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WORKING METHODS PAPER

Certification of Trimethyl-lead in an Urban Dust Reference Material (CRM 605)

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In order to control the quality of trimethyl-lead determination in urban dust, the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission organized interlaboratory studies of which the final aim was to certify a Reference Material. This paper describes the preparation of an urban dust reference material (CRM 605), the homogeneity and stability studies, and the analytical work performed for the certification of the trimethyl-lead content ($7.9 \pm 1.2\ \mu g\ kg^{-1}$ by mass). Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Although the use of leaded gasoline (petrol) is being increasingly discontinued in many countries, the use of tetraalkyl-lead compounds as antiknock agents remains the largest application of organolead compounds[1] and, 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 tetraalkyl-lead are subject to atmospheric breakdown to trialkyl- and dialkyl-lead and all three forms are scavenged from the atmosphere by rainfall.[3] Therefore, trimethyl- and triethyl-lead are found in road drainage and surface water.[4] As a consequence, a number of laboratories are performing analyses of rainwater and urban dust, for example, to monitor the levels of trialkyl-lead compounds in the environment.

The techniques used are generally based on a combination of different analytical steps including extraction, derivatization (e.g. ethylation or Grignard reactions), separation (e.g. gas chromatography or high-performance liquid chromatography) and detection (e.g. atomic absorption or atomic emission spectrometry) which all pose risks of systematic errors (e.g. insufficient extraction, inhibition of derivatization reaction, incomplete separation etc.). In order to verify the performance of analytical techniques used in lead speciation and the quality control of trimethyl-lead determinations, Certified Reference Materials are needed. This paper describes the preparation and certification of trimethyl-lead in an urban-dust reference material, CRM 605, prepared within the framework of a project launched by the Standards, Measurements and Testing programme (formerly BCR) of the European Commission.

FEASIBILITY STUDY

One of the most critical points in organometallic chemical analysis is the availability of calibrants of suitable purity and verified stoichiometry. This aspect was recognized at an early stage of the project and the purity of alkyl-lead compounds used in the feasibility study was verified carefully.[3] Additional experiments were performed on calibrants during the first interlaboratory exercise. Trimethyl- (TriML) and triethyl-lead (TriEL)

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compounds 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; chloride concentration was determined by ion chromatography. Total lead was determined in the calibrants by electrothermal atomic absorption (ET AAS) 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 l^{-1} level were prepared in distilled deionized water (DDW) and analysed; a 200 μl aliquot of each of these solutions was added to a solution containing NaCl (2 g), 0.5 mol l^{-1} sodium diethyldithiocarbamate (NaDDTC) (2 ml) and 0.1 mol l^{-1} ethylenediaminetetra-acetate (EDTA) (1 ml) in 30 ml DDW, and the mixtures were shaken manually in a separating funnel. Hexane (5 ml) was added to the funnel and the aqueous phase was removed after shaking for 4 min. The extracted alkyl-lead compounds were then re-extracted into dilute nitric acid and hydrogen peroxide, and determined by ET AAS.

An aqueous solution containing 500 ng l^{-1} of TriML and TriEL was prepared and extracted as above (except for the addition of nitric acid and hydrogen peroxide). The hexane extract was transferred to a 25 ml conical flask and 0.5 ml propylmagnesium chloride (Grignard) reagent was added, followed by gentle shaking for 8 min. The extract was then washed with 0.5 mol l^{-1} H_2SO_4 (5 ml) to destroy any excess Grignard reagent present. The organic phase was separated and dried with a minimum of anhydrous Na_2SO_4 and transferred to a 4 ml vial. TriML and TriEL were determined by gas chromatography (GC AAS). Student's *t*-tests were used to compare the experimental results obtained with the predicted values.

The results showed that the content of alkyl-lead in the calibrants was slightly less than 100%, and that extraction/analytical losses were the likely causes for this, rather than inorganic lead (since this was not significantly different from the expected concentration). In addition, if there was contamination by inorganic $PbCl_2$ in the standards, the concentration of chloride obtained by microanalysis and ion chromatography would have been higher than expected. In the two chloride analyses, it was found that the chloride concentration was slightly lower than expected, probably due in part to the tetra-alkyl-lead detected in the calibrants (around 2% of the total lead content). In the light of these results, it was thought unlikely that significant amounts of either inorganic lead or other ionic alkyl-lead compounds were present. It was concluded, therefore, that the two trialkyl-lead calibrants were not less than 98% pure. These calibrants were used in the interlaboratory studies.

INTERLABORATORY STUDIES

Two interlaboratory studies were organized, the first dealing with the analysis of artificial concentrated rainwater solutions[6] and the second dealing with artificial rainwater and urban dust.[7] The preparation of the urban dust and the analytical results are described below. Results of the artificial rainwater exercise are described elsewhere.[6]

Preparation of urban-dust samples used in the interlaboratory study

The sample preparation was performed by the Institute of Public and Environmental Health, University of Birmingham, UK. Urban dust was collected from the Queensway road tunnel in Birmingham city centre. After being passed through a 500 μm sieve to remove large particles of debris, the dust was first treated by air-drying for 4–5 days and then ground with a ballmill for 3 min. The ground dust was further sieved through a 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 material was bottled immediately into 30 ml amber glass bottles, each of which contained approximately 25 g of the dust; they were then sealed in plastic bags.

Results of the interlaboratory study

In most cases, the pretreatment techniques used were based on complexation and GC separation, and employed various detection techniques (e.g. MIP–AES, AAS, ICP–MS). The extraction recovery was considered to be one of the most critical points in urban-dust analysis. Direct ultrasonic extraction of TriML from the urban dust into water gave poor recoveries and in extreme cases led to negligible or even negative recoveries (in comparison with spike recovery tests); 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, a milder extraction procedure (shaking) was used to ensure complete recovery of the TriML spike, whilst inorganic lead was only partly extracted.

Some doubts were expressed on the procedure used by one laboratory, which filtered the suspension and recovered TriML from the filtrate. Indeed, it was suspected that losses could have occurred, for example, by adsorption on the filter. The extraction recovery was not necessary as standard additions were performed before extraction; recovery values of 66 and 77% were obtained. At this stage, it was not possible to confirm the doubts expressed over 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. Recommendation was made to spike the dust in a slurry which should be freeze-dried, rather than oven-dried, in order to avoid losses of TriML.

The preparation of samples for a possible certification exercise was discussed. The participants agreed that a Candidate Reference Material could be prepared, following a similar approach to the interlaboratory study, with the addition of a second spiked material in order 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.

PREPARATION OF THE CANDIDATE CRM

Around 15 kg of surface road dust was collected by sweeping a lay-by in the central section of the Queensway tunnel in Birmingham (UK). The tunnel is approximately 850 m in length and is a major traffic route through Birmingham from the motorway system. The dust was passed through a 500 μm sieve to remove large particles of debris. Then the sample was treated by air-drying at room temperature for five days on a flat tray lined with clean paper in a well-ventilated and dark place. Further, the dust was ground in a ballmill for a period of 3 min and sieved through a 125 μm sieve.

About 10 kg of the pre-treated dust sample was homogenized by the following procedure: the whole amount of dust was divided in four subsamples of about 2.5 kg; each subsample was stored in a 5 l dark-glass bottle and shaken on the mechanical shaker for few hours (using different shaking directions). When all four subsamples had been homogenized, they were redistributed again into a second four subsamples in such a way that each of the first four subsamples contributed equally to each of the second four. This procedure was repeated three times, after which the final four subsamples were again combined in one sample. The homogenized dust sample was freeze-dried at −50 °C and 8 mbar pressure for 24 h. The bottling procedure followed immediately. Each of the 600 30 ml amber glass bottles, provided with screw-caps, was filled with *ca* 15 g of the dust sample, sealed in a plastic bag and stored in the coldroom at 4 °C.

A separate batch of material was set aside for the preparation of spiked samples to be used for the verification of extraction recoveries by the certifying laboratories. A solution (250 ml) of trimethyl-lead chloride calibrant containing 20 μg as Pb was first prepared, and then added to 400 g of candidate urban road dust. The slurry was placed in a 1 l wide-necked amber glass bottle and was stirred manually for several hours with two glass rods, and then stored over 48 h at 4 °C. After being freeze-dried over two nights, the dust was gently ground in a porcelain mortar, and then transferred into another 1 l wide-necked amber glass bottle. The bottle was then shaken mechanically to homogenize the whole sample of the spiked road dust before it was distributed into 25 bottles, each containing *ca* 15 g of the dust. The spiking level of trimethyl-lead in the urban road doast was 50 μg kg^{-1} (as Pb).

HOMOGENEITY

The between-bottle homogeneity of the candidate CRM 605 was verified by a single determination of trimethyl-lead in each of 15 bottles set aside during the bottling procedure (five bottles out of each set of 200 bottles). The within-bottle homogeneity was verified by 10 replicate analyses from one bottle.

Samples (1 g) were transferred to 250 ml screw-cap glass bottles containing Milli-Q water (100 ml) and NaCl (10 g). The bottles were shaken on a mechanical shaker for 30 min. The slurry was filtered through two pieces of glass microfibre filter (Whatman GF/C) and rinsed with 50 ml of Milli-Q water. The combined filtrates were then transferred to a second clean 250 ml glass bottle. After the pH was adjusted to 9.0 with an ammonia solution, EDTA (3 g), 5 ml of 0.5 mol l^{-1} NaDDTC and 15 ml hexane were added. After 30 min of agitation, the organic phase was removed and the extraction was repeated with a second aliquot of hexane. The combined hexane extracts were then passed through anhydrous Na_2SO_4 with hexane rinses. The hexane extracts were transferred to a 25 ml conical flask and evaporated by purging with an N_2 stream in a water bath set at 35 °C, until approximately 5 ml of the hexane extract remained. This was transferred into a 10 ml concentrator receiver tube with a hexane rinse and evaporated by purging with an N_2 stream until 0.5 ml of the extract remained. Grignard reagent (0.3 ml propylmagnesium chloride) was added and the concentrator tube was shaken in a ultrasonic bath for 5 min. H_2SO_4 (5 ml of 0.5 mol l^{-1}) was added to destroy the excess Grignard reagent and the mixture was shaken in the ultrasonic bath for a further 5 min. The hexane layer was removed from above by means of a 200 μl pipette. A small amount of anhydrous Na_2SO_4 was placed within the pipette tip to dry the extract. This 25 μl of the final extract was injected into a GC AAS system. The extraction recovery of trimethyl-lead in road dust was verified by spiking road dust material at a level of 4 μg kg^{-1}. The range of recovery was from 66.5 to 91.3% for four replicates (mean of 77.6 ± 9.5%).

The coefficients of Variation (CVs) for trimethyl-lead analysis in CRM 605 are presented in Table 1. An *F*-test at a significance level of 0.05 did not reveal significant differences between the within-bottle and the between-bottle variances and the method CV. On the basis of these results, no inhomogeneity was suspected and the material was considered to be homogeneous at a level of 1 g and above.

Table 1 Between-bottle homogeneity and method CV for CRM 605: (CV ± U_{CV}) %

Component	Within-bottle[a]	Between-bottle[b]	Method[c]
Trimethyl-lead	8.2 ± 1.5	8.4 ± 1.9	8.2 ± 1.8

[a] 10 replicate determinations on the contents of one bottle. Uncertainty on the CVs: $U_{CV} \approx CV/\sqrt{2n}$.

[b] Single determination on the contents of each of 15 bottles.

[c] 10 replicate determinations on an extract solution.

STABILITY

The stability of the trimethyl-lead content was tested to determine the suitability of this material as a candidate CRM. Bottles were kept in the dark at −20 °C, +20 °C and +37 °C and trimethyl-lead was determined at the beginning of the storage period and after 1, 3, 6, 12 and 37 months. Samples were analysed using the same procedures as for the homogeneity study. Trimethyl-lead was determined in triplicate (one replicate analysis in each of three bottles stored at −20, +20 and +37 °C) on each occasion of analysis.

Any change with time in the content of a element or compound indicates an instability, provided that a good long-term analytical reproducibility is obtained. Instability may be detected by comparing the concentrations of different elements or compounds in samples stored at different temperatures with those stored at a low temperature on the various occasions of analysis.

The samples stored at −20 °C were used as a reference for the samples stored at +20 and +37 °C respectively. Table 2 gives the ratios (R_T) of the mean values (X_T) of three measurements made at +20 and +37 °C to the mean value ($X_{-20°C}$) from three determinations made on the same occasion of analysis at a temperature of −20 °C, i.e. $R_T = X_T/X_{-20°C}$

The uncertainty U_T has been obtained from the coefficient of variation (CV) of five measurements obtained at each temperature:

$$U_T = (CV_T{}^2 + CV_{-20°C}{}^2)^{1/2}.\ R_T/100 \qquad [1]$$

Table 2 Normalized results of the stability study

Component	Time (months)	$R_T \pm U_T$ (+20 °C)	$R_T \pm U_T$ (+37 °C)
Trimethyl-lead	1	1.06 ± 0.10	0.83 ± 0.14
	3	0.98 ± 0.18	0.84 ± 0.14
	6	1.01 ± 0.14	0.83 ± 0.13
	12	1.00 ± 0.13	0.80 ± 0.10
	37	0.98 ± 0.12	0.73 ± 0.08

Table 3 Carbon, hydrogen and chlorine analysis of the trimethyl-lead calibrant

	Composition (%) Found	Calcd.
Carbon	12.62	12.51
Hydrogen	3.24	3.14
Chlorine	12.04	12.30

In the case of ideal stability, the ratio R_{T} should be 1. In practice, however, there are some random variations due to the error on the measurement. In almost all cases, the value 1 falls between $R_{\mathrm{T}}^{-} U_{\mathrm{T}}$ and $R_{\mathrm{T}} + U_{\mathrm{T}}$. On the basis of the results, it was concluded that no instability of the material could be demonstrated over a period of 37 months for the material stored at +20 °C. However, a significant decrease in trimethyl-lead content was observed to occur at +37 °C.

On the basis of these results, it was concluded that the material is stable at +20 °C whereas storage temperatures above this level should be strictly avoided.

METHODS USED IN THE CERTIFICATION

After a preparatory meeting in which all the requirements for certifying Reference Materials were discussed and restated, two bottles of the candidate CRM were shipped to the participating laboratories listed in the Acknowledgements. Each laboratory that took part in the certification exercise was requested to perform six independent replicate determinations on at least two different bottles of the CRM on different days.

A trimethyl-lead calibrant was prepared by the University of Plymouth for the purpose of the certification campaign in order to enable participating laboratories to verify their own calibrants. A portion of 39 g of tetramethyl-lead and toluene (80%, w/w) was placed in a round-bottomed flask and hexane (250 ml) was added. Dried hydrogen chloride gas was bubbled through the mixture for 10 min at a flow rate of 150 ml min^{-1}. A heavy white precipitate was formed and was removed by filtration; it was first washed with hexane (300 ml) and finally rinsed with pentane before being dried under reduced pressure. The original reaction mixture was discarded, the apparatus was cleaned with hexane and a fresh preparation was undertaken in order to produce sufficient trimethyl-lead chloride for the purpose of the project. The purity of the product was assessed by NMR spectroscopy and was found to be greater than 99%. The product was also sent to an accredited external laboratory for carbon, hydrogen and chlorine analysis and the results are shown in Table 3. Good agreement was obtained between the observed percentage composition for these components and their theoretical values, providing confirmatory evidence of the purity of the product.

This calibrant was used in all cases by the participants in the certification campaign. In addition to the purity checks performed by the University of Plymouth, some laboratories cross-checked this calibrant using the calibrant from the interlaboratory studies.

The methods used in the certification campaign are described in Table 4.

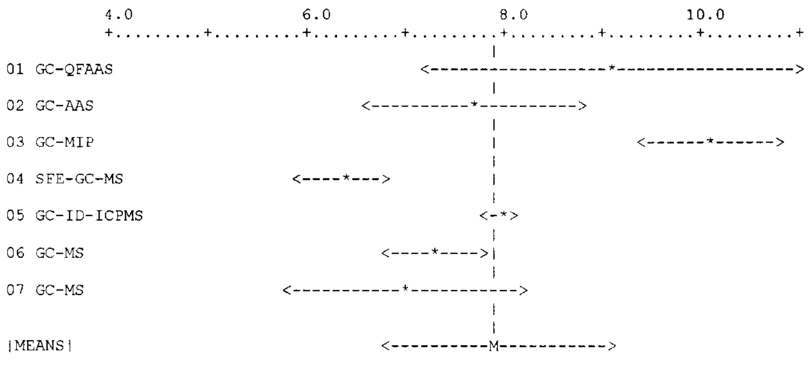

Fig. 1. Trimethyl-lead (μg/kg^{-1}) in urban dust; laboratory mean values and 95% confidence intervals.

Table 4 Summary of techniques used in the certification

Laboratory	Method
01	Addition of NaCl/H_2O; derivatization with 4% $NaBEt_4$; separation by cryogenic trapping in a U-tube filled with chromatographic material; detection by QF AAS
02	Complexation with EDTA and DDTC; hexane extraction; derivatization by addition of 2 mol/L propylmagnesium chloride; elution with hexane; separation with U-tube filled with chromatographic material; detection by QF AAS
03	Addition of ammonium citrate/EDTA; derivatization with $NaBEt_4$; separation by CGC; detection by MIP–AES
04	Supercritical fluid extraction using CO_2 with methanol: liquid–liquid extraction of SFE eluate with *n*-hexane after complexation with DDTC; derivatization by addition of propylmagnesium chloride; separation by CGC; detection by MS
05	Addition of NaCl, EDTA and hexane; separation by CGC; derivatization with $NaBEt_4$; detection with ID–ICP–MS of isotopes ^{206}Pb and ^{208}Pb
06	Addition of DDTC; extraction with pentane; clean-up with 100% active alumina followed by elution with hexane/diethyl ether; derivatization with pentylmagnesium bromide; separation by CGC; detection by MS
07	Extraction with pentane after buffering with ammonium acetate and DDTC complexation; clean-up with deactivated alumina; redissolution into hexane; derivatization with butylmagnesium bromide; separation by CGC; detection by MS

Abbreviations:
CGC Capillary gas chromatography
DDTC Diethyldithiocarbamate
ICP–MS Inductively coupled plasma mass spectrometry
ID–ICP–MS Isotope dilution–inductively coupled plasma mass spectrometry
MIP–AES Microwave-induced plasma atomic emission spectrometry
MS Mass spectrometry
QF AAS Quartz furnace (electrothermally heated) atomic absorption spectrometry
SFE Supercritical fluid extraction

TECHNICAL AND STATISTICAL EVALUATION OF THE RESULTS

The sets of results found acceptable after both the technical and statistical evaluation are presented in Fig. 1. Each set of results is identified by the code number of the laboratory.

Technical discussion

Results produced by hydride generation/ZET AAS were withdrawn; this method is capable of speciating between inorganic and organic lead but does not have the specificity to differentiate between organolead species. The candidate CRM was likely to contain a variety of organolead compounds, so these results were not used.

The recoveries obtained by the various laboratories were discussed most were in the range 70–95%, with standard deviations of 3–8%. It was agreed that the best practice was to conduct recovery studies alongside the analytical measurement. Trimethyl-lead in the spiked sample was determined as the difference between the spiked and the unspiked results.

General statistical discussion

For each set of results the mean value and the standard deviation were calculated after having passed technical scrutiny. The sets of results were submitted to the following statistical tests: Kolmogorov–Smirnov–Lilliefors tests to assess the conformity of the distributions of individual results and of laboratory means to normal distributions; the Nalimov test to detect ‘outlying’ values in the population of individual results and in the population of laboratory means; the Bartlett test to assess the overall consistency of the variance values obtained in the participating laboratories; the Cochran test to detect ‘outlying’ values in the laboratory variances (S_i^2); the one-way analysis of variance (F-test) to compare and estimate the between- and the within-laboratory components of the overall variance of all the individual results.

The estimates of the within-laboratory standard deviation (S_W) and the between-laboratory standard deviation (S_B), as derived from one-way analysis of variance, demonstrated that the between-laboratory variation was not significant. For reasons of uniformity, it was decided to base the certification on the laboratory means rather than all individual results. The half-width of the 95% confidence interval of the mean of the data set means was adopted as the uncertainty.

In Fig. 1 the length of a bar corresponds to the 95% confidence interval of the laboratory mean. The certified value was calculated as the arithmetic mean of the laboratory means (taking into account the number of sets accepted for certification after both statistical and technical scrutiny); this value is featured as a vertical dotted line on the bargraphs (the uncertainty is given by the half-width of the 95% confidence interval).

The population of results accepted for certifica-

Table 5 Certified mass fractions (dry matter) of trimethyl-lead in CRM 605 (μg kg^{-1} as TriML)

Component	Certified value (μg kg^{-1} as TriML)	Uncertainty (μg kg^{-1} as TriML)	p[a]
Trimethyl-lead	7.9	1.2	7

[a] p = number of sets of results.

tion had a normal distribution before the 95% confidence interval of the means of means is calculated (Kolmogorov–Smirnov–Lilliefors tests). In addition, no outlying mean values were detected (Nalimov test). The set of variances was not homogeneous; owing to the fact that different methods were used, each having a different repeatability and reproducibility, this was not surprising and it was fully acceptable. No outlying variances were detected.

CERTIFIED VALUE

The certified value (unweighted mean of p accepted sets of results) and its uncertainty (half-width of the 95% confidence interval) is given in Table 5 as mass fractions. Trimethyl-lead is certified as the mass fraction of $(CH_3)_3Pb^+$ (μg kg^{-1} as TriML).

AVAILABILITY

CRM 605 is available at the Institute for Reference Materials and Measurements (IRMM), Retieseweg, B-2440 Geel, Belgium [Fax: (+32)14 590406], along with a certification report which contains the information given in this paper as well as all the individual results and a full description of the methods used in the certification.

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University of Plymouth, Department Environmental Sciences, Plymouth (UK).
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