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Determination of Trialkyllead Species in Water Samples

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An analytical compound procedure is described for the determination of trimethyl- and triethyllead in water samples like rain, melted snow, and surface waters. The method consists of an enrichment step (adsorption onto and elution from silica gel), a chromatographic separation with column switching (HPLC including pre-column enrichment), and a spectrophotometric detection (chemical reaction detector). The detection limits for the whole procedure, starting with 500 ml sample volume, are 15 pg/ml and 20 pg/ml for trimethyl- and triethyllead resp. The standard deviation for repeated analysis of a sample containing 90 pg Et_3Pb^+ /ml is calculated to $\pm 4\%$. The method also covers the analysis of the chemically mixed trialkyllead species Me_2EtPb^+ and MeEt_2Pb^+ . The investigation of several water samples taken from different locations shows the presence of trimethyl- and triethyllead in the concentration range of 20–100 pg/ml.

KEY WORDS: Trialkyllead, water, enrichment, HPLC, chemical reaction detector.

INTRODUCTION

Although activities to eliminate or reduce health hazards due to lead are in progress, especially tetraalkyllead compounds used as anti-knock additives still play an important role in the discussion of environmental risks due to lead toxicity. These compounds, mainly

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tetramethyl- (Me_4Pb) and tetraethyllead (Et_4Pb) being emitted into the atmosphere are converted to inorganic lead through the formation of trialkyl- and dialkyllead species. These are fairly soluble in water and subject to wash-out processes leading to their presence in rain, snow, and surface waters. Within the group of the alkyllead salts, the triethyllead species turned out to be the most toxic of all important lead compounds. Environmental health aspects of organolead compounds are reviewed by Grandjean and Nielsen¹ whereas the analytical procedures known so far are summarized by De Jonghe and Adams.² The method mostly used for the quantitative determination of ionic alkyllead species in water samples is based on liquid-liquid extraction, derivatization by alkylation, and separation and detection by GC-AAS. This procedure is applied with slight variations by several groups.³⁻⁸ We have developed an analytical compound procedure which allows the determination of trialkyllead species in urine. The main aim of our studies is the biological monitoring of human exposure to organolead compounds under occupational health aspects. Slight variations of the method, however, make possible also the measurement of tetraalkyllead decomposition products in the environment.

EXPERIMENTAL

The collection of rain water was carried out with narrow-necked amber glass bottles (2 l volume) provided with polyethylene funnels 30 cm in diameter. Snow was either collected in the same manner or picked up cautiously from the ground with subsequent melting. Surface water was directly filled into the bottles. Amber glass was used to protect the sample from daylight to avoid decomposition of trialkyllead compounds. After sampling the water was acidified with 1 ml/l of concentrated hydrochloric acid to minimize wall adsorption and deterioration of the analytes. The samples were stored in the dark and kept cold until analysis.

The first step of the analytical procedure is the enrichment of the interesting lead species. After the addition of EDTA (10^{-3} moles/500 ml) as a complexing agent for metal ions, the water sample (500 ml starting-volume) is adjusted with NaOH to pH 10 and then conveyed by a peristaltic pump at a flow-rate of 10 ml/min

through an extraction-column (8 mm inner diameter), packed with 500 mg of silica gel (Merck). The adsorbed lead compounds are eluted with 2 ml of an acetate-buffer (pH 3.7) containing 10% of methanol. The eluate is adjusted to pH 8 and simultaneously diluted to an end-volume of 6 ml by adding 4 ml of a borate-buffer. Further concentration takes place by injecting 5 ml of this eluate onto a pre-column (20 × 4 mm) packed with Nucleosil 10-C₁₈ (Macherey and Nagel). The adsorbed trialkyllead compounds are eluted in a back-flush mode onto a RP-C₁₈ column and separated with methanolic acetate-buffers as mobile phases.⁹

The detection is carried out on-line by a post column chemical reaction detector,^{10,11} where the separated lead species are decomposed (Eq. 1) and measured spectrophotometrically via their PAR (4-(2-pyridylazo)-resorcinol) complexes (Eq. 2).

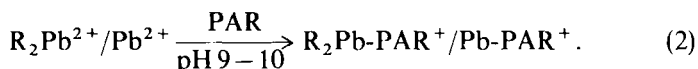
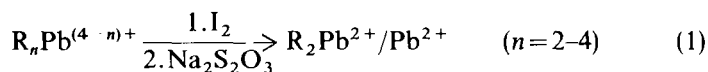


Figure 1 shows the experimental set-up of the chromatographic system with pre-column enrichment and the chemical reaction detector. The various steps of the procedure and the analytical conditions are described elsewhere in detail.⁹ The chromatogram shown in Figure 2 belongs to a sample of tap water which was spiked with a mixture of four trialkyllead compounds prior to analysis. It can be seen that not only the triethyl- and trimethyllead-ions are analysed but in addition the two chemically mixed trialkyl-

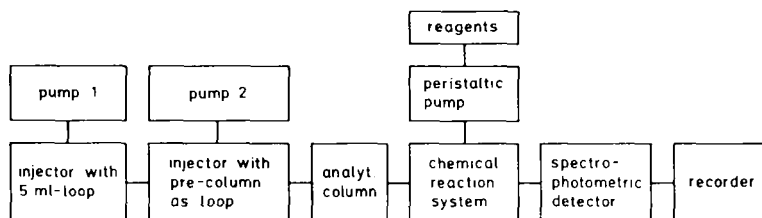


FIGURE 1 Experimental set-up of the analytical system with column switching, HPLC and chemical reaction detector.

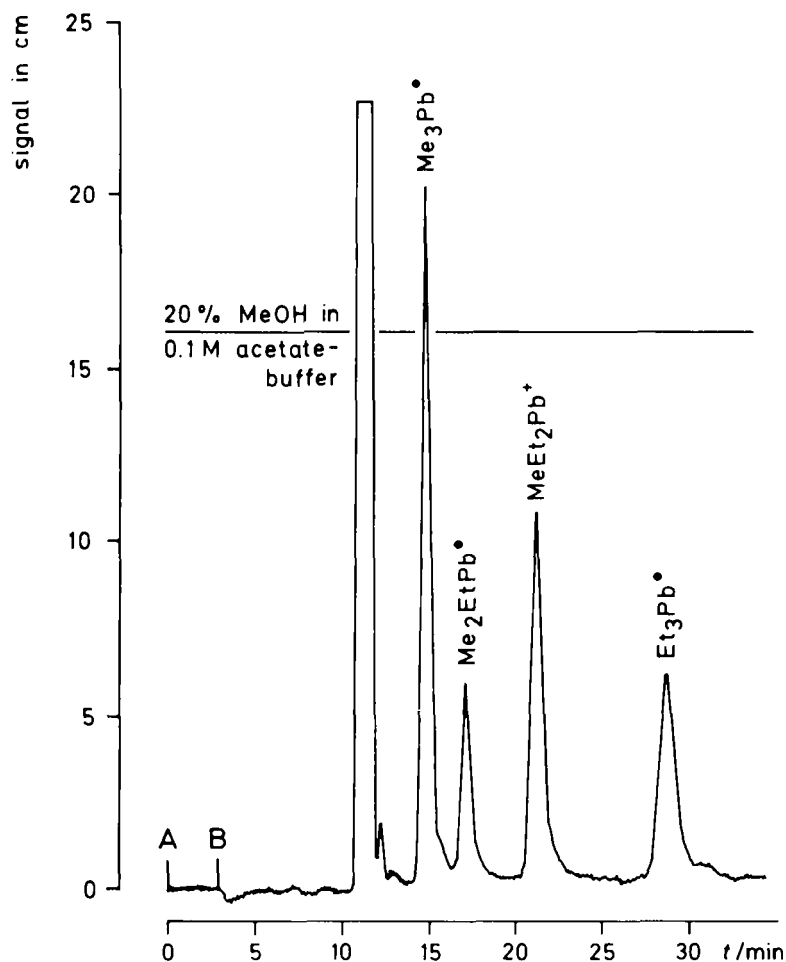


FIGURE 2 Chromatographic trace of four trialkyllead species. Sample: Trialkyllead standard in a 500 ml tap water sample. Column: Whatman Partisil ODS3 $5\mu\text{m}$ ($250 \times 4.6\text{ mm}$). Flow: 1 ml/min. Detection: Chemical reaction detector: 0.02 AUFS. A, B see Table I.

lead species Me_2EtPb^+ and MeEt_2Pb^+ . Under isocratic conditions the most retarded Et_3Pb^+ is eluted after about 30 min.

Table I gives the technical details of the pre-column enrichment and the time scale of the chromatographic separation.

TABLE I

Technical details of the pre-column enrichment and the time scale of the chromatograms.

Enrichment by pre-column technique	
Injection loop:	5 ml (knitted PTFE-tubing (10 m × 0.8 mm i.d.))
Pre-column :	Nucleosil 10-C ₁₈ (20 × 4 mm)
Flow :	2 ml/min
Pressure :	7 bar
Elution :	backflush mode
Chromatographic time scale	
A:	Loading of the pre-column
B:	Elution of the pre-column onto the analytical column
C:	Change of the mobile phase (step gradient)

RESULTS AND DISCUSSION

Applying the above described procedure various environmental water samples (rain, melted snow, and surface water) were analysed and showed no detectable amounts of the chemically mixed species. Therefore, in order to save time, the isocratic conditions were changed into a step gradient which reduces the runtime of a chromatogram to ~23 min. Further analyses of environmental water samples were carried out using either an external standard or the standard additions method for quantitative evaluation of the chromatographic peaks. Figure 3 shows two chromatograms of a real sample of melted snow, with the upper one spiked with 65 pg/ml Me_3Pb^+ and 70 pg/ml Et_3Pb^+ .

The peak at the flank of the Me_3Pb^+ signal probably belongs to the $\text{Et}_2\text{Pb}^{2+}$ species. This, however, has not been confirmed until now. The detection limits for the whole procedure starting with 500 ml sample volume are 15 pg/ml and 20 pg/ml for trimethyl- and triethyllead compounds resp. The standard deviation for repeated analysis of a sample containing 90 pg Et_3Pb^+ /ml is calculated to $\pm 4\%$. Sampling was carried out in Dortmund (about 600,000 inhabitants) situated in the East of the Ruhr area (FRG) in the period between November 1985 and March 1986.

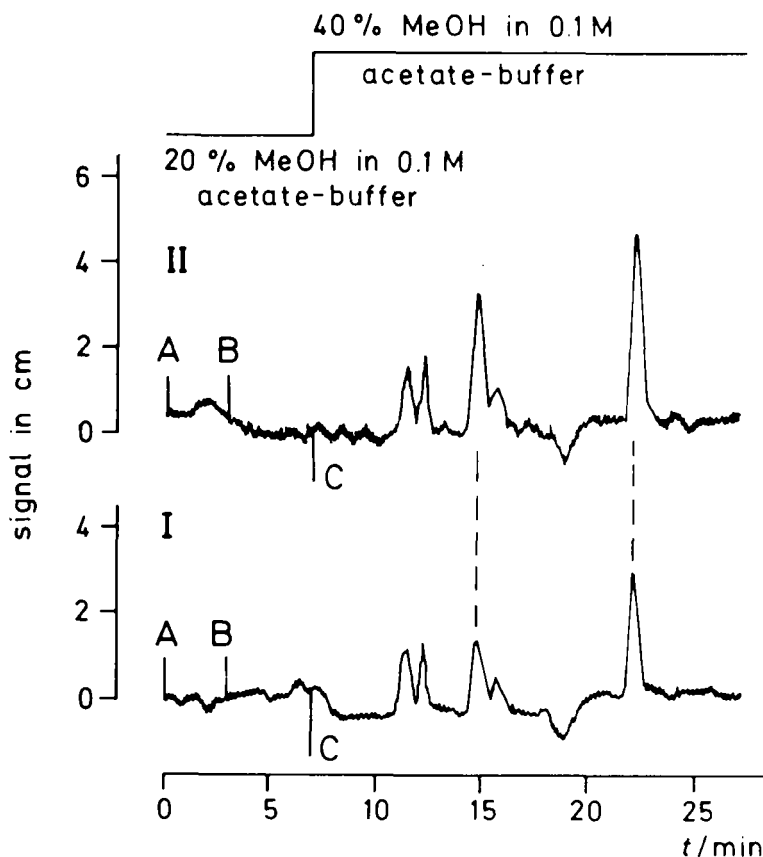


FIGURE 3 Chromatographic trace of trimethyl- and triethyllead species in melted snow sample. Sample: I. 500 ml melted snow; II. 500 ml melted snow spiked with 65 pg Me_3Pb^+ /ml and 70 pg Et_3Pb^+ /ml. Column: Whatman Partisil ODS3 $5\mu\text{m}$ ($250 \times 4.6\text{mm}$). Flow: 1 ml/min. Detection: Chemical reaction detector, 0.02 AUFS. A, B, C see Table I.

Table II summarizes the results of 31 samples taken from different locations of the town. Total lead was determined by electrothermal atomic absorption spectrometry with Zeeman-background correction. Despite the fact, that the total lead content of the samples exceed the concentrations of the trialkyllead species by a factor of 100, it should be mentioned for completeness that the standard

TABLE II
Trimethyl- and triethyllead concentrations in water samples.

Location	Sample	Concentration pg / ml		Concentration ng / ml total lead	Remarks
		Me ₃ Pb*	Et ₃ Pb*		
urban (300 m from highway)	rain	n.a.	107	n.a.	ext. std.
	rain	n.a.	44	n.a.	ext. std.
	rain	n.a.	24	n.a.	std. add.
	rain	n.a.	<20	n.a.	ext. std.
	rain	<15	30	n.a.	ext. std.
	rain	18	34	n.a.	ext. std.
	rain	74	34	n.a.	ext. std.
	rain	27	34	0.92	std. add.
	rain	19	<20	n.a.	std. add.
	rain/melted snow	<15	<20	0.29	std. add.
	rain/melted snow	28	69	0.78	std. add.
	rain	45	71	0.86	std. add.
	rain	18	<20	0.30	std. add.
residential	rain	n.a.	72	n.a.	ext. std.
	rain	n.a.	62	n.a.	ext. std.
	melted snow	23	39	n.a.	ext. std.
	melted snow	23	112	n.a.	ext. std.
	rain	62	<20	n.a.	ext. std.
	rain	42	33	n.a.	ext. std.
	rain	18	147	n.a.	ext. std.
main street	melted snow	16	65	0.69	std. add.
	melted snow	<15	78	0.82	std. add.
main street/crossing	rain	<15	52	0.22	std. add.
	melted snow	61	133	3.26	std. add.
	melted snow	27	82	n.a.	std. add.
highway/petrol station	melted snow	22	56	0.46	std. add.
residential	rain	<15	74	43.3	std. add.
rural	river water	<15	<20	2.5	std. add.
recreation park	creek water	<15	<20	11.4	std. add.
harbor	harbor water	123	40	5.1	std. add.
laboratory	drinking water	<15	<20	n.a.	std. add.

n.a. = not analysed; ext. std. = external standard calibration; std. add. = standard additions method
analysis of total lead by GFAAS and standard additions method

conditions for ETAAS-analysis of inorganic lead are not optimized for quantitative determination of organolead compounds. As can be taken from the table, none of the samples analysed exceeded the concentration of 150 pg/ml for both trialkyllead species. This result is in good agreement with values published for similar urban and rural regions.^{6,7,12} The analytical procedure described here, is totally

different from all others known so far. Therefore it can be used as an independent method for rating the accuracy of trialkyllead concentration values, e.g. of the published data on triethyllead in the rain of the Black Forest, which are still controversially discussed.¹³⁻¹⁵

More than that, the procedure which is simple and easy to perform should be used for a general monitoring of organolead compounds in the environment, because increasing information about lead species enables a better, more differentiated judgement of potential risks and the effectiveness of governmental regulations.

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