APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 89–93 (1995)

WORKING METHODS PAPER:

Interlaboratory Programme for the Quality Control of Trimethyllead Determination in the Environment

Ph. Quevauviller,* Y. Wang,† A. B. Turnbull,† W. M. R. Dirkx,‡ R. M. Harrison† and F. C. Adams‡
* European Commission, Measurements and Testing Programme (BCR), rue de la Loi 200, B-1049 Brussels, Belgium, † University of Birmingham, School of Biological Sciences, Edgbaston, Birmingham B15 2TT, UK, and ‡ University of Antwerp, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Determinations of the trimethyllead moiety in environmental samples are carried out by a number of laboratories in Europe. To verify the quality of such determinations, the Measurements and Testing Programme (formerly BCR) of the European Commission organised an interlaboratory exercise which allowed discussion and comparison of the different techniques used so far in lead speciation analyses. In addition, this first step enabled a study of the feasibility of the preparation of candidate reference materials (CRMs) for the determination of the trimethyllead moiety in simulated rainwater to be carried out. The solutions used in this study were carefully prepared and their homogeneity and stability verified. This paper describes the organisation and the results of the intercomparison and discusses the further development of the project.

Keywords: trimethyllead; interlaboratory study; quality control; simulated rainwater

INTRODUCTION

Environmental contamination by lead is widespread, the major anthropogenic source of this element being the combustion of leaded gasoline. Although their use has been discontinued in some countries, the use of tetraalkyllead compounds as antiknock agents still remains the largest appliction of organolead compounds.[1] It is recognized that, owing to the ubiquity of lead and concern over the toxicity of organolead compounds in the environment,[2] the monitoring of lead species will need to be continued over the next decade. Vehicular emissions of tetraalkylead are subject to atmospheric breakdown to trialkyl- and dialkyllead and all three forms are scavenged from the atmosphere by rainfall.[3–6] Therefore, trimethyl- and triethyllead are found in road drainage and surface water.[7] As a consequence, a number of laboratories are performing analyses of, e.g. rainwater and urban dust to monitor the levels of trialkyllead compounds in the environment. The techniques are generally based on a combination of different analytical steps including extraction, derivatization (e.g. ethylation, Grignard reaction), separation [e.g. gas chromatography (GC) or high performance liquid chromatography (HPLC)] and detection (e.g. atomic absorption or atomic emission spectrometry).

In view of the urgent need to establish the level of expertise in lead speciastion analysis, a project has been discussed and designed with a group of European laboratories within the framework of the Measurements and Testing Programme (formerly BCR) of the European Commission. A feasibility study has been carried out to investigate the stability of alkyllead compounds in solution[8] showing that dialkyllead compounds and triethyllead were not sufficiently stable to be kept in water; the only compound which could be stored without significant degradation was trimethyllead and this compound was, therefore, selected for the preparation of lead-containing solutions. This interlaboratory exercise was designed as the first step in a larger project whose aim is to produce reference materials of simulated rainwater and urban dust certified for their content of trimethyllead. This paper gives a summary of the results obtained in this first exercise.

CCC 0268–2605/95/010089–05

Received 7 December 1993
Accepted 23 February 1994

Aim of the exercise

The major task of the Measurements and Testing Programme consists of organizing projects in which participating laboratories collaborate to improve the measurement or analysis process. An intercomparison can be held (i) to detect the problems of a commonly applied method and to ascertain its performance in practice, (ii) to measure the quality of a laboratory or a part of a laboratory (e.g. audits for accreditation of laboratories), (iii) to improve the quality of a laboratory in collaborative work in a mutual learning process and (iv) to certify the content of a reference material (CRM).[9] The work described here is of type (iii); such an exercise is one of the most powerful tools by which to detect and remove sources of error due to a particular technique as applied within a laboratory.[10, 11] In general, analytical errors in all analyses may stem from:

(a) inadequate sample storage;
(b) method of sample pretreatment (e.g. digestion, pre-concentration, dilution);
(c) method of final measurement (e.g. calibration, removal of spectral interferences, background corrections);
(d) laboratory infrastructure (e.g. training and educational level of workers, awareness of potential problems, management, clean bench facilities);
(e) data treatment.

When different laboratories participate in an intercomparison, different sample pre-treatment methods and different techniques of final determination are compared and discussed as well as the actual analytical results from the laboratories.

Preparation and verification of calibrants

One of the most critical areas in organometallic chemistry is the availability of calibrants of suitable purity and verified stoichiometry. This aspect was recognised at an early stage of the project and the purity of alkyllead compounds used in the feasibility study was carefully verified.[3] Additional experiments were performed on calibrants within the framework of the first interlaboratory exercise as described below.

EXPERIMENTAL

Trimethyl- (TriML) and triethyllead (TriEL) were obtained from Alfa products (Johnson Matthey) and their purity was verified as follows: carbon, hydrogen and chloride relative masses in the TriML and TriEL calibrants were determined by elemental microanalysis and the chloride concentration was determined by ion chromatography. Total lead was determined in the calibrants by electrothermal atomic absorption spectrometry (ETAAS) using two different acid digestion procedures (concentrated nitric acid and mixture of nitric acid/hydrogen peroxide). Calibrant solutions of TriML and TriEL at the 25 mg dm^{-3} level were prepared in deionized distilled water (DDW) and analysed; a 200 μl aliquot of each of these solutions was added to a DDW solution (30 cm^3) containing NaCl (2 g), 0.5 mol dm^{-3} sodium diethyldithiocarbamate (NaDDTC) (2 cm^3) and 0.1 mol dm^{-3} EDTA (1 cm^3) and the mixtures were shaken manually in a separating funnel. Hexane (5 cm^3) was added to the funnel and the aqueous phase was removed after a 4 min shaking time. The extracted alkyllead compounds were then each re-extracted into dilute nitric acid and hydrogen peroxide and determined by ETAAS.

An aqueous solution containing 500 ng dm^{-3} of TriML and TriEL was also prepared and extracted as above (except for the addition of nitric acid and hydrogen peroxide). The hexane extract was transferred to a 25 cm^3 conical flask and 0.5 cm^3 propyl magnesium chloride (Grignard) reagent was added, followed by gentle shaking for 8 min. The extract was then washed with 0.5 mol dm^{-3} H_2SO_4 (5 cm^3) to destroy any excess Grignard reagent present. The organic phase was separated and dried with a minimum of anhydrous sodium sulfate (Na_2SO_4) and transferred to a 4 cm^3 vial. TriML and TriEL were determined by gas chromatography GC/AAS.[12] Students t-tests were applied for comparing the experimental results obtained with those expected.

RESULTS

The results are listed in Tables 1 and 2. Inorganic lead contamination of the calibrants can be estimated by subtracting the total organic lead from total lead concentration determined by acid digestion.[4] It was found that the content of alkyllead in the calibrants was slightly less than 100%, and that extraction/analytical losses were likely causes for this, rather than inorganic lead (as this was not significantly different from the expected

Table 1 Trimethyllead chloride solution

			Found (%)		
Components	Expected (%)	Mean	σ	n	Significance in t-test
C[a]	12.5	13.0	0.36	3	—
H[a]	3.1	3.1	0.05	3	—
Cl[a]	12.3	10.5	0.02	2	S
Cl[b]	12.3	11.8	0.2	3	S
Total Pb[c]	72	73.5	5.0	4	—
Total Pb[d]	72	72.4	1.7	4	—
TriML[e]	100	98.8	3.9	4	—
TriML[f]	0	1.8	0.08	2	S
$MeEt_3Pb$[f]					
Other alkyl Pb[g]					
DML[h]	0	1.8	0.12	2	S

[a] Microanalysis. [b] Ion chromatography (Dionex). [c] HNO_3 digestion followed by ETAAS. [d] HNO_3/H_2O_2 digestion followed by ETAAS. [e] Hexane extraction, HNO_3/H_2O_2 back-extraction followed by ETAAS. [f] Hexane extraction followed by GC/AAS. [g] Hexane extraction, propylation, followed by GC/AAS. [h] Dimethyllead.

abundance). In addition, if there was contamination by inorganic lead(II)chloride ($PbCl_2$) in the calibrants, the concentration of chloride as obtained by microanalysis and ion chromatography would be higher than the one expected. In the two chloride analyses, it was found that the chloride concentration was slightly lower than that expected, probably due in part to the tetraalkyllead detected in the calibrants (around 2% of the total lead content). In the light of the other results (Table 1 and 2), it was thought unlikely that significant amounts of either inorganic lead or other ionic alkyllead compounds were present. It was concluded, therefore, that the two trialkyllead calibrants were not less than 98% pure.

Table 2 Triethyllead chloride solution

			Found (%)		
Components	Expected (%)	Mean	σ	n	Significance in t-test
C[a]	21.8	21.3	0.28	2	—
H[a]	4.6	4.4	0.09	2	—
Cl[a]	10.8	11.3	0.11	2	S
Cl[b]	10.8	10.2	0.20	3	S
Total Pb[c]	62.8	63.1	1.6	3	—
Total Pb[d]	62.8	62.6	1.4	3	—
TriEL[e]	100	97.7	4.7	3	—
TriEL[f]	0	1.6	0.08	2	S
$MeEt_3Pb$[f]	0	0.2	0.06	2	—
Other alkyl Pb[g]	0	0			

[a] Microanalysis. [b] Ion chromatography (Dionex). [c] HNO_3 digestion followed by ETAAS. [d] HNO_3/H_2O_2 digestion followed by ETAAS. [e] Hexane extraction, HNO_3/H_2O_2 back-extraction followed by ETAAS. [f] Hexane extraction followed by GC/AAS. [g] Hexane extraction, propylation, followed by GC/AAS.

Preparation of solutions

Preliminary investigations have shown that ethyllead compounds are more sensitive towards degradation than the corresponding methylated compounds;[8] TriML was found to be stable in solutions kept at ambient temperature in the dark. Consequently, a batch of solutions containing 40 mg dm^{-3} of TriML chloride (as lead) and 100 mg dm^{-3} of lead nitrate (as lead) added as interferent was prepared and the stability was verified over a period of six months.

Analytical techniques used in the intercomparison

Nine laboratories from six European countries participated in the intercomparison (see Acknowledgements). The techniques used are summarized below:

(a) *Laboratory 01* used a diethyldithiocarbamate complexation with EDTA/hexane solvent, followed by a Grignard derivatization (with propylmagnesium chloride), capillary gas chromatographic (GC) separation and detection by microwave inductively plasma-atomic emission spectrometry (MIP/AES).

(b) *Laboratory 02* used a pyrrolidinedithiocarbamate complexation with n-hexane solvent followed by HPLC and detection by quartz furnace ETAAS.

(c) *Laboratory 03* carried out a complexation of lead(II) (Pb^{2+}) with EDTA in citrate buffer with a determination by differential pulse anodic stripping voltammetry (DPASV).

(d) *Laboratory 04* performed a diethyldithiocarbamate and pentane extraction followed by a Grignard derivatization (with butylmagnesium chloride), a capillary GC separation and detection by mass spectrometry (masses 208, 223 and 253).

(e) *Laboratory 05* carried out a complexation of lead(II) with EDTA in citrate buffer and extraction in n-hexane, followed by a capillary GC separation and detection by quartz furnace ETAAS.

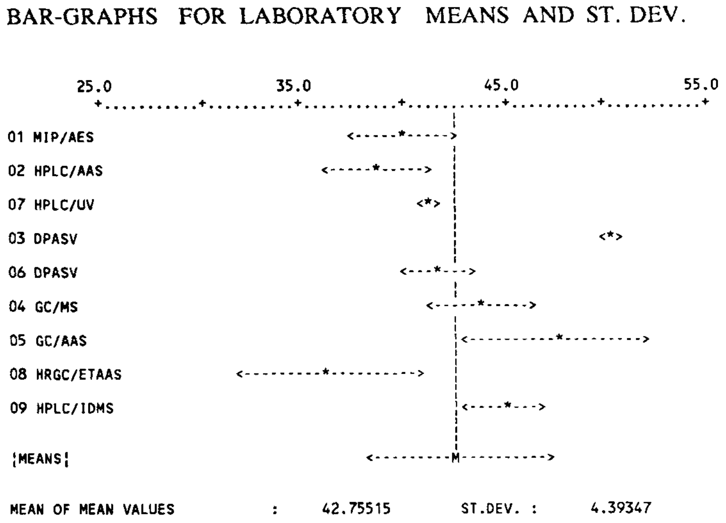

Figure 1 Bar graphs for laboratory means and standard deviation.

(f) *laboratory 06* added a sodium buffer solution at pH 5 and performed the final determination by DPASV.

(g) *Laboratory 07* added HCl and carried out a pre- and on-column derivatization with methylthioglycolate, followed by HPLC separation and final determination by UV/vis spectrometry.

(h) *Laboratory 08* added EDTA and sodium citrate and carried out a diethyldithiocarbamate complexation and a pentane extraction, followed by a Grignard derivatization (with butylmagnesium chloride), separation by high resolution GC and ETAAS detection.

(i) *Laboratory 09* diluted with a mobile phase buffer and carried out a HPLC separation followed by an ICPMS detection of mass 208.

DISCUSSION

The results submitted in the intercomparison were discussed amongst all participants at a technical meeting. Each laboratory which participated in the exercise was requested to make a minimum of five independent replicate determinations. The results were presented in the form of bar-graphs showing the laboratory codes and the methods used, the mean and standard deviation of each laboratory and the mean of laboratory means with its standard deviation (Fig. 1). For the intercomparison exercise, participants were asked to dilute the solution 1000 times, i.e. to determine levels of TriML of ca 40 $\mu g\, dm^{-3}$. Some laboratories (Labs. 01, 02, 03 and 06) analysed the solutions after a 10 000-fold dilution.

The participants considered it impossible to correct the results for impurities in the calibrant matrix.

The high result and small standard deviation of Lab. 03 were questioned. The small standard deviation is inherent to the technique used but interferences and suspected adsorption problems on the mercury drop electrode were suspected which could explain the higher value found (50.4 $\mu g\, dm^{-3}$).

A small standard deviation was also noticed for Lab. 07 which was due to the use of means of replicates instead of the individual results. Lab. 05 observed slightly higher coefficient of variance (CV) values than normal (ca 5%). Lab. 08 observed a double peak in their chromatogram eluting at the retention time of inorganic lead which was not reproducible. It was suspected that the derivatization step was not fully optimized which could explain the low value found (36 $\mu g\, dm^{-3}$). Lab. 02 suspected a systematic error which could explain higher values found at the 4 $\mu g\, dm^{-3}$ level (10 000-fold dilution). This error could not be seen at the higher level (1000-fold dilution). Indeed, in the case of a small systematic error the calibration slope would be the same and standard additions could not correct for non-additive errors. The laboratory mentioned that a hydride generation procedure was successfully used in their laboratory for lead speciation analysis. No interferences were observed between inorganic lead, Me_3PbCl and TriEL using this method. However, this system is still under development and its durability should be further tested. This method was based on earlier work by Blais and Marshall.[13]

No problems due to interferences from inorganic lead were mentioned by any of the participants.

Future development

Feasibility studies are currently being carried out at the University of Birmingham, UK to test the preparation of an artificial rainwater and urban dust contaminated with TriML. Artificial rainwater solutions enriched with TriML were prepared and diluted to obtain solutions containing three different levels: 50 ng dm^{-3}, 500 ng dm^{-3} and 5 μg dm^{-3}. These solutions were stored at room temperature and −20 °C. The composition of the artificial rainwater samples simulated the composition of real samples (addition of NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, NO_3^- and H_3O^+ ions). The pH of the solutions upon storage was 3.84. The stability was studied during six months with determinations performed every month. The results showed that the decomposition of TriML was most rapid in the low concentration samples (50 ng dm^{-3}). There was only a small degree of decomposition at the 500 ng dm^{-3} level both in the dark at ambient temperature and at −20 °C. The 5 μg dm^{-3} samples were stable for at least 6 months under both storage conditions. On the basis of these results, the preparation of a candidate reference material of artificial rainwater was discussed. The participants agreed that the levels should be representative of natural concentrations but that, however, the preparation of solutions containing 50 ng dm^{-3} of TriML would not be feasible. To overcome the instability problems it was decided to store a ten-fold concentrated artificial rainwater solution (500 ng dm^{-3}) in 100 cm^3 Nalgene bottles and dilute to 1 dm^3 prior to analysis. The pH corresponding to the storage conditions of the artificial rainwater solution should be 3.5 to arrive at a pH of 4.5 after dilution. Any further dilution would require use of artificial rainwater of similar composition.

An extensive study on the preparation of artificial rainwater solutions and of urban dust has been carried out on the basis of these findings. Samples were prepared for a second intercomparison, the results of which were discussed in February 1994 and are described in detail elsewhere.[14] A certification campaign on TriML in an artificial rainwater and urban dust is contemplated in 1994/95.

Acknowledgements The authors gratefully acknowledge all the participants in this interlabortory exercise, namely: D. Baxter (University of Umeå, Sweden), J. Bettmer (University of Münster, Germany), A. A. Brown (University of Plymouth, UK), P. Colombini (CNR-ICAS, Pisa, Italy), R. Lobinski (University of Antwerp, Belgium), B. Neidhart (Philipps-Universität Marburg, Germany), C. Nerin (University of Zaragoza, Spain), O. Nygren (National Institute of Occupational Health, Umeå, Sweden) and A. Slater (The Associated Octel Company, South Wirral, UK).

REFERENCES

1. C. N. Hewitt and R. M. Harrison. In: *Organometallic Compounds in the Environment*, Craig, P. J. (ed), Longman, London (1986), p. 160.
2. R. J. C. Van Cleuvenbergen and F. C. Adams. In: *Handbook of Environmental Chemistry*, Hutzinger, O. (ed), Springer Verlag (1990), p. 97.
3. R. M. Harrison and D. P. H. Laxen, *Environ. Sci. Technol.* **12**, 1384 (1978).
4. C. N. Hewitt and R. M. Harrison, *Environ. Sci. Technol.* **20**, 797 (1986).
5. C. N. Hewitt and R. M. Harrison, *Environ. Sci. Technol.* **21**, 260 (1987).
6. A. G. Allen, M. Radojevic and R. M. Harrison, *Environ. Sci. Technol.* **22**, 517 (1988).
7. R. M. Harrison, M. Radojevic and S. J. Wilson, *Sci. Total Environ.* **50**, 129 (1986).
8. R. J. C. Van Cleuvenbergen, W. M. R. Dirkx, Ph. Quevauviller and F. C. Adams, *Int. J. Environ. Anal. Chem.* **47**, 21 (1992).
9. E. A. Maier, *Trends Anal. Chem.* **10**, 340 (1991).
10. Royal Society of Chemistry, Analytical Methods Committee, *Analyst* **112**, 679 (1987).
11. B. Griepink and M. Stoeppler. In: *Hazardous Metals in the Environment*, Stoeppler, M. (ed), Elsevier, vol. 17 (1992) p. 517.
12. M. Radojevic, A. G. Allen, S. Rapsomanikis and R. M. Harrison, *Anal. Chem.* **58**, 658 (1986).
13. J. S. Blais and W. D. Marshall, *J. Anal. At. Spectrom.* **4**, 641 (1989).
14. Ph. Quevauviller, Y. Wang and R. M. Harrison, *Appl. Organometal. Chem.*, **8**, 703–708 (1994).