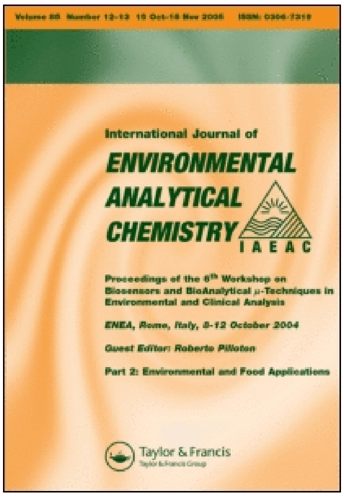

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Speciation of Ionic Alkyllead in Aerosols by Gas Chromatography-Atomic Absorption Spectrometry

D. Chakraborti[a,b]; R. Van Cleuvenbergen[a]; F. Adams[a]
[a] Department of Chemistry, University of Antwerp (U/A), Wilrijk, Belgium [b] Department of Chemistry, Jadavpur University, Calcutta, India

To cite this Article Chakraborti, D. , Van Cleuvenbergen, R. and Adams, F.(1987) 'Speciation of Ionic Alkyllead in Aerosols by Gas Chromatography-Atomic Absorption Spectrometry', International Journal of Environmental Analytical Chemistry, 30: 3, 233 — 242

To link to this Article: DOI: 10.1080/03067318708075471

URL: http://dx.doi.org/10.1080/03067318708075471

Intern. J. Environ. Anal. Chem., 1987, Vol. 30, pp. 233–242
Photocopying permitted by license only

Printed in Great Britain

Speciation of Ionic Alkyllead in Aerosols by Gas Chromatography–Atomic Absorption Spectrometry

D. CHAKRABORTI,* R. VAN CLEUVENBERGEN and F. ADAMS

Department of Chemistry, University of Antwerp (UIA), B-2610 Wilrijk, Belgium

(*Received October 2, 1986; in final form January 21, 1987*)

A sensitive method is described to determine the individual ionic alkyllead species associated with the air particulate matter fraction. The optimization of the procedure and the application to residential aerosols are discussed.

KEY WORDS: Ionic alkyllead, aerosols, gas chromatography–atomic absorption spectrometry (GC–AAS).

INTRODUCTION

The determination of the individual alkyllead compounds has become important in studies related to toxicity and environmental geochemistry. The organolead compounds are more toxic than inorganic lead and between the species there are appreciable differences in environmental behaviour and toxicity.[1]

Of commercially important use are five tetraalkyllead (TAL) compounds: tetramethyllead (TML), tetraethyllead (TEL), and the combined alkyllead species, trimethylethyllead (TMEL), dimethyl-

---

*On leave from Department of Chemistry, Jadavpur University, Calcutta-32, India.

diethyllead (DMDEL) and methyltriethyllead (MTEL). These apolar species are present in the air as a result of emission in leaded gasoline consumption and are readily determined with gas chromatography–atomic absorption spectrometry (GC–AAS) or other related hyphenated methods.[2,3] The compounds undergo degradation to a number of corresponding polar tri- and dialkyllead species (triAL and diAL) on their way to the final conversion to inorganic lead.[3–5] The ionic alkyllead compounds are considered to be highly toxic to mammals.[6] The environmental chemistry of the organolead compounds in general, and the ionic products in particular is still poorly understood since there is a lack of reliable data on their occurrence in many environmentally important types of samples.

Until a few years ago the determination of the ionic degradation products was difficult at the trace levels typical for environmental samples, but recently successful procedures were developed based on chelate extraction followed by species-specific derivatization of the compounds to more volatile tetraalkyl homologues for subsequent separation and determination by GC–AAS.[7–10] The procedure developed in our laboratory[9] includes a highly efficient enrichment step of the compounds from water samples and detection limits are very low, at the $\mathrm{ng\,l^{-1}}$ level. The importance of this preconcentration is well illustrated by a recent review on ionic alkyllead in the environment[5] showing the inability of most of the other existing methods to detect the species in sea water, lake water and ground water. We have applied our procedure with positive results so far for environmental samples such as rain, snow, road run-off and various types of surface water and after leaching from solid materials such as sediments and road dusts.[11,12]

In the present paper we will describe the method of analysis and a few results for the determination of the ionic alkyllead compounds associated with the particulate matter fraction of the air. Our measurements demonstrate that with the procedure adopted, a sample of about $1000\,\mathrm{m}^3$ in a residential area is sufficient for the determination of almost all organolead species. Earlier investigations by Harrison *et al.* allowed the determination of TriML and TriEL in urban aerosols, but the detection of the corresponding diAL species was impossible due to an incomplete recovery of these compounds.[13,14]

EXPERIMENTAL

Equipment

The instrumentation as well as the interface between the GC and the AAS have been described in detail elsewhere.[9,11] In this study we positioned both instruments to make the transfer line as short as possible (60 cm).

Sampling

Air particulates were collected on 11 cm diameter GF/A Whatman glass fiber filters with a standard high volume sampler at a flow rate of about 400 l min^{-1}. The sampling time was 12 to 48 h to allow for air volumes of 300 to 1000 m^3. The samples were all collected in February and March 1986 at an altitude of 6 meters above ground on a balcony of a building of the university campus which is in a residential area of Antwerp at about 7 km south of the city centre.

Procedure

After sampling the filter is folded with the exposed side inside for storing until analysis. Just before analysis it is cut into small pieces and placed in a 1 l beaker. Thirty ml of hexane is added and the slurry is stirred for 5 to 10 min in order to extract the TAL compounds, then 300 ml of water is added and again stirred, before the mixture is filtered on Whatman 41 with a Buchner filter. After washing with a further 100 ml of water, the filtrate is collected into a 1 l separating funnel. Organic and water layers are separated and the aqueous phase is transferred again to the 1 l beaker together with the residue of the filtration. To this are added 4 g of citric acid and 1 g of EDTA and the mixture is stirred for 90 min on a magnetic stirrer before it is again filtered in the same way as before. To the filtrate is added a further 10 g of EDTA and pH is adjusted to 9.0 with ammonia. To the solution is then added 5.0 ml of 0.25 M sodium diethyldithiocarbamate and the complexes formed are extracted twice with 30 ml of pentane after which the separating funnel is rinsed with 10 ml of pentane. To the combined pentane layers a minimum amount of anhydrous sodium sulphate is added to remove traces of water and the organic phase is then roto-evaporated to dryness in an Erlenmeyer flask at 20°C. Next, the chelates in the dry residue are dissolved in 250 μl of nonane before butylation and determination are carried out as has been described earlier.[9, 11]

RESULTS AND DISCUSSION

The recovery of the ionic alkyllead compounds from the air particulate matter was tested in two ways. First, experiments were performed in which loaded filters were spiked with a known amount of the compounds and dried before application of the procedure. The original filters were divided in two equal parts so that blank determinations could be carried out simultaneously with those of the spiked samples. The results which are summarised in Table I indicate that in these circumstances the recovery is nearly quantitative. This, however, does not necessarily prove the completeness of extraction from original atmospheric particulates. Hence, sequential extractions were performed in which the procedure was repeated on the residue on the filter after the first treatment, with omission of the hexane extraction. In the second extraction only about 4% of diEL was recovered whereas other species were undetectable.

Water alone is not appropriate for the extraction of the compounds and the citric acid and EDTA as employed in the procedure appeared to be the most effective extracting agent tried. Longer extraction times than 90 min become detrimental for complete recovery of the DiML species. Co-extraction of the ionic organolead during the hexane removal of the TAL could be expected as it was reported earlier that with hexane 20% of TriEL is extracted from water solution using a 1:1 ratio.[15] In the present procedure involving a 1:10 hexane–water ratio the recovery of the triethyllead compound was nearly quantitative; spiking experiments provided a recovery of 96 ± 7%.

The procedure as described here is somewhat less complicated and lengthy than the one described earlier for the analysis of the same compounds in road dust[12] in which extreme care was taken to separate the considerable inorganic lead fraction from the ionic alkyllead compounds. In this procedure there is a less complete separation from inorganic lead but this does not interfere with the

Table I Recovery of spiked alkyllead species from loaded aerosol filters 1 (first row) and 2 (second row)

Blank (ng)				Amount spiked (ng)				Recovery (%)			
$PbMe_3^+$	$PbMe_2^{++}$	$PbEt_3^+$	$PbEt_2^{++}$	$PbMe_3^+$	$PbMe_2^{++}$	$PbEt_3^+$	$PbEt_2^{++}$	$PbMe_3^+$	$PbMe_2^{++}$	$PbEt_3^+$	$PbEt_2^{++}$
2.0	nd[a]	14.5	89.6	59	71	124	96	101	86	88	95
1.4	nd	6.7	57.7	118	142	301	258	96	95	94	96

[a] nd = not detected.

determination by GC–AAS. In case aerosol samples with a very high inorganic lead content are measured, the amount of EDTA added can be increased up to 20 g without adverse effects on the overall recovery.

Considerable preconcentration is, in general, an attractive feature of this method. In aerosol samples and considering standard sampling of 1000 m^3 of air and a 20 μl injection in the GC, detection limits of the four ionic alkyllead species are 0.6 pg m^{-3} for TriML, 1.0 pg m^{-3} for DiML, 1.2 pg m^{-3} for TriEL and 4.2 pg m^{-3} for DiEL respectively.

APPLICATION

As a preliminary environmental application, eight air particulate samples collected at the university campus were analysed, as a representative example for the aerosol in a residential area in Western Europe. Figure 1 shows the chromatogram obtained from one of the samples. The TriAL and DiAL compounds are identified and quantitatively determined with available standards. Other compounds in the chromatograms are identified through the systematics of the chromatographic retention times.[11] Table II summarizes the results obtained for the individual species. The concentrations of the mixed methyl-ethyl compounds were calculated assuming a complete extraction and sensitivities inferred from those of the other compounds taking into account their time of appearance in the chromatograms. Laboratory experiments confirmed that these mixed methyl-ethyl species do not result from rearrangement reactions during butylation.

The results can be compared with the concentration of the TAL precursors in the gaseous fraction of the atmosphere of which TML is considered to be the most stable compound. We have published an extensive survey on these compounds in the gas phase of the environmental air in 1981[2] and then found an average concentration of the combined TAL compounds of 7 ng m^{-3} of which *ca* 76% corresponded to TML, 20% to TMEL, and 6% to DMDEL with low concentrations of the other species. Significant in that survey is that TEL was not detected although it was one of the most prominent species in the gasoline used at that time.[2] Although caution should be taken in a detailed comparison as the composition of organolead additives and its total concentration together with traffic density in general may have changed considerably between 1981 and 1986, a rough estimate is that the concentration of the ionic compounds associated with the air particulates is an order of magnitude lower than that of the TALs in the gas phase. Also, the comparison of the individual species detected in the air with those in the aerosols points to a minor stability of the TEL species. In the aerosol about 75% of the organolead detected is diethyllead and most of the remainder is triethyllead. This could explain the missing TEL compound in our earlier survey through the fast decomposition into its corresponding tri- and dialkyllead decomposition products.

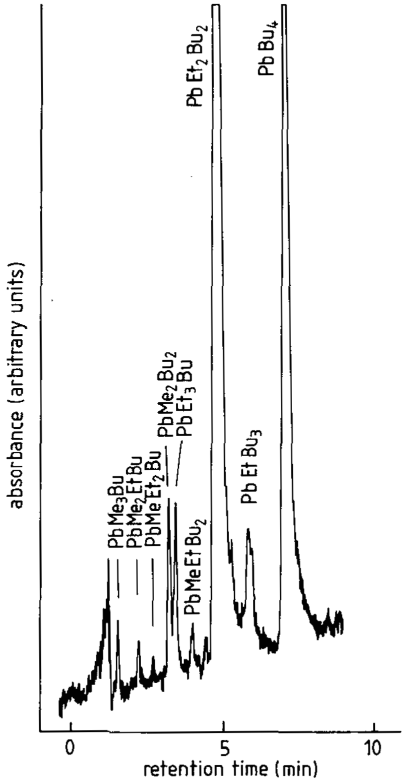

Figure 1 Typical chromatogram of a residential aerosol sample.

Table II Ionic alkyllead on aerosol particles in a residential area

Sample	Volume air (m^3)	Weight particles (mg)[a]	Concentration ($pg\,m^{-3}$)						
			$PbMe_3^+$	$PbMe_2Et^+$	$PbMeEt_2^+$	$PbMe_2^{++}$	$PbEt_3^+$	$PbMeEt^{++}$	$PbEt_2^{++}$
1	472	—	4.5	nd[b]	nd	10.0	20.0	nd	104.0
2	550	—	nd	nd	nd	nd	14.0	nd	60.0
3	517	81.2	5.2	5.5	nd	9.5	25.0	nd	86.0
4	504	100.6	10.4	3.2	nd	nd	94.0	4.0	146.0
5	293	79.0	4.8	5.2	nd	nd	23.0	nd	197.0
6	425	61.6	4.6	5.1	nd	nd	34.0	3.0	211.0
7	884	151.1	2.5	3.0	nd	nd	43.0	5.0	111.0
8	1040	171.2	2.5	1.7	1.1	9.3	8.0	2.6	295.0
Average aerosol ($pg\,m^{-3}$)			4.3	3.0	0.1	3.6	32.6	1.8	151.2
Average road dust ($ng\,g^{-1}$)			3.2	0.5	0.5	0.9	10.7	1.3	86.9

[a] Before weighing, filters were conditioned in a silicagel desiccator until constant weight was obtained.

[b] nd – not detected.

It may be expected that a non-negligible amount of the ionic alkyllead compounds is present in the gas phase of the air. At present, there is no specific method of detection available for the determination of this fraction. Several measurements, however, have indirectly suggested its importance.[2,14] A recent method describing the direct speciation of gas-phase alkyllead[16] may not be completely free from interferences, as the possible *in situ* formation of trialkyllead through rapid degradation of the TAL species collected was not investigated.

The levels of ionic organolead in the air particulate fraction can be compared with the concentration of these compounds in road dust,[12] which is a similar environmental matrix. The average concentration in these materials is included in Table II. The high concentration of diethyllead, which we have also detected in various water samples[11] contrasts with earlier statements on the rareness of detection of the dialkyllead compounds in the environment.[17] The ranking order in decreasing concentration is DiEL > TriEL > TriML > DiML in both the air particulates and the road dust samples. This emphasizes the importance of the diethyllead species in the environment. According to volatility of the compounds DiML should rank before TriML in the aerosol; the high stability of the latter species probably explains this reverse sequence.

Acknowledgements

This research was sponsored by the NFWO, Belgium, through a research assistant grant to R. Van Cleuvenbergen and through FKFO grant 2.0091.85.

References

1. P. Grandjean, (ed.), *Biological Effects of Organolead Compounds* (CRC Press, Boca Raton, Florida, 1984).
2. W. De Jonghe, D. Chakraborti and F. Adams, *Env. Sci. Technol.* **15,** 1217 (1981).
3. W. R. A. De Jonghe and F. C. Adams, *Talanta* **29,** 1057 (1982).
4. F. G. Noden, *Lead in the Marine Environment* (M. Branica and Z. Konrad, eds.), (Pergamon Press, Oxford, 1980), p. 83.
5. M. Radojevic and R. M. Harrison, *Sci. Tot. Env.* **59,** 157 (1987).
6. P. Grandjean and T. Nielsen, *Res. Rev.* **72,** 97 (1979).
7. S. A. Estes, P. C. Uden and R. M. Barnes, *Anal. Chem.* **54,** 2402 (1982).
8. Y. K. Chau, P. T. S. Wong and O. Kramar, *Anal. Chim. Acta* **146,** 211 (1983).

9. D. Chakraborti, W. R. A. De Jonghe, R. J. A. Van Cleuvenbergen, W. E. Van Mol and F. C. Adams, *Anal. Chem.* **56,** 2692 (1984).
10. M. Radojevic, A. Allen, S. Rapsomanikis and R. M. Harrison, *Anal. Chem.* **58,** 658 (1986).
11. R. J. A. Van Cleuvenbergen, D. Chakraborti and F. C. Adams, *Env. Sci. Technol.* **20,** 589 (1986).
12. D. Chakraborti, R. Van Cleuvenbergen and F. Adams, *Proc. Int. Conf. Chemicals in the Environment* (J. N. Lester, R. Perry and R. M. Steritt, eds.), (Selper Ltd, London, 1986) p. 298.
13. R. M. Harrison and M. Radojevic, *Env. Technol. Lett.* **6,** 129 (1985).
14. R. M. Harrison and M. Radojevic, *Sci. Tot. Env.* **44,** 235 (1985).
15. W. R. A. De Jonghe, W. E. Van Mol and F. C. Adams, *Anal. Chem.* **55,** 1050 (1983).
16. C. N. Hewitt and R. M. Harrison, *Proc. Int. Conf. Heavy Metals in the Environment, Athens* (T. D. Lekkas, ed.), (CEP Consultants, Edinburgh, 1985) p. 171.
17. J. R. Grove, *Lead in the Marine Environment* (M. Branica and Z. Konrad, eds.), (Pergamon Press, Oxford, 1980), p. 45.