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Flow injection atomic absorption spectrometery for the standardization of arsenic, lead and mercury in environmental and biological standard reference materials

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Abstract Results of a thorough study and application of flow injection atomic absorption spectrometry for the determination of As, Pb and Hg in parts per million to subparts per billion levels in environmental and biological samples have been described. Various standard reference materials from the National Bureau of Standards, USA, the National Institute of Standards and Technology, USA, the Community Bureau of Reference, Brussels, Belgium and the National Institute for Environmental Studies, Japan and Standard Chinese river sediment were used. By flow injection hydride generation AAS the standard reference materials were analyzed for As and Pb. Mercury was determined by cold vapour flow injection AAS from environmental and biological standard reference materials. The technique is fast, simple and highly sensitive. It takes only 30 s for each analysis from the digested solution. The detection limits of As, Pb and Hg are 1.8 μg L^{-1} and 2.0 μg L^{-1} and 1.5 μg L^{-1}, respectively. The results show good agreement with the certified values.

Introduction

Flame atomic absorption spectrometry is a very simple and reliable technique with high accuracy and precision, its sensitivity for the determination of arsenic, lead and mercury is very poor [1]. Therefore other analytical techniques have been used for very low concentrations as GF-AAS, ICP-AES, XRF, NAA, AFS [2–11] etc. Among them GF-AAS has been widely used for the determination of Pb and As in biological and environmental samples [12–16]. A matrix modifier is essential in this technique [14, 17–19]. However some experts are of the opinion that due to large matrix interferences the GF-AAS technique is not too selective and is time consuming [20]. Hydride generation atomic absorption spectrometry has appeared as an alternative method for the determination of hydride forming elements as As, Pb, Sb, Bi, Se etc. [21–24]. This method was first proposed by Holak [25] in 1969 for the determination of As, Bi, Ge, Sb, Se, Sn, Te, Pb. But it has been less investigated for those elements where hydrides are difficult to generate and are unstable, e.g. Pb. The hydride generation technique is not so selective because of the interference by metals and slow reaction kinetics and it is time consuming [26, 27]. To improve the selectivity and sensitivity flow injection coupled with hydride generation AAS has been introduced [28]. The FI-HG-AAS methods are characterized by high efficiency, low sample volume and reagent consumption and improved tolerance of interference [20, 29, 30]. In case of mercury, instead of hydride formation volatile Hg is formed and this technique is called cold vapour flow injection AAS. In this paper the results of a thorough study and application of FI-AAS for the determination of As, Pb and Hg levels in environmental and biological samples are described.

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Experimental

Apparatus

The analytical system was assembled from commercially available instruments and accessories in our laboratory. A Perkin Elmer model 3100 atomic absorption spectrometer (USA) was interfaced with a Hewlett-Packard Vectra 386/25 N computer with GEM software (Perkin Elmer) and a printer Wipro EX-1000 (India). The peristaltic pump VGA-76 was from Varian (Australia). Details of the instrumentation have been discussed in our earlier publication [31].

Reagents

All reagents used were of analytical reagent grade. Distilled deionized water was used throughout.

Reducing solutions. For arsenic, sodium tetrahydroborate with concentrations 0.25%, 0.50%, 0.75%, 1.0%, 1.25% and 1.50% (w/v) was prepared by dissolving the compound (Merck, Germany) in 0.5% (w/v) NaOH (BDH, India). For lead, 2%, 4%, 6%, 8%, 10% and 12% (w/v) $NaBH_4$ (Merck, Germany) solutions were prepared in 1% (w/v) NaOH solution. For the reduction of mercury in alkaline medium, 0.1%, 0.2%, 0.4%, 0.5%, 0.6% and 0.8% (w/v) stannous

chloride solutions were prepared by dissolving the compound (E. Merck, India) and 0.035% (w/v) L-cystein (Renal, Hungary) in 100 mL of sulfuric acid-sodium chloride solution. Sulfuric acid-sodium chloride solution was prepared from 0.2 g of sodium chloride (Qualigen, India) and 1.5 mL of conc. sulfuric acid (BDH, India) in 100 mL water. For acid reduction, 1%, 2%, 3%, 4%, 5%, 6% and 8% (w/v) $SnCl_2$ solutions were prepared by dissolving stannous chloride in 10 mL conc. HCl (BDH, India) and diluted to 100 mL with water.

Carrier solutions. For arsenic, HCl (Merck, India) solutions of 2, 3, 4, 5, 6 and 8 mol/L were prepared by proper dilution. For lead determination, 4%, 6%, 8%, 9%, 10% and 12% (w/v) of ammonium persulfate solutions were prepared by dissolving ammonium persulfate (E. Merck, India) in 2%, 4%, 5%, 6%, 8% and 10% (v/v) nitric acid solution.

For mercury in alkali reduction sodium hydroxide (BDH, India) was prepared by dissolving 1%, 2%, 3%, 4%, 5% and 6% (w/v) NaOH in water and for acid reduction 0.5%, 0.75%, 1.0%, 1.25%, 1.5%, and 2.0% (v/v) nitric acid was prepared.

Standard solution of arsenic (1000 mg L^{-1}) was prepared by dissolving 1.320 g As_2O_3 (Merck, Germany) in about 10 mL water containing 4 g NaOH and diluted to 1000 mL with water.

Standard lead and mercury solutions (1000 mg L^{-1}) were prepared from standard lead and mercury Titrisol (Merck, Germany), respectively.

The Standard reference materials used for the analyses were: River sediment SRM 1645, Urban particulate matter SRM 1648, and Citrus leaves SRM 1572 of the National Bureau of Standards, Washington, D.C.; Oyster tissue SPM 1566(a) of the National Institute of Standards and Technology, Gaithersburg, USA; Sewage sludge of industrial origin CRM 146, Coal CRM 040, Fly ash from pulverized coal CRM 038, Mussel tissue CRM 278 and Lagarosiphon major (aquatic plant) CRM 060 of the Community Bureau of Reference, Brussels, Belgium; Pond sediment NIES 2 and Vehicles exhaust particulate NIES 8 of the National Institute for Environmental Studies, Japan, and Standard Chinese river sediment 81–101.

Digestion of the standard reference materials for arsenic, lead and mercury

The method of digestion (HNO_3– H_2O_2) for the reference materials has been described in earlier publications [2, 9, 32].

Digestion of standard reference materials by HNO_3– H_2SO_4 for arsenic only

Another simple method for the digestion of standard reference materials for arsenic is as follows: 0.1–0.2 g of standard sample was taken in a 50 mL conical flask; then 4 ml 1:1 HNO_3 and 1 mL conc. H_2SO_4 were added. The whole was placed on a sand bath with a small funnel on the mouth of the conical flask. Heating was continued until fumes of SO_3 evolved. Then, heating was discontinued and after cooling 2–3 mL of water were added, the solution filtered through a Millipore filter and finally made up to 10 mL. Blanks were prepared under the same conditions.

Procedure

The sample was injected into a carrier solution by means of a six-port sample injection valve fitted with a 50 µL sample loop for Pb and As and 100 µL sample loop for Hg. The injected solution along with the carrier solution was subsequently mixed with a continuous stream of reducing solution. Lead and arsenic formed lead hydride and arsine, respectively, which subsequently entered into the gas-liquid separator. The procedure for As was discussed earlier [31]. Cooling is necessary to increase the stability of the hydride, especially for lead. But for mercury cooling was not required. Inside the gas-liquid separator a continuous flow of N_2 carrier gas was introduced for mixing and carrying the hydrides or volatile mercury to the quartz tube. For Pb and As, an air acetylene flame is required for the AA measurement. The peak height signals were measured. The concentrations of Pb, As and Hg were measured against a standard curve.

Results and discussions

Table 1 gives the optimum parameters for the Pb and As determination as hydride and volatile Hg^0 generation in the flow injection system.

Table 1 Optimum parameters for lead, arsenic and mercury determination by the FI-system

Pb		As		Hg	
Lamp current	10.0 mA	Lamp current	20.0 mA	Lamp current	6 mA
Wave length	283.3 nm	Wave length	193.7 nm	Wave length	253.7 nm
Ammonium persulfate flow rate	1 mL min^{-1}	HCl solution flow rate	1 mL min^{-1}	NaOH/HNO_3 flow rate	1 mL min^{-1}
Ammonium persulfate concentration	9% (w/v) in 6% (v/v) HNO_3	HCl solution concentration	5 mol L^{-1}	NaOH concentration	4% (w/v)
$NaBH_4$ flow rate	1 mL min^{-1}	$NaBH_4$ flow rate	1 mL min^{-1}	HNO_3 concentration	1.5% (v/v)
$NaBH_4$ concentration	8% (w/v) in 1% NaOH soln.	$NaBH_4$ concentration	1% (w/v) in 0.5% (w/v) NaOH soln.	$SnCl_2$ solution flow rate	1 mL min^{-1}
				$SnCl_2$ concentration for acid reduction	5% (w/v) in 10% (w/v) HCl
Carrier gas	nitrogen	Carrier gas	nitrogen		
Carrier gas flow rate	100 mL min^{-1}	Carrier gas flow rate	200 mL min^{-1}	$SnCl_2$ concentration for alkali reduction	0.5% (w/v) $SnCl_2$+ 0.035% (w/v) L-cystein in 1.5% (v/v) H_2SO_4 solution
Flame	air-acetylene	Flame	air-acetylene		
				Carrier gas	nitrogen
				Carrier gas flow rate	50 mL min^{-1}

Optimization of the parameters for lead hydride generation

The effect of sodium tetrahydroborate on the efficiency of hydride generation is more marked for lead than for other elements such as arsenic or selenium [20]. The concentration range 2–12% (w/v) $NaBH_4$ was chosen for the study. The absorbance increased rapidly upto 7% (w/v) $NaBH_4$; higher concentrations of $NaBH_4$ only slightly affect the efficiency of lead hydride generation. To minimize the cost of analysis, 8% was taken as optimum $NaBH_4$ concentration.

The optimum persulfate concentration was 9% (w/v). The absorbance increased upto 8% (w/v) of persulfate in a particular HNO_3 concentration, then the change of absorbance was not significant.

The nitric acid concentration plays an important role in lead hydride generation. With an increase of HNO_3 concentration the absorbance increased and above 6% (v/v) the change of absorbance was not so significant. The carrier gas flow rate was optimized at 100 mL min^{-1}.

Optimization of parameters for the arsenic determination

Low acid concentrations showed lower sensitivity probably due to an incomplete reaction. The optimum HCl concentration was 5 mol/L HCl. A further increase of HCl concentration caused a small increase in sensitivity and worse precision occurred.

1% (w/v) $NaBH_4$ produced the maximum sensitivity using 5 mol/L HCl. For higher concentrations of $NaBH_4$ the sensitivity decreased. The optimum concentration was 1% (w/v).

A gas flow rate of 150 to 225 mL min^{-1} produced the most sensitive measurement. The optimum flow rate was selected at 200 mL min^{-1}.

Optimization of parameters for the Hg determination

In alkaline medium. The sensitivity is very much influenced by the NaOH concentration. The absorbance increased sharply from 1% to 3% (w/v) NaOH. Then its effect was insignificant. The optimum NaOH concentration was fixed to 4% (w/v).

The influence of $SnCl_2$ within the range 0.1% to 0.6% was studied in presence of 4% NaOH. At 0.5% (w/v) $SnCl_2$ concentration the signal was maximum and almost stable above 0.5% (w/v).

In acid medium. HNO_3 influenced the sensitivity of mercury. At high concentrations sensitivity decreased. The optimum acid concentration was selected at 1.5% (v/v).

The optimum concentration of $SnCl_2$ was 5% (w/v).

The effect of the N_2 flow was studied in both media. The sensitivity decreased with increasing flow rate. At lower flow rates the sensitivity was high, but the noise was maximum. So the optimum flow rate was selected at 50 mL min^{-1}.

The physical experimental parameters (reagent flow rate, length of reaction coil) did not significantly influence the overall improvement of the sensitivity.

Interferences

A number of transition metals can interfere with the determination of Pb and As during hydride generation [20, 24]. A detailed study was carried out by several investigators [20, 33]. The flow injection system showed a better tolerance towards hydride forming elements than the batch system [20]. This might be due to shorter reaction time and smaller sample volume. In such a short reaction period most of the interfering transition metal ions could not be reduced to metal, which could then not absorb or decompose the hydride [34]. In acid medium Hg determination, Ag, Cu, Pt, Se, Sb interfere and low values have been reported [35, 36]. Hydrogen chloride and nitrogen dioxides also interfere [37, 38].

Analytical performance. The analytical characteristics for the determination of Pb, As and Hg under the optimum conditions are listed in Table 2. The detection limits for Pb, As and Hg were 2 μg L^{-1}, 1.8 μg L^{-1} and 1.5 μg L^{-1}, respectively. The sampling frequency was 80 samples per hour in each case.

Determination of Pb, As and Hg in environmental and biological standard reference materials

The digested environmental and biological standard reference materials were analyzed using the FI-HG-AAS technique. River sediment, sewage sludge, urban particulate, pond sediment and vehicles exhaust particulate were

Table 2 Analytical performance of lead, arsenic and mercury determination by the FI-system

Parameters	Pb	As	Hg	
			Alkaline reduction	Acid reduction
Charateristic mass (ng/0.0044 U.A.)	0.25	0.22	0.19	0.17
Detection limit (10)	2.0 μg L^{-1}	1.8 μg L^{-1}	1.5 μg L^{-1}	2.4 μg L^{-1}
Quantification limit (10)	7.0 μg L^{-1}	6.0 μg L^{-1}	5.0 μg L^{-1}	8.0 μg L^{-1}
RSD (%)[a]	4.0%	3.0%	2.0%	2.5%
Sample frequency	80 per hr.	80 per hr.	80 per hr.	80 per hr.

[a] Relative standard deviation for 10 replicated determinations

Table 3 Analysis of standard reference materials (SRM) for lead, arsenic and merucry by FI-HG-AAS (μg g^{-1})

Samples	Concentration of Lead		Concentration of Arsenic			Concentration of Mercury		
	Certified value	FI-HG-AAS value	Certified value	FI-HG-AAS value		Certified value	FI-AAS value	
				PTFE vessel digestion (HNO_3-H_2O_2)	Sand-bath digestion (NNO_3-H_2SO_4)		Alkaline reduction	Acid reduction
SRM-1645 (River Sediment)	714 ± 25	694.71 ± 13.0				1.10 ± 0.5	1.126 ± 0.07	0.838 ± 0.15
CRM 146 (Sewage sludge of industrial origin)	1270 ± 28	1235.79 ± 25.0				9.49 ± 0.76	9.028 ± 0.30	7.420 ± 0.45
SRM-1648 (Urban particulate matter)	0.655 ± 0.008[a]	0.629 ± 0.006[a]	115.0 ± 10.0	109.93 ± 3.0	108.53 ± 2.5			
NIES-2 (Pond sediment)	105 ± 6.00	99.89 ± 7.00	12.0 ± 2.0	9.85 ± 0.5	14.59 ± 0.8	1.3[b]	1.311 ± 0.06	1.184 ± 0.09
NIES-8 (Vehicles exhaust particulate)	219 ± 9.00	217.70 ± 5.00						
Chinese river sediment 81-101 (of 1981)			56.0 ± 10.0	53.79 ± 2.0	50.09 ± 2.0			
CRM 038 (Fly ash from pulverized coal)			48.0 ± 2.3	48.29 ± 1.5	47.95 ± 1.0	2.10 ± 0.15	1.923 ± 0.08	1.695 ± 0.09
CRM 040 (coal)			13.2 ± 1.1	12.64 ± 0.5	13.59 ± 0.6	0.35 ± 0.06	0.378 ± 0.03	0.290 ± 0.04
SRM 1566 (a) (Oyster tissue)			14.0 ± 1.2	13.6 ± 0.5				
SRM 1572 (Citrus leaves)			3.1 ± 0.3	4.05 ± 0.5				
CRM 060 (Lagaro-siphon major, aquatic plant)						0.34 ± 0.04	0.350 ± 0.04	
CRM 278 (Mussel tissue)						0.188 ± 0.007	0.206 ± 0.01	

[a] Result in %, [b] Not certified

analyzed for Pb. The results are given in Table 3. The lead concentration in the standard samples was also analyzed by flame AAS and ICP-AES [2]. These were in good agreement with the certified values. For the determination of arsenic in standard reference materials two different digestion procedures were followed and the FI-HG-AAS system was used. The results are also given in Table 3. The oyster tissue was digested in a microwave oven by $HNO_3/H_2O_2/H_2SO_4$ [32] only and measured by the FI-HG-AAS system. The results obtained by these digestion procedures are well comparable with the certified values. For high arsenic contents, the spectrophotometric method [31] was used to compare the results with FI-HG-AAS.

For mercury, the digestion procedure is very important. Depending on the power of the oxidizing agents and the temperature, a considerable amount of mercury may be lost. Wet digestion in open vessels even at low temperature may cause losses of mercury. The loss during digestion can be reduced using closed PTFE vessels under pressure [39–42]. Closed vessels have several advantages over open vessels: no acid is lost during the digestion, so that the loss is reduced and the blank can be minimized; air borne contamination is eliminated and the power of oxidizing agent is considerably enhanced at elevated temperature. After digestion in closed PTFE vessels, the standard samples were analyzed by the FI-system in alkaline and acid medium. In alkaline medium the stannous chloride reduces mercury to Hg^0. The results are also given in Table 3. They agreed quite well with the certified values. The reason may be the low partition coefficient (0.4–0.7) of Hg between the gas phase and the aqueous solution of hydrochloric acid and nitric acid at room temperature upto 1 mol/L [35, 43]; it decreases with increasing acid concentration [44]. In alkaline solution the coefficient is somewhat higher than in acid ones [45]. Another important use of NaOH in the determination of Hg is to contribute to the volatilization of Hg by the heat of neutralization generated [46, 47]. Low recovery in acid medium has been obtained due to interferences by As, Cu, Pt, Se, Sb [35, 36], hydrogen chloride and nitrogen dioxides [37, 38]. Cystein was used in alkaline medium to minimize the loss of mercury during the reduction process [48]. In acid medium cystein suppresses the signal of mercury.

Conclusion

The mineralization procedures are well suitable for the recovery of Pb, As and Hg from any environmental and biological sample. For arsenic, the sand bath HNO_3/H_2SO_4 digestion procedure is very simple and for routine analysis, where a PTFE vessel and a microwave oven are not available, large numbers of samples can be digested at a time by this technique. For mercury, closed PTFE vessel digestion is recommended for routine analysis. Further, the described flow-injection hydride technique is very simple and fast with high precision and sensitivity. The proposed technique can thus be well used for the routine analysis of Pb, As and Hg in soils, sediments, water and different biological samples.

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