

Flow injection-hydride generation-infrared spectrophotometric determination of Pb

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Abstract

A novel analytical technique has been suggested for determination of Pb using formation of $\text{PbH}_4(\text{g})$ by chemical reduction and its subsequent spectrophotometric measurement in IR region, using the peak at 1821.4 cm^{-1} . The range of measurements is $1.0\text{--}30.0 \text{ mg l}^{-1}$ using a sample of 1.0 ml in flow injection mode. The 3σ limit of detection is 0.28 mg l^{-1} . The method has been applied to standard reference materials of Waste Water, EU-L-1, lead-base bearing metal 53e and Soil/Sediment #4 as well as soil samples collected from heavy traffic areas in Ankara. © 2004 Elsevier B.V. All rights reserved.

Keywords: Pb; Flow injection; Hydride generation; Molecular absorption; Dispersive infrared; FTIR; Soil

1. Introduction

Metallic Pb and its compounds are toxic. Lead poisoning can affect many systems of the body such as hematopoietic, vascular, renal, peptic, cardiovascular, immunological, reproductive, gastrointestinal, endocrine and central nervous systems [1]. The main source of organolead compounds in the environment is their use as antiknocking agents for gasoline. The determination of Pb in environmental samples is important so as to assess the degree of pollution due to the emission of this element by the vehicles.

Hydride generation atomic absorption spectrometry (HGAAS) is a well established technique for the determination of elements which form volatile hydrides [2]. Lead can be determined by hydride generation (HG) but with difficulty because of its low yield and stability. Various oxidizing agents have been tried to increase the efficiency of the reaction such as potassium dichromate, potassium permanganate, ammonium cerium(IV) nitrate, hydrogen peroxide, peroxodisulfate and potassium hexacyanoferrate(III) [2]. The

highest sensitivity was obtained when potassium hexacyanoferrate(III) was used as hydride generating medium [3].

In recent years, gas phase molecular absorption spectrometry applied for the determination of hydride forming elements has appeared in literature. Hydrides of As, Sb, Se and Sn have been detected simultaneously by gas phase UV–vis molecular absorption spectrometry [4,5]. The polar nature of the metal hydrogen bond and the specific molecular symmetry cause some hydrides to be active in IR region. Most recently, Gallignani et al. [6] developed a novel and powerful flow analysis technique using HG and FTIR coupling for the individual and simultaneous determination of Sb, As and Sn via generation of stibine, arsine and stannane, respectively. This hybridized system enhanced the analytical potentialities of FTIR instrumentation. The developed methodology was also applied for determination of Sb in pharmaceuticals [7].

Chemical interferences resulting from co-existing ions are one of the main problems commonly associated with HG techniques. Such interferences are mostly due to transition metals that are usually present in great excess relative to the analyte. In principle, analyte may react with interferent and be converted to a compound which is not reduced to hydride, analyte or hydride may be captured by the product formed

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by the reaction of interferent with tetrahydroborate, formed hydride may be bonded by the dissolved interferent, or the reducing agent may be consumed by the interferent. In order to eliminate such chemical interferences, one of the most widely used methods is binding the interferent in a nonreactive compound by a masking agent [2]. The efficient masking action of oxalate ion on interfering ions such as Cu(II), Fe(III) and Ni(II) by forming complexes is known [8]. Another way to minimize interferences is solvent extraction which is used for the separation of analyte from the sample matrix. One of the most well known methods for separative concentration of Pb is dithizone extraction [9]. This method has the advantages of good selectivity at appropriate pH and high recovery. In addition, flow injection analysis provides the advantages of reduced interferences as well as less memory effects, low reagent consumption and high sample throughput.

In this study, a hydride generation gas phase molecular absorption spectrophotometric method was developed for the determination of Pb. To the best of our knowledge, this is the first report on the IR spectrometric detection of lead hydride for qualitative and quantitative purposes. FI mode was successfully adapted to the proposed method. After optimizations, the method was tested by the determination of Pb in three SRMs involving waste water, soil/sediment and alloy and applied to the analysis of real soil samples.

2. Experimental

2.1. Instrumentation and apparatus

A Mattson 1000 FTIR instrument was employed to obtain the IR spectrum of generated hydride at a resolution of 2 cm^{-1} in the region of $1700\text{--}1900\text{ cm}^{-1}$. Flow injection experiments were conducted by using a Shimadzu IR-470 dispersive infrared spectrophotometer; this instrument was operated in time scan mode at a fixed wavenumber. A Mile-

stone Ethos Plus microwave sample preparation system with TFM[®] vessels was used to dissolve lead-base bearing metal SRM. A 3 ml inner volume gas–liquid separator with a forced outlet was employed. The detailed description of gas–liquid separator can be found elsewhere [10]. The schematic diagram of the set-up is given in Fig. 1.

2.2. Reagents

All reagents were analytical grade. Deionized water ($18\text{ M}\Omega\text{ cm}$) was obtained from Milli-Q water purification system. A 1000 mg l^{-1} Pb stock solution (Aldrich) was used to prepare working solutions. Dilutions of Pb working solutions were done with 0.5% (m/v) potassium hexacyanoferrate(III) (Merck) in 0.12 mol/l HCl (Merck) unless stated otherwise. A solution containing 0.01% (m/v) dithizone (Merck) was prepared daily in chloroform. Sodium tetrahydroborate (Merck) solution, 1 or 3% (m/v), was in 0.2% (m/v) NaOH. A 35% (m/v) sodium dihydrogen citrate (Riedel de Haen), 34% (m/v) hydroxylamine hydrochloride (Carlo Erba) and 10% (m/v) potassium cyanide (Merck) were used for liquid phase extraction. The pH of the solutions was adjusted to 8.5–9.0 with concentrated ammonia (Merck) by using few drops of thymol blue indicator. A solution containing 0.12 mol/l HCl was prepared for the back extraction of Pb. An amount of 1% (m/v) oxalic acid (AnalaR) was employed for interference reduction. Pure Ar was used as carrier gas in flow systems.

2.3. Procedure

Lead contents in Soil/Sediment #4 (Ultra Scientific), lead-base bearing metal 53e (NBS) and Waste Water, Low Level Concentrate, EU-L-1 (SCP Science) standard reference materials were determined in order to validate the method. The method was also applied for the analysis of soil samples collected from high traffic areas.

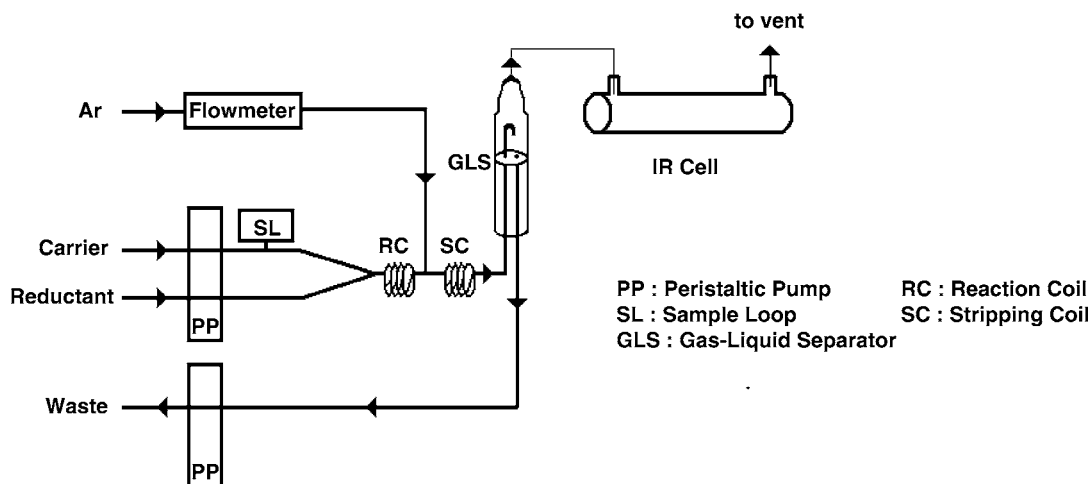


Fig. 1. Experimental set-up.

A 25.0 ml aliquot from waste water standard reference material was evaporated to dryness to remove HNO_3 and the residue was dissolved in 25.0 ml 0.12 M HCl. A 2.0 ml portion of the resultant solution was diluted to 10.0 ml; the final solution contained 1% (m/v) oxalic acid, 3% (m/v) potassium hexacyanoferrate(III) and 0.12 mol/l HCl. A solution containing 3% (m/v) sodium tetrahydroborate was used as reductant for the analysis of waste water. Standard addition method was applied for analysis.

For the analysis of lead-base bearing metal 53e (NBS), 8.0 ml of concentrated HCl was added on 0.050 g sample and the following microwave digestion program was applied. The temperature was brought to and kept at 120, 170 and 180 °C for 10, 10 and 30 min, respectively; maximum power applied was 1000 W throughout these periods. The final solution was analyzed after appropriate dilutions with 0.12 mol/l HCl. Direct calibration method was used.

For soil/sediment SRM analysis, Pb in 1.0 g of sample was extracted with a 10.0 ml mixture of concentrated HNO_3 and concentrated HCl (1:1) on hot plate at moderate temperature for 30 min. The leachate was filtered and diluted to 25.0 ml with deionized water. In the analysis of collected soil samples, the extraction procedure was modified as 10.0 g sample, 50 ml of HNO_3 –HCl mixture and a final volume of 100 ml. The following dithizone extraction was applied to the filtrates to eliminate the severe interferences due to high transition metal content of both soil/sediment SRM and collected soil samples.

Dithizone extraction procedure was modified by Jin and Taga [9]. An amount of 20.0 ml of solution were transferred to a separatory funnel onto which 10.0 ml of ammonium citrate and 2.0 ml of hydroxylamine hydrochloride were introduced followed by a few drops of thymol blue indicator. Then the pH was adjusted to 8.5–9.0 by successive additions of aqueous ammonia until the color of solution just became green. An amount of 2.0 ml of potassium cyanide and 10.0 ml of dithizone were added. The mixture was shaken for 20 min with a shaker. After separating the organic phase, the extracted Pb was back-extracted to aqueous phase with 20.0 ml of 0.12 mol/l HCl by shaking again for 20 min.

Wavelength scanning was done employing FTIR instrument in continuous flow hydride generation mode. After determining the absorption band of PbH_4 , the experiments were carried out in flow injection mode using the dispersive IR spectrophotometer. Carrier and reductant solutions were fed continuously with a peristaltic pump. An amount of 1.0 ml sample/standard solution was injected to the carrier stream with a six port injection valve (Supelco). Generated hydride was separated from the aqueous phase in gas–liquid separator and was swept to the measurement cell by Ar as carrier gas. The longest pathlength for IR cell physically tolerable by the instrument's sample compartment was constructed from glass with circular CaF_2 windows. All the transfer tubings and coils were made up of 0.8 mm i.d. polytetrafluoroethylene tubings. Measurements were done in triplicates. Peak height absorbance values were measured. Operating condi-

Table 1

The operating conditions of instruments and optimum HG parameters

	Value
Dispersive IR spectrophotometer	
Wavenumber (cm^{-1})	1821.4
Resolution (cm^{-1})	8
IR cell dimension, length \times diameter (cm)	16×1.7
IR cell window material	CaF_2
Thickness of CaF_2 window (mm)	4
FTIR	
Resolution (cm^{-1})	2
Spectral range (cm^{-1})	1100–4000
Number of scans	10
Optimized HG conditions	
%($\text{K}_3\text{Fe}(\text{CN})_6$) (w/v)	0.5
% NaBH_4 (w/v)	1.0
Carrier ($\text{K}_3\text{Fe}(\text{CN})_6$) flow rate (ml min^{-1})	3.0
Reductant (NaBH_4) flow rate (ml min^{-1})	3.0
Argon flow rate (ml min^{-1})	75
Reaction coil (cm)	35
Stripping coil (cm)	30
Distance between GLS-IR cell (cm)	15
Sample loop (ml)	1.0

tions of the instruments and optimized HG parameters are given in Table 1.

3. Results and discussion

3.1. Optimization of hydride generation conditions

The optimized hydride generation conditions are given in Table 1. Since the generation of lead hydride is difficult, use of potassium dichromate, nitroso R-salt, ammonium cerium(IV) nitrate and hydrogen peroxide were tried. Highest sensitivity was obtained when potassium hexacyanoferrate(III) was used in the hydride-generating medium. The analytical signal did not improve significantly when the concentration of potassium hexacyanoferrate(III) was increased above 0.5% (m/v). The reductant concentration was optimized to be 1.0% (m/v). Ar flow rate did not affect the response considerably provided that it was in between 50 and 150 ml min^{-1} . Further increments of the flow caused dilution effect. Thus flow rate of the carrier was selected as 75 ml min^{-1} for the transportation of generated hydride to the measurement cell. The signal could be increased by using higher flow rates of carrier and reductant streams. However, this was avoided since higher flow rates flooded the gas–liquid separator because of its 3.0 ml inner volume. On the other hand use of small inner volume was favorable since then less water vapor reaches the measurement cell; high humidity resulted in elevated background absorption. The highest sensitivity was obtained when the reaction and stripping coil lengths were 35 and 30 cm, respectively. The distance between GLS and cell was kept at minimum in order to avoid transport losses. No precipitation of PbCl_2 was observed.

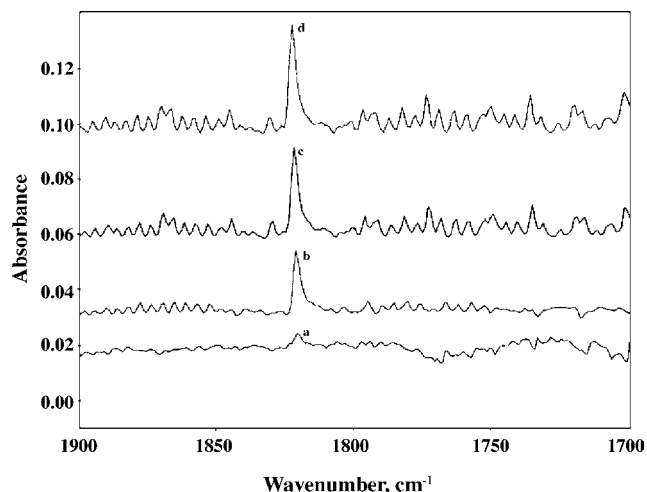


Fig. 2. FTIR spectra of PbH_4 in continuous flow HG: (a) 1.0 mg l^{-1} , (b) 10.0 mg l^{-1} , (c) 30.0 mg l^{-1} , (d) 50.0 mg l^{-1} Pb.

3.2. FTIR measurements

All FTIR spectra were obtained in continuous flow (CF) mode. The disadvantage of CF mode is precipitation of metallic Pb which then sticks on the walls of both GLS and transfer tubings. Since relatively high amounts of analyte were introduced, metallic Pb accumulated in transport zone caused a significant decrease in sensitivity unless GLS was frequently washed with dilute HNO_3 . FTIR spectra of plumbane for varying concentrations are shown in Fig. 2. Absorption at 1821.4 cm^{-1} was determined as the analytical band for PbH_4 ; this value is in agreement with the wavenumber values reported [11]. No other absorption band was observed in the spectral range scanned.

3.3. Dispersive IR spectrophotometric measurements

After determining the absorption band to be used for quantitation, the measurements were conducted using double beam dispersive IR spectrophotometer. The instrument was operated in time scan mode at 1821.4 cm^{-1} . Among the preset slitwidths of the instrument, the choice was made in order to have the optimum S/N. When the slit was adjusted to its narrowest value (1), the signal was not distinguishable because of extremely high noise level. Slit 4, corresponding to a bandwidth of 8 cm^{-1} , provided the best S/N so it was selected for further measurements. At narrower slitwidths, the

noise level was excessively high since the total energy reaching to detector decreased. When the slitwidth was adjusted to its widest value, the spectral bandwidth was significantly larger than that of absorption band, resulting in a decrease in the absorbance.

The experiments were done in flow injection mode to prevent the loss of sensitivity due to precipitates in the GLS and transfer tubings. Less amount of Pb was introduced as this is one of the main advantages of FI. In fact, the precipitate formation was lessened significantly and washing frequency of GLS was reduced. The effect of injection volume is depicted in Fig. 3. The signal increased up to 1.0 ml injection volume reaching a plateau for higher volumes. The inner volume of measurement cell was 36 ml and the hydrides spent 29 s in measurement cell, neglecting the volume of H_2 generated in the reaction of decomposition of reductant.

3.4. Analytical figures of merit

The calibration plot obtained using 1.0 ml injection volume and aqueous standards is linear between 1.0 and 30.0 mg l^{-1} with a best line equation of $y = 0.000733 (\pm 0.000019)x + 0.001049 (\pm 0.000257)$ and correlation coefficient of 0.9986 . The reproducibility is better than 2% RSD for aqueous standard solutions in the dynamic range. The repeatability of the measurements was also better than 2% . Reproducibility is the closeness of agreement between independent results obtained with the same method on identical test material but under different conditions. Repeatability, on the other hand, is the closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions [12]. The 3σ limit of detection is 0.28 mg l^{-1} ($n = 10$). The sampling frequency is 60 h^{-1} .

In an effort to enhance the detection power, an attempt was made to concentrate lead hydride in cryogenic trap. However, the trapped species could not be revolatilized, probably due to the unstable nature of lead hydride; formation of a black precipitate was observed in cold trap indicating the presence of metallic Pb. It has been reported that PbH_4 is thermodynamically unstable and loses one molecule of H_2 [11]; in the same study, however, it is also suggested that the rate of decomposition is sufficiently slow so that PbH_4 can be observed in gas phase.

The accuracy of the method was checked by analyzing standard reference materials. The results given in Table 2

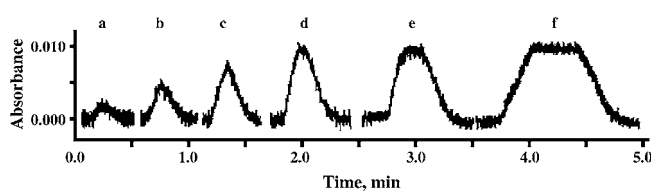


Fig. 3. The effect of injection volume in FI mode, 10.0 mg l^{-1} Pb: (a) 0.10 ml , (b) 0.50 ml , (c) 0.70 ml , (d) 1.0 ml , (e) 2.0 ml , (f) 3.0 ml .

Table 2

The results of standard reference values and the certified values

Standard reference material	Certified	Confidence interval	Found
Waste Water, EU-L-1 (mg l^{-1})	10	9.8–10.2	10.1 ± 0.5
Soil/Sediment #4 (mg kg^{-1})	95.3	90.0–101	96 ± 2
Lead-base bearing metal 53e (g g^{-1})	0.84	–	0.82 ± 0.02

Table 3

Determination of Pb in soil samples ($n=3$)

Soil	Pb (mg kg^{-1})
1	36.3 ± 2.0
2	21.1 ± 2.0
3	9.4 ± 1.0
4	41.8 ± 2.0
5	9.4 ± 1.0
6	17.7 ± 1.0
7	10.1 ± 0.2
8	19.8 ± 0.3
9	14.3 ± 0.2
10	9.4 ± 1.0
11	34.3 ± 1.0

were found to be in good agreement with the certified ones. Direct calibration method was used for the analysis of Soil/Sediment #4, lead-base bearing metal SRMs and soil samples. However, in the analysis of waste water SRM samples, the method of standard additions was employed. In addition, 3% potassium hexacyanoferrate(III) was used due to severe interference effect of the content of matrix. In such a medium, the decomposition of potassium hexacyanoferrate(III) was visually observed. The adverse effect of presence of excessive transition metals was prevented by addition of 1% (m/m) oxalic acid as a masking agent to the medium.

Uses of L-cystine, potassium iodide-ascorbic acid, thiourea, tartaric acid-potassium dichromate were unsuccessful when added as potential masking agents to potassium hexacyanoferrate(III) solutions. These reagents decomposed potassium hexacyanoferrate(III) and/or formed a precipitate.

As an application, the developed methodology was used for the determination of Pb in highly contaminated soil samples collected from road side. The results are given in Table 3.

4. Conclusions

The IR spectrometric quantitative determination of Pb was performed for the first time, by using absorption by PbH_4 molecule formed by chemical reduction. Since quantitative IR measurements rely on detection of absorbance at a single wavenumber, spectral advantages of using a dispersive

IR instrument should be obvious. Therefore, FTIR was not preferred in this study as the unnecessarily scanned portion of spectrum will not bring any advantage from S/N point of view. The method was validated using three different SRM samples that have different matrices showing that it can be applied to environmental and metallurgical samples. The developed method has also been applied to soil samples taken from high traffic locations in Ankara where the use of leaded gasoline is still permitted. Relatively high Pb concentration values in soil samples allowed the use of IR technique.

Regarding the concentration range applicable, the method proposed in this work is about four orders of magnitude less sensitive than HGAAS, when the performance obtained in our laboratories is taken as a reference [13]. However, flame AAS for Pb has a useful range of concentration that is very similar to the novel IR method. Therefore, the laboratories equipped with an IR instrument, but lacking an AA spectrometer can employ this method as a substitute for flame AAS for elemental determination of lead.

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