, whereupon 3 ml IER, 1 ml $NaBEt_4$ solution and 0.5 ml hexane were added. The mixture was shaken for 10 min and centrifuged for 3 min (4000 min^{-1}) to hasten phase separation. The hexane phase was collected with a micropipette, transferred to an autosampler glass vial and analysed by GC MIP-AES.

GC MIP-AES analysis

The operating conditions of gas chromatograph, injection system and detector are summarized in Table 2.

Calibration

A calibration solution of trimethyl-lead chloride issued in the framework of the first BCR intercomparison study on trimethyl-lead was used. The input concentration of trimethyl-lead was revealed to be 40 mg l^{-1} (as Pb) and corresponded to the value found earlier in our lab (39.98 mg l^{-1}).[27] The average of nine participating laboratories was 42.89 μg l^{-1}.

Quantification was done by the method of standard additions. The samples were spiked with appropriate volumes of the diluted standard solution prior to analysis so that standard addition curves of three points were obtained. The results from the road dust analysis were corrected to dry weight. The humidity was found to be 0.96 ± 0.12%.

RESULTS AND DISCUSSION

Optimization of the operating variables

Nonpolar tetra-alkyl-lead compounds ($Me_nEt_{4-n}Pb$, $n = 1, 2, 3, 4$) were demonstrated to be readily extracted into organic solvents, e.g. hexane.[28] Hence, only the conditions for a quantitative formation of trimethylethyl-lead from trimethyl-lead needed to be optimized. The relevant parameters included pH, concentration of $NaBEt_4$ and reaction time. The number of parameters was much smaller than in a purge-and-trap system[9] so that the use of the univariate optimization strategy instead of the simplex method was considered justified.

The pH was changed from 1 to 12 at one-unit intervals by carrying out the reaction in suitable 0.1 M buffers. The recovery was calculated by comparing the net signal measured with the one obtained after Grignard derivatization (with propylmagnesium chloride) of the same amount of standard in hexane, known to occur with 100% efficiency.[29] The maximum signals measured after $NaBEt_4$ derivatization were *ca* 5% higher than those obtained after Grignard propylation because of signal discrimination (Me_3EtPb is slightly more volatile than Me_3PrPb).[8] The pH dependence of the recovery (Fig. 2) shows a relatively broad optimum range, in contrast to the purge-and-trap method.[9] There, a fairly sharp maximum at $pH = 4.1$ was observed, which seemed to interact with a number of other parameters. Sturgeon *et al.*,[30] however, found quantitative formation of Et_4Pb from lead(II) (Pb^{2+}) at pH values higher than 4. In comparison with the derivatization of organotin, the ethylated compound is formed at lower pH values, which indicates its higher stability.

Ethylated organolead species were found to be formed and extracted quantitatively even at very low borate concentrations (*ca* 0.01% at pH 7) but in the presence of excess inorganic lead, ubiquitous in real samples, a large fraction of the borate is consumed in the lead(II) derivatization. Therefore much larger concentrations need to be applied. A slightly basic pH value (*ca* 7–8) was

Table 2 GC MIP-AES operating conditions

Parameter	Water analysis	Dust analysis
Gas chromatography		
Injection volume	1 µl	
Injection temperature program	40 °C→ 12 °C s^{-1}→260 °C (1 min)	
Column head pressure	130 kPa	
Oven program	45 °C (1 min)→ 20 °C min^{-1}→80 °C →60 °C min^{-1}→240 °C (0.5 min)	45 °C (1 min)→ 20 °C min^{-1}→80 °C →60 °C min^{-1}→280 °C (1 min)
Atomic emission detector		
Transfer line temperature	280 °C	
Wavelength	405.783 nm	
helium make-up flow rate	300 ml min^{-1} (measured at the cavity vent)	
Hydrogen pressure	90 psi (621 kPa)	
Oxygen pressure	20 psi (138 kPa)	
Spectrometer purge flow rate	2 l nitrogen min^{-1}	
Solvent vent-off program	On (1.8 min)→off (6 min)→on	On (1.7 min)→off (2.5 min)→on
Cavity temperature	280 °C	

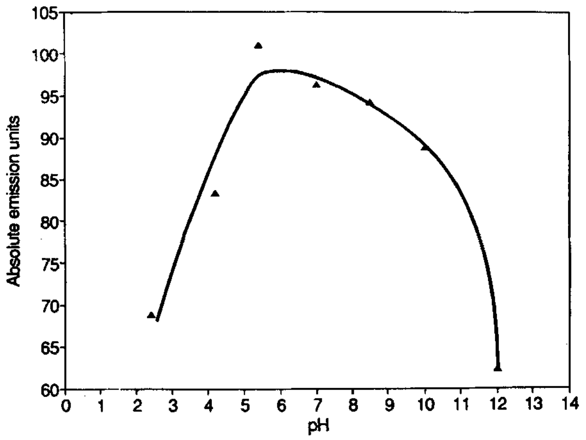

Figure 2 Effect of pH on the derivatization efficiency of trimethyl-lead. Injected: 6.75 pg of Me_3Pb^+.

chosen for real sample analyses as this enabled an efficient use of EDTA as masking agent for inorganic lead,[31] and on the other hand it enabled the effective use of DDTC as a releasing agent for trimethyl-lead bound to dust.

An extraction time of 1 min was found sufficient for the quantitative recovery of trimethyl-lead from standard solutions. Longer times were applied in the case of real sample analyses.

Analysis of water samples

The developed method was applied to the synthetic rainwater samples issued by the BCR in the framework of the second round-robin exercise for trimethyl-lead in environmental matrices. The results for the different dilutions of the solutions I and II, together with the statistical figures of merit, are given in Tables 3 and 4, respectively.

Table 3 Analytical figures of merit for the standard addition curves $y = a + bx$ of trimethyl-lead in solution A (dilution of solution I)

	a	*b*	*r*	Me_3Pb^+ concn[a] (µg l^{-1})
Solution A				
Mean	15.19	0.0121	0.9991	**49.68**
Range	12.92–19.58	0.0108–0.0142	0.9963–1.0000	46.56–54.46
SD	2.3496	0.0012	0.001392	3.050
RSD	15.5%	10.1%	0.1%	6.1%

Definitions: *a* = intercept; b = slope; r = regression coefficient of the standard addition curves; SD = standard deviation; RSD = relative standard deviation.

[a] In the undiluted solution I

Table 4 Analytical figures of merit for the standard addition curves $y=a+bx$ of trimethyl-lead in solutions B–D (dilutions of solution II)

	a	b	r	Me_3Pb^+ concn[a] ($\mu g\ l^{-1}$ as Pb)
Solution B				
Mean	15.62	0.0107	0.9997	**6.436**
Range	13.09–19.38	0.091–0.0120	0.9989–0.9999	6.430–6.538
SD	2.1008	0.0010	0.000385	0.099
RSD	13.5%	9.5%	0.0%	1.5%
Solution C				
Mean	14.41	0.0112	0.9957	**6.524**
Range	13.63–15.34	0.0094–0.0138	0.9895–1.0000	5.531–7.530
SD	0.5766	0.0015	0.004735	0.642
RSD	4.0%	13.1%	0.5%	9.8%
Solution D				
Mean	5.796	0.0177	0.998330	**6.593**
Range	5.337–5.981	0.0151–0.0202	0.9944–1.0000	5.895–7.579
SD	0.2752	0.0017	0.002026	0.586
RSD	4.7%	9.3%	0.2%	8.9%

Definitions: as in Table 3.

[a] In the undiluted solution II.

The average standard deviation of *ca* 6% can be regarded as satisfactory if it is taken into consideration that the results were obtained on different days and always with a fresh diluted sample and standards, so that they include all possible sources of error. The linearity of the standard addition curves is satisfactory in the investigated range. The results show very good consistency at different dilution levels ($6.5 \pm 0.2\ \mu g\ l^{-1}$).

Analysis of road dust

It was initially attempted to apply the same procedure as for the water samples to the road dust. Instead of being shaken for 2 min, the mixture was placed in an ultrasonic bath for *ca* 1 h. As an increase in the borate concentration did not improve the recoveries, 0.2 M NaDDTC was introduced as releasing agent. As a result, the signals were considerably higher but no linearity of the standard addition curves was observed. The results showed very poor precision and the spikes were recovered with mixed success. It was concluded that either trimethyl-lead was strongly bound to the matrix or the derivatization agent was consumed by a large content of inorganic lead in the sample whose release was at the same time stimulated by the added DDTC. Carrying out the reaction under milder conditions (10 min shaking instead of the ulotrasonic treatment) solved this

Table 5 Analytical figures of merit for the standard addition curves $y=a+bx$ of trimethyl-lead in road dust

Sample	Sample intake (g)	a	b	r	Me_3Pb^+ concn ($ng\ g^{-1}$ as Pb)
Road dust	0.2036	21.12	0.0159	0.9988	6.527
	0.0990	7.61	0.0109	0.9929	7.065
	0.0990	10.60	0.0159	0.9992	6.735
	0.1142	11.38	0.0138	0.9985	7.219
	0.1014	9.60	0.0140	0.9989	6.776
Mean		—[a]	—[a]	0.9979	6.864
SD		—[a]	—[a]	0.0026	0.247
RSD		—[a]	—[a]	0.3%	3.6%

Definitions: as in Table 3.

[a] Cannot be calculated because of different sample intake.

Table 6 Comparison of the results obtained in our laboratory with those of the second interlaboratory study on lead speciation

	Concentration of Me_3Pb^+ (as Pb)		
Sample	Result from our laboratory	Result from the intercomparison study[a]	No. of participating laboratories
A	4.97 ± 0.31 μg l^{-1}	4.91 ± 0.20 μg l^{-1}	8
B	0.64 ± 0.01 μg l^{-1}	0.62 ± 0.07 μg l^{-1}	7
C	65.2 ± 6.4 ng l^{-1}	60.0 ± 5.7 ng l^{-1}	5
D	6.6 ± 0.6 ng l^{-1}	not given	2
Road dust	6.9 ± 0.2 ng g^{-1}	5.4 ± 1.1 ng g^{-1}	5

[a] From Ref. 26.

problem. It also improved the precision as the shaking led to a better homogenization of the mixture in the centrifuge tube.

The detection of the trimethyl-lead was seriously interfered with by the large concentration of inorganic lead in the road dust, which could not be entirely masked by the added EDTA. This resulted in a very high detector background, which increased with every injection. By the development of a suitable solvent-venting program, which switched the effluent stream from the column away from the detector immediately after the trimethyl-lead signal had been registered, an acceptably constant background could be achieved. The column was cleaned by heating it to 280 °C after each run.

The results of the road dust analaysis together with the statistical figures of merit are summarized in Table 5.

Comparison with the results from the interlaboratory study

Table 6 contrasts the results obtained in our laboratory with those of the second round-robin exercise on lead speciation.[26] The results from the analysis of the different rainwater dilutions showed very good agreement with the mean values of the interlaboratory study. A difference was observed between the results of the road dust analysis. The intercomparison results showed a serious variation which can possibly be explained by uncertainties concerning the extraction efficiencies of the different methods employed. Another factor was the high amount of inorganic lead in the sample which caused great detection interferences. Under these circumstances the agreement of our result with the mean of the intercomparison results was satisfactory.

CONCLUSIONS

It was shown that the time needed for the determination of trimethyl-lead in the environmental samples can be considerably reduced and the sample handling simplified by using *in situ* derivatization of trimethyl-lead with $NaBEt_4$ followed by extraction, instead of purge-and-trap processing. Contrary to the purge-and-trap method, however, only a tiny fraction of the sample is finally used for the analysis, so a highly sensitive detector (e.g. MIP-AES or MS) is necessary. An increase in the detection limits by *in-line* solvent venting[32] is hardly possible because of the relatively high background from inorganic lead (derivatized to Et_4Pb and co-extracted) ubiquitous in environmental samples. The method was demonstrated to be applicable to the analysis of artificial rainwater and road dust, and its accuracy was validated in a rond-robin exercise on lead speciation.

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