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Interlaboratory Study for the Quality Control of Trimethyl-lead Determination in Simulated Rainwater and Urban Dust

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An interlaboratory programme has been started within the Measurements and Testing Programme (formerly BCR) of the European Commission to evaluate the performance of analytical techniques used for the determination of trimethyl-lead in simulated rainwater and urban dust. A first interlaboratory study on solutions was successfully concluded in 1993 and a second exercise was organized, focusing on simulated rainwater and urban dust analysis. This paper reports the results of this second interlaboratory study, which is a preparatory step for a certification campaign of simulated rainwater (with representative contamination levels) and urban dust.

Keywords: Trimethyl-lead, interlaboratory study, analytical performance, quality control, simulated rainwater, urban dust

INTRODUCTION

Although the use of leaded gasoline has considerably decreased in the past few years, environmental contamination by lead is still widespread owing to the ubiquity of lead and lead compounds. Consequently it is expected that the monitoring of lead and lead species will need to be continuously carried out over the next decade. Trialkyl-lead compounds are currently monitored owing to their higher toxicity; in particular, a number of laboratories are determining trimethyl-lead in environmental compartments likely to be contaminated by lead compounds such as rainwater (as an index of atmospheric contamination) and urban dust. The need to evaluate the techniques used for lead speciation analysis has resulted in the organization of an interlaboratory study on lead in solutions by the Measurements and Testing Programme (formerly BCR) in 1993.[1] The results obtained by different analytical methods (hyphenated and electrochemical techniques) were in good agreement and it was decided to organize a second interlaboratory study on samples resembling more closely natural samples, i.e. simulated rainwater with low trimethyl-lead (TriML) levels, and urban dust. This paper gives a summary of the second exercise, which was carried out in the framework of the Measurements and Testing Programme in 1993–1994.

DESIGN OF THE INTERLABORATORY STUDY

Interlaboratory studies are one of the most powerful tools to detect and remove sources of error due to a particular technique.[2] Indeed, all methods have their own source of error; for instance, for some techniques errors may occur due to an incomplete derivatization, a step which is not necessary for other techniques involving high-performance liquid chromatography (HPLC); the latter technique, however, may suffer from errors such as incomplete separation, which is not encountered, or only to a lesser extent, in the former technique. If the results of different methods are in good agreement, it can be concluded that the results are unlikely to be affected by an error of a systematic nature (e.g. insufficient extraction). However, if the methods have similarities, such as an extraction step, a comparison of results leads to conclusions concerning the accuracy of the method of final determination.

When laboratories participate in an interlaboratory study, different analytical techniques are compared and discussed, as well as the performance of the laboratories. If the results of such an intercomparison are in good statistical agree-

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ment, the collaboratively obtained value is likely to be the best approximation of the truth.

The participating laboratories received two sets of solutions containing respectively *ca* 50 and 5 $\mu g\ l^{-1}$ of trimethyl-lead chloride ((TriML). They were requested to perform five replicate analyses of, respectively:

(a) 10-fold dilution of the 50 $\mu g\ l^{-1}$ solution (solution A);
(b) 10-fold dilution of the 5 $\mu g\ l^{-1}$ solution (solution B);
(c) 100-fold dilution of the 5 $\mu g\ l^{-1}$ solution (solution C);
(d) 1000-fold dilution of the 5 $\mu g\ l^{-1}$ solution (solution D).

In addition, the participants had to perform five replicate analyses of an urban dust sample.

Nine laboratories participated in the intercomparison (see acknowledgements).

SAMPLE PREPARATION

The sample preparation was performed by the School of Biological Sciences, University of Birmingham. Two sets of simulated rainwater solutions were prepared with the composition listed in Table 1. Aliquots of solution (100 ml) were transferred into 18 100-ml Nalgene bottles for each of the samples. The bottles were wrapped with aluminium foil, and then sealed in plastic bags.

Urban dust was collected from the Queensway road tunnel in Birmingham city centre (UK). After being passed through a 500 μm sieve to remove large particles of debris, the dust was first treated by air-drying for several (4–5) days and then ground with a ballmill for 3 min. The ground dust was further sieved through an 80 μm sieve. Around 600 g of treated road dust was homogenized thoroughly in a 1 kg glass jar and then stabilized by freeze-drying for 20 h. The bottling procedure followed immediately into 30-ml amber glass bottles containing approximately 25 g of the dust, which were sealed in plastic bags.

Table 1 Composition of the solutions used in the interlaboratory study

Composition	Sample A	Sample B
TriML ($\mu g\ l^{-1}$)	54.8	6.39
Pb^{2+} ($\mu g\ l^{-1}$)	100	100
10-fold concentrated artificial rainwater (concn in $\mu mol\ l^{-1}$):		
NH_4^+	600	600
K^+	50	50
Ca^{2+}	120	120
Mg^{2+}	100	100
Na^+	600	600
Cl^-	900	900
SO_4^{2-}	300	300
NO_3^-	400	400

ANALYTICAL TECHNIQUES USED IN THE INTERCOMPARISON

Table 2 summarizes the different techniques of final determination used by the participating laboratories. The pretreatment techniques were in most cases based on complexation, GC separation and different detection techniques (e.g. MIP–AES, AAS, ICP–MS; abbreviations are defined in the footnote to Table 2).

TECHNICAL DISCUSSION

The results submitted in the interlaboratory study were discussed amongst all participants at a technical meeting (Rome, 19–22 February 1994); they 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. The bar-graphs obtained for solutions A, B and C, and for the urban dust sample are shown in Figs 1–4.

Solution A: 10-fold dilution of 50 $\mu g\ l^{-1}$ solution

The bar-graph presentation is shown in Fig. 1. The technique used by Laboratory 03 did not include a separation step but the participant mentioned that EDTA extraction would extract only organic lead compounds; this technique was considered to be suitable for the analysis of a simple solution containing only one lead compound but would not be adapted to mixtures of lead species, e.g. the techniques would not allow for the sepa-

Table 2 Summary of techniques of final determination

Sample pretreatment, derivatization, separation and calibration[a]	Final determination[a]	Series
Diethyldithiocarbamate complexation with EDTA/hexane solvent; ammonia/citrate buffer (pH 8.3)–derivatization with sodium tetraethylborate; extraction with hexane–capillary GC separation–calibration by standard additions (aqueous calibrant solution of Me_3PbCl)	MIP–AES	1
Diphenylthiocarbazone extraction in CH_2Cl_2/hexane; addition of KCN and EDTA; ammonium phosphate/citrate buffer (pH 9.0)–Grignard reaction (butylmagnesium chloride); excess destroyed with HNO_3–packed GC separation–calibration graph (Me_3BuPb, purity 99%)	GC–AAS with quartz T-tube, wavelength 217 nm	2
Addition of HCl–hydride generation; addition of EDTA–no separation step–calibration graph and standard additions (aqueous solution of Me_3PbCl)	ETAAS	3
Complexation of Pb^{2+} with EDTA in citrate buffer–calibration by standard additions (aqueous solution of Me_3PBCl, purity 99%)	DPASV	4
Addition of sodium buffer soluton (pH 5)–calibration by standard additions (aqueous solution of Me_3PbCl)	DPASV	5
Ion-exchange using Chelex resin micro-columns	ICP–MS	6
Addition of NaCl–ethylation with $NaBEt_4$; cryogenic trapping–packed GC separation (U-tube)–calibration graph (aqueous solution of Me_3PbCl, purity 98%)	ETAAS with quartz T-tube, wavelength 283.3 nm	7
Diethyldithiocarbamate complexation and pentane extraction–Grignard reaction (butylmagnesium chloride 2 mol^{-1}; excess decomposed with H_2SO_4–capillary GC–calibration graph (aqueous solution of Me_3PbCl); internal standard Et_4Pb	MS of masses 208, 223 and 253	8
Complexation of Ph^{2+} with EDTA in citrate buffer; pH adjusted to 9 with ammonia; diethyldithiocarbamate complexation followed by pentane extraction–Grignard reaction (butylmagnesium chloride, excess decomposed with acid)–calibration by standard additions (aqueous solution of Me_3PbCl)	GC–AAS with graphite furnace	9

[a] Abbreviations: DPASV, differential pulse anodic stripping voltammetry; GC, gas chromatography; ETAAS, electrothermal atomic absorption spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; MIP-AES, microwave-induced plasma atomic emmision spectrometry; MS, mass spectrometry.

ration of TriML and triethyl-lead (TriEL) in a natural rainwater sample. In cases where organolead compounds are to be determined in natural samples or solutions containing different lead compounds, ETAAS (used here) should be coupled to a separation technique, e.g. GC or HPLC. Laboratory 05 had some doubt over the results obtained considering a poor standard deviation, and repeated the analysis with a well-conditioned electrode. The new mean was 6.52 ± 0.22 μg kg^{-1}. Laboratory 07 mentioned that sample A was used there as a preliminary analysis, which could explain the slightly higher results and a high standard deviation; this result was considered only as an indicative value ad was not incuded in the bar-graph (7.52 ± 0.87 μg kg^{-1}).

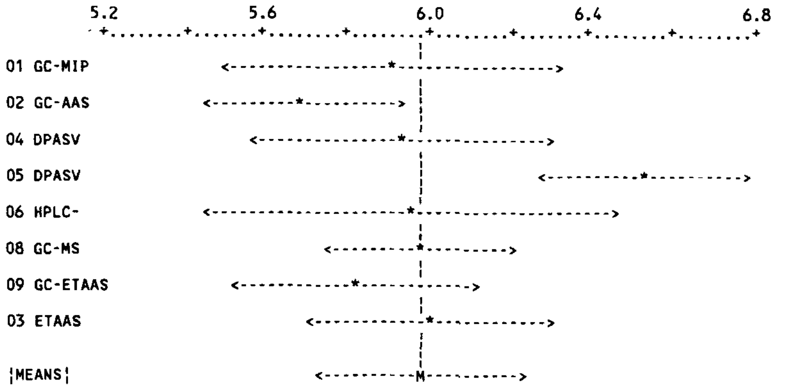

Figure 1 Bar-graphs of results of TriML in solution A. The mean of laboratory means was 5.98 ± 0.24 μg kg^{-1}.

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        .65                   .75                   .85                   .95
         +..........+..........+..........+..........+..........+..........+
                                  |
01 GC-MIP                       <--*-->
                                  |
02 GC-AAS <--*-->                 |
                                  |
07 GC-AAS         <-----------*--------->
                                  |
05 DPASV               <-----------*---------->
                                  |
08 GC-MS                          | <--------*-------->
                                  |
09 GC-ETAAS                       |                <------------*----------->
                                  |
03 ETAAS   <--------*-------->    |
                                  |
                                  |
|MEANS|          <----------------M---------------->
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Figure 2 Bar-graphs of results of TriML in solution B. The mean of laboratory means was 0.76 ± 0.08 µg kg^{-1}.

Laboratory 04 also repeated the analysis and observed a systematic difference due to two different sets of calibrants. The second set of data (5.94 ± 0.33 µg kg^{-1}) was obtained with a calibrant solution made with a newer calibrant from the same producer. This highlighted the need to verify the calibrant, i.e. not to rely on the calibrants from one producer of which the quality could vary from one set to another. Most of the laboratories used their own calibrants which were not verified for purity and stoichiometry. Only one laboratory used the calibrant previously verified and distributed in the first interlaboratory study.[1] It was stressed that calibration was an important issue and that more effort should be put into the verification of calibrants in future exercises. It was agreed that the coordinator of the project would purchase calibrant from a chemical company and verify its purity; sets of verified primary calibrants would then be made available to participants in a further exercise to verify their own calibrants.

The verification of extraction recoveries was also questioned. Most of the laboratories performed standard addition procedures and hence did not need to correct for recovery. Laboratory 02 did not correct for recovery and mentioned that its set of results would be higher by *ca* 10% after correction.

The coeficient of variation (CV) between laboratories was originally 20.9%. After technical scrutiny and elimination of certain laboratories' results, the CV decreased to *ca* 4%, which was found to be an excellent agreement.

Solution B: 10-fold dilution of 5 µg l^{-1} solution

The bar-graph for solution B is presented in Fig. 2. Laboratory 06 mentioned that the technique was under development and still not optimized at the level of concentration considered and the ICP–MS result was therefore withdrawn (0.49 ± 0.16 µg kg^{-1}). Laboratories 01 and 02 had standard deviations lower than usual. For Laboratory 01, this was not easily explainable. For Laboratory 02, the reason was probably that the analyses were carried out on a single day and that, therefore, the day-to-day variability was not a factor. Laboratory 04 (DPASV) could not submit results as its technique was below the detection limit required. Laboratory 05 (DPASV) succeeded in producing reliable results by doubling the deposition time (240 s instead of 120 s); the participant mentioned, however, that this concentration corresponded to the limit of determination of his technique.

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        55.0                65.0                75.0                85.0
          +.........+.........+.........+.........+.........+.........+.........+
                                              |
01 GC-MIP                             <----------------*---------------->
                                              |
02 GC-AAS                   <-----*---->      |
                                              |
07 GC-AAS                 <-----------*----------->
                                              |
08 GC-MS                                      |       <-----------*------------>
                                              |
03 ETAAS                <-------------*------------->
                                              |
                                              |
|MEANS|                         <-------------M------------->
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Figure 3 Bar-graphs of results of TriML in solution C. The mean of laboratory means was 73.1 ± 7.0 ng kg^{-1}.

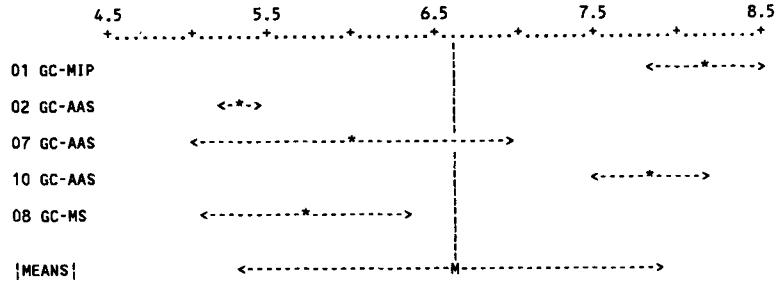

Figure 4 Bar-graphs of results of TriML in urban dust. The mean of laboratory means was 6.6 ± 1.3 ng g^{-1}.

The CV between laboratories was 14.8% before the evaluation and dropped to 10% after elimination of certain results. This degree of agreement was found acceptable at this level of TriML concentration.

Solution C: 100-fold dilution of 5 μg l^{-1} solution

As shown in Fig. 3, a good agreement was obtained between laboratories at this level of concentration (CV *ca* 10% between laboratories).

Urban dust

Figure 4 shows the bar-graph for urban dust analyses.

The extraction recovery was considered to be the most critical point in urban dust analysis. Laboratory 01 found that ultrasonic extraction gave poor recoveries and in extreme cases led to zero or even highly negative recoveries. This was probably because such a treatment leads to the release of inorganic lead from the sample which consumes the reagent ($NaBEt_4$) despite the EDTA masking. In addition, the high amount of inorganic lead extracted creates important interferences at the detection step, which requires the addition of EDTA. Therefore, it was preferable to use a milder extraction procedure (shaking) to allow the complete recovery of the TriML spike to be obtained, whereas inorganic lead was only partly extracted.

Laboratory 02 verified its recovery by spiking a different road dust material and found values of 86 and 89% respectively; the results submitted were, however, not corrected and would be slightly higher after correction. Here again, the analyses were perfomed on a single day, which explained the small standard deviation.

Some doubts were expressed on the procedure used by Laboratory 07 which filtered the suspension and took back TriML in water. Indeed, TriML is not stable in water and it was suspected that losses could have occurred, e.g. by adsorption on the filter. An extraction recovery experiment was not necessary as standard additions were performed prior to extraction; recovery values of 66 and 77% were obtained.

Laboratory 08 did not verify the extraction recovery, which again allowed some doubt over the possibly low results.

At this stage, it was hardly possible to confirm the doubts expressed on the extraction recovery of TriML in this material. The participants recommended that emphasis be put on the verification of extraction recovery in a further exercise, i.e. that a small batch of candidate reference material of urban dust be spiked with a known amount of TriML, left to equilibrate, homogenized and made available to the participants so that the extraction recovery may be verified. A recommendation was made to spike the dust in a slurry which should be freeze-dried, not dried, in order to avoid losses of TriML.

CONCLUSIONS

The preparation of samples for a possible certification excerise was discussed. The participants agreed that a solution containing 500 ng l^{-1} of TriML in a ten-fold concentrated artificial rainwater solution would be a suitable candidate reference material. The bulk solution should be analysed as such and after a ten-fold dilution in order to obtain values matching the concentration levels found in natural rainwater samples (*ca* 50 ng l^{-1}). The analysis of different sample intakes was recommended in order to investigate possible interferences and as a method of optimizing the analytical techniques.

With respect to urban dust, it was proposed that a candidate reference material should be prepared as well as a spiked material to verify the extraction recoveries. Particular attention was recommended to be paid to this verification as well as to the verification of calibrant purity and stoichiometry. Other requirements would be that five replicate determinations should be performed on two bottles on at least two separate days. A possible certification campaign could be contemplated by the end of 1994 or the beginning of 1995.

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