APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 8, 615–620 (1994)

Transversely Heated Graphite Atomizer–Atomic Absorption Spectrometry (THGA AAS) in Combination with Flow Injection Analysis System-Hydride Generation (FIAS HG) as a Reliable Screening Method for Organolead Compounds

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The combination of a flow injection analysis system-hydride generation (FIAS HG) and transversely heated graphite atomizer–atomic absorption spectrometry (THGA AAS) has been applied for the sensitive detection of organolead compounds [e.g. detection limit of trimethyl-lead species (TriML): 32 ng l^{-1} for a 0.5 ml sample loop] in the presence of inorganic lead. A mixture of hydrochloric acid and ethylenediaminetetra-acetic acid (EDTA) as a carrier solution in the flow injection system suppressed interferences of inorganic lead. Calibration with various organolead compounds in the range 0.25–8 μg l^{-1} was carried out in the presence of 10 mg l^{-1} Pb^{2+} without any interferences. Additionally, statistical aspects of the determination of trimethyl-lead have been studied. Different parameters, e.g. working range, detection limit, recovery function etc., were calculated with respect to quality assurance in metal speciation.

Keywords: Organolead compounds, flow injection analysis, hydride generation, graphite furnace atomization, atomic absorption spectrometry

INTRODUCTION

Today the main purpose of metal speciation is the specific and sensitive determination of single compounds, e.g. methylmercury or tributyltin species, and is often performed by coupling chromatographic methods with element-specific detectors.[1] Before analysis with these time-intensive and expensive systems, it is desirable to be sure about the existence of organometallic compounds in the sample. For this purpose, in the 1970s and 1980s several methods were developed to differentiate inorganic and organometallic compounds.[2–5] This differentiation was made possible by the determination of a total metal concentration parameter, and especially its inorganic metal percentage.

In contrast to some former methods, this paper presents an analysis method which performs the detection of organolead compounds in the presence of high amounts of inorganic lead without any separation steps. The determination is accomplished by transversely heated graphite atomizer–atomic absorption spectrometry (THGA AAS) in combination with flow injection analysis system-hydride generation (FIAS HG). Examination of ionic organolead compounds has previously demonstrated the great efficiency of this commercially available system.[6] The observation of low detection limits for these compounds and small sensitivity for inorganic lead interferences suggested verification of whether it is possible to determine the more toxic organoleads in the presence of inorganic lead.

In this work a mixture of hydrochloric acid and ethylenediaminetetra-acetic acid (EDTA) is used as a carrier solution in the FIAS. Due to the complexation with EDTA, interferences of inorganic lead are not observed, because only the hydride products of the organolead compounds are introduced and enriched in the graphite furnace. However, it has to be supposed that the ionic alkyl-lead compounds are partially complexed, too. In addition, a statistical treatment according to Funk *et al.*[7] is carried out for the determination of trimethyl-lead. Important

CCC 0268–2605/94/070615–06

Received 21 February 1994
Accepted 15 July 1994

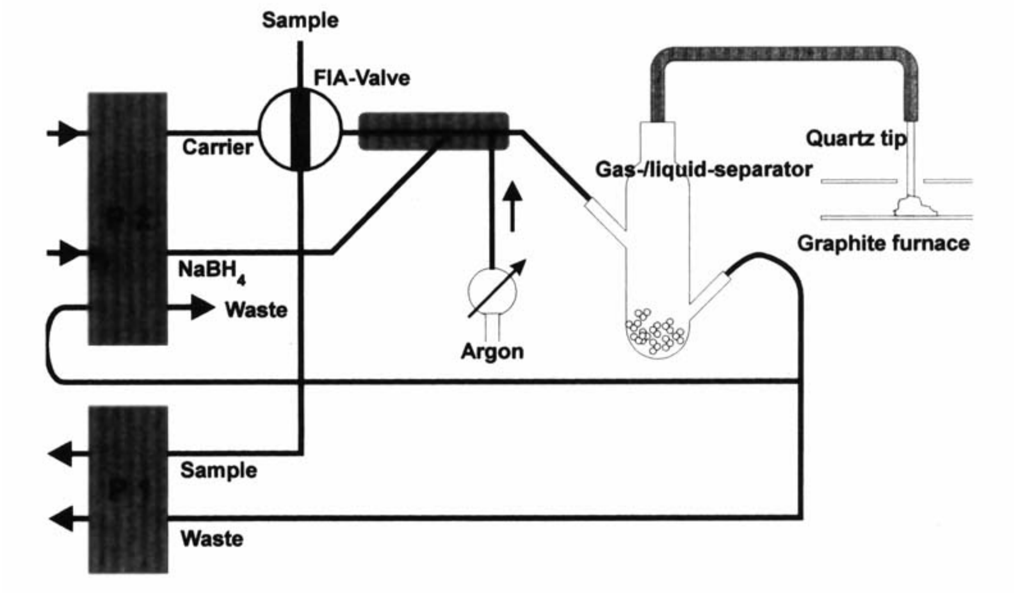

Figure 1 Flow injection analysis system (FIAS).

parameters and statistical values are calculated to assure quality in metal speciation.

EXPERIMENTAL

Instrumentation

The measurements were carried out with a Perkin–Elmer model 4100ZL atomic absorption spectrometer in combination with the FIAS 200. The EDL for lead (wavelength 283.3 nm, slit 0.7 nm L (low)) was operated at 440 mA. The measurement parameters were specified as follows: integration time 5 s; measurement type, peak height and area; BOC time 2 s; sample loops 0.5 ml and 1.5 ml for the synthetic rainwater sample. The flow injection system is described in Fig. 1.

Reagents and standard solutions

Ethylenediaminetetra-acetic acid, disodium salt, (EDTA) dihydrate (99%; Aldrich-Chemie, Steinheim, Germany), sodium hydroxide (p.a.), sodium borohydride (p.a.), hydrogen peroxide (30% medical extrapure), L(+)-tartaric acid (p.a.) (all obtained from Merck, Darmstadt, Germany) and hydrochloric acid (37% p.a.; (Riedel-de Haën, Seelze, Germany) were used in the flow injection system. The hydride products were introduced into the graphite furnace with 99.996% argon (Westfalen AG, Münster, Germany). The analytes—trimethyl-lead chloride (Alfa Products, Karlsruhe, Germany), tetraethyl-lead (AK Chemie, Biebesheim, Germany) and dimethyl-lead chloride (in this laboratory)[9]—were stored at 4 °C. The standard solutions were about 100 mg l^{-1} (as Pb) in twice-distilled (except for tetraethyl-lead dissolved in methanol p.a.; Merck, Darmstadt, Germany) and diluted daily for the examinations. The lead

Table 1 Furnace temperature program

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (ml min^{-1})
Injection enrichment	350	1	20	250
Pretreatment	600	10	20	50
Atomization	1600	0	5	0
Glow-out	2400	1	2	250

standard ($1\,g\,l^{-1}$ as Pb) was also obtained from Merck.

RESULTS AND DISCUSSION

Furnace temperature control and FIAS parameters

The temperature programme for the graphite furnace is given in Table 1. Earlier investigations have shown that these conditions lead to the best signal forms.[6] Also, a modification of the graphite furnace proved to be unnecessary.

The flow rates of reduction and carrier solutions used in the flow injection system were those listed in the manual for FIAS 200[8] and are given in Table 2. The optimization of the FIAS parameters was performed elsewhere[6] and is summarized in Table 2. Only the composition of the carrier solution used for these examinations was changed. A mixture of hydrochloric acid and disodium ethylenediaminetetra-acetate (Na_2EDTA) was optimized as well as possible to reduce the sensitivity for inorganic lead, as shown in Fig. 2. Formation of a Pb–EDTA complex prevents the inorganic lead from reacting with sodium borohydride, so that it was not detected, even at concentrations of $10\,mg\,l^{-1}$. Tartaric acid in combination with Na_2EDTA was of no use, due to its limited solubility in water. Depending on the conditions mentioned above, the calibration with three organolead species (dimethyl-lead, trimethyl-lead and tetraethyl-lead) was recorded in the presence of $10\,mg\,l^{-1}$ Pb^{2+} (Fig. 3). The highest sensitivity was obtained for trimethyl-lead, in agreement with earlier examinations.[6] It should be mentioned that the sensitivity for all analytes considerably decreased on addition of Na_2EDTA (e.g., for trimethyl-lead, by a factor of five). But nevertheless, the complexation of lead(II) (Pb^{2+}) made it possible to detect selectively organolead compounds in the presence of high amounts of lead(II) (Pb^{2+}). In the following the determination of trimethyl-lead as an example is treated statistically to confirm the analytical results using FIAS HG–THGA AAS.

Table 2 FIAS parameters
Argon gas flow: $75\,ml\,min^{-1}$

Solution	Reagent	Concentration (%, w/w)	Flow rate ($ml\,min^{-1}$)
Reduction	$NaBH_4$	0.5	6
Reduction	NaOH	0.05	6
Carrier	HCl	4	11
Carrier	Na_2EDTA	0.7	11

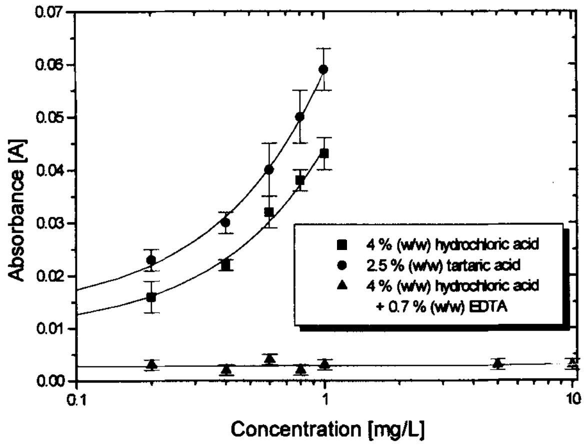

Figure 2 Influence of different carrier solutions on the absorbance of Pb^{2+}.

Fundamental calibration of the analytical method

The necessity of statistical protection is often neglected in analytical chemistry. In this paper the statistical treatment of the method used was carried out according to Doerffel[10] and Funk *et al.*[7]

The first step on the way to quality assurance was the determination of some characteristic data, e.g. the linearity of the calibration function and the analysis of variance. For this purpose a

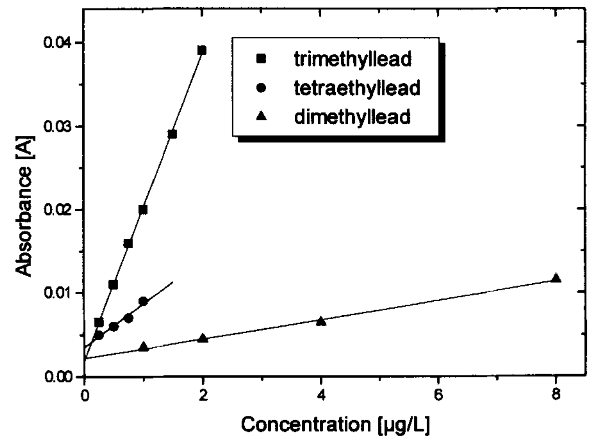

Figure 3 Calibration with various organolead compounds in the presence of $10\,mg\,l^{-1}$ Pb^{2+}.

Table 3 Fundamental calibration and characteristic data

	Linear regression 0.25–5 $\mu g\ l^{-1}$	Quadratic regression 0.25–5 $\mu g\ l^{-1}$	Linear regression 0.25–2 $\mu g\ l^{-1}$	Quadratic regression 0.25–2 $\mu g\ l^{-1}$
Intercept a (A)	2.62×10^{-3}	2.26×10^{-3}	2.34×10^{-3}	2.29×10^{-3}
Slope b A l μg^{-1}	1.836×10^{-2}	1.720×10^{-2}	1.841×10^{-2}	1.729×10^{-2}
Quadratic coefficient c (Al^2 μg^{-2})	—	1.952×10^{-4}	—	4.935×10^{-4}
Coefficient of regression R	0.999	0.999	0.999	0.999
Residual standard deviation s_y (A)	1.08×10^{-3}	1.04×10^{-3}	3.60×10^{-4}	3.60×10^{-4}
Operation standard deviation s_{XO} ($\mu g\ l^{-1}$)	5.89×10^{-2}	5.74×10^{-2}	1.96×10^{-2}	1.97×10^{-2}
Relative operation standard deviation V_{XO} (%)	2.95	2.87	1.96	1.97
Sensitivity E (A l μg^{-1})	1.836×10^{-2}	1.811×10^{-2}	1.841×10^{-2}	1.828×10^{-2}
No. of measurements N	9	9	6	6

calibration with trimethyl-lead chloride in doubly distilled water was recorded in the working range between 0.25 and 5 $\mu g\ l^{-1}$ (as Pb). Nine calibration solutions (0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4 and 5 $\mu g\ l^{-1}$ as Pb) were measured with FIAS HG–THGA AAS and the peak heights were evaluated.

Table 3 summarizes the characteristic data for the calibration. With the use of Mandel's test for goodness of fit, we checked whether a quadratic regression fits significantly better than a linear one. In this case the F-test demonstrated that linear regression was statistically permissible (Table 3), In order to verify the accuracy of the calibration the homogeneity of the variances had to be checked. For this, solutions of the lowest (0.25 $\mu g\ l^{-1}$ as Pb) and the highest concentration (5 $\mu g\ l^{-1}$ as Pb) were measured ten times and the variances s_1^2 and s_9^2 were compared. The F-test resulted in a significant inhomogeneity (Table 4), so that the working range was lowered to between 0.25 and 2 $\mu g\ l^{-1}$ (as Pb) (Fig. 4). As demonstrated in Table 4, a new verification of the homogeneity of the variances removed the inhomogeneity, so that the statistical data for the newly defined working range were calculated (Table 3).

Table 4 Verification of linearity and homogeneity of variances

	Working range 0.25–5 $\mu g\ l^{-1}$	Working range 0.25–2 $\mu g\ l^{-1}$
Difference of variance DS^2 (A^2)	1.68×10^{-6}	1.30×10^{-7}
Check value for Mandel's test	1.43	1.00
$F(f_1 = 1, f_2 = N - 3; P = 99\%)$	13.75	34.12
Variance s_1^2 (A^2)	3.21×10^{-7}	3.21×10^{-7}
Variance s_n^2 (A^2)	5.57×10^{-6}	9.89×10^{-7}
Check value for inhomogeneity of variances	17.34	3.08
$F(f_1 = f_2 = N - 1; P = 99\%)$	5.35	5.35

The next step in the statistical treatment was the verification of the low working range. For analytical determinations, results obtained from the calibration function have to be significantly different from zero. With the use of a mathematical algorithm and the values given in Table 3, the parameter x_P was calculated.[7] The check value x_P was 0.0949 $\mu g\ l^{-1}$ and so smaller than the lowest calibration concentration (0.25 $\mu g\ l^{-1}$). This result assured the statistical protection of the calibration and consequently the ability to analyze in the total working range.

The three important characteristic values to describe the low concentration range are the criterion of detection L_C, the detection limit XN and

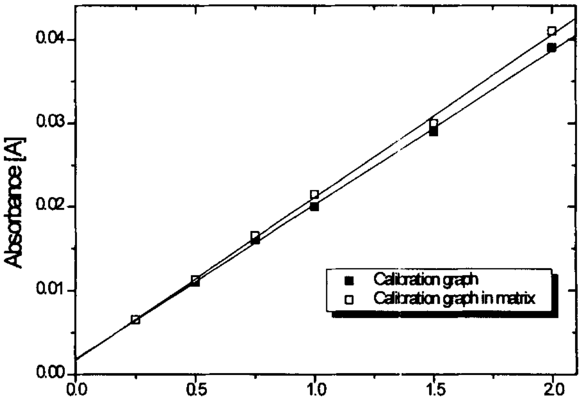

Figure 4 Calibration with trimethyl-lead in doubly distilled water and matrix.

Table 5 Characteristic values for low concentrations. ^{a} VB_{rel} = confidence interval

Criterion of detection L_C	0.0031 A	t_α ($\alpha = 5\%$, $f = 9$, one-sided) = 1.83
Detection limit XN	0.032 $\mu g\, l^{-1}$	t ($f = 8$, P = 95%, one-sided) = 1.86
Limit of determination XB	(a) 0.200 $\mu g\, l^{-1}$	(a) $VB_{rel.} = 10\%$ t ($f = 8$, $P = 95\%$) = 2.306
	(b) 0.040 $\mu g\, l^{-1}$	(b) $VB_{rel.} = 50\%$ t ($f = 8$, $P = 95\%$) = 2.306

the limit of determination XB. These values were calculated as described by Funk *et al.*[7] and are presented in Table 5. The definitions of these parameters can be found elsewhere.[7, 11] It should be mentioned that all these parameters, e.g. the detection limit, could be lowered by increasing the sample volume. Earlier investigations have shown the high efficiency of FIAS HG–THGA AA using a 1.5 ml sample loop.[6]

All values calculated in this paper apply to fundamental calibrations in doubly distilled water. Determination of the influence of the matrix on the characteristic data is described below, to prove the possibility of the method for real water sample analysis.

Influences of matrix

To simulate a real water sample we used a synthetic rainwater sample. The composition according to Harrison[12] was as follows: NO_3^- 156.6 $\mu mol\, l^{-1}$, SO_4^{2-} 30 $\mu mol\, l^{-1}$, Cl^- 90 $\mu mol\, l^{-1}$, NH_4^+ 60 $\mu mol\, l^{-1}$, Na^+ 60 $\mu mol\, l^{-1}$, K^+ 5 $\mu mol\, l^{-1}$, Ca^{2+} 12 $\mu mol\, l^{-1}$, Mg^{2+} 10 $\mu mol\, l^{-1}$, H^+ 31.6 $\mu mol\, l^{-1}$ (pH = 4.5) and Pb^{2+} 48.3 $\mu mol\, l^{-1}$ (10 $mg\, l^{-1}$).

A calibration using the same conditions as above was recorded to discover possible deviation from the fundamental calibration (Fig. 4). For this purpose a recovery function seems to be the easiest way.[7] The values obtained were -0.0728 $\mu g\, l^{-1}$ for the intercept a_f and 0.9579 for the slope b_f. Having no deviation the recovery function would be linear with an intercept $a_f = 0$ and a slope $b_f = 1$. For the assessment of the recovery function both calibrations were compared. The F-test to control the precision showed no significant deviation between the operation standard deviation s_{XO} for the fundamental calibration (Table 3) and the residual standard deviation $s_{yf} = 0.004$ $\mu g\, l^{-1}$ for the recovery function. But the verification for systematic deviation resulted in a proportional systematic error ($0.957 < b_f < 0.9588$). A constant systematic error was not found ($-0.1538 < a_f < 0.0082$). Consequently the effect of the matrix has to be considered. The best possibility of eliminating this influence is use of the standard addition method. This would make the technique suitable for water analysis.

Real sample analysis

Our laboratory has taken part in an interlaboratory study for the quality control of trimethyl-lead species in simulated rainwater and urban dust to evaluate the performance of the technique.[12] One of the rainwater samples contained about 50 $ng\, kg^{-1}$ of trimethyl-lead. With the use of a 1.5 ml sample loop this solution was analyzed. The result obtained was 68.9 ± 7.2 $ng\, kg^{-1}$ ('true' value 64 $ng\, kg^{-1}$, mean value of the participating laboratories[12] 73.1 ± 7.0 $ng\, kg^{-1}$). This indicates the performance and the efficiency of the method developed.

CONCLUSIONS

The combination of FIAS HG and THGA AAS has been used for the determination of organolead compounds. The method makes it possible to detect selectively trimethyl-lead with a detection limit of 0.032 $\mu g\, l^{-1}$ in the presence of 10 $mg\, l^{-1}$ inorganic lead without any separation steps. The determination of trimethyl-lead is treated statistically to prove the suitability of the method for water analysis. It should be mentioned that further investigations are needed to complete the statistical protection, e.g. the verification of the influence of time and the analysis of standard reference materials. Additionally, the method should be prepared for a reliable screening analysis including an increase in sensitive detection for dialkyl- and tetra-alkyl-lead compounds.

Acknowledgements The authors gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft and the Land Nordrhein–Westfalen, and the help of D. Erber.

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