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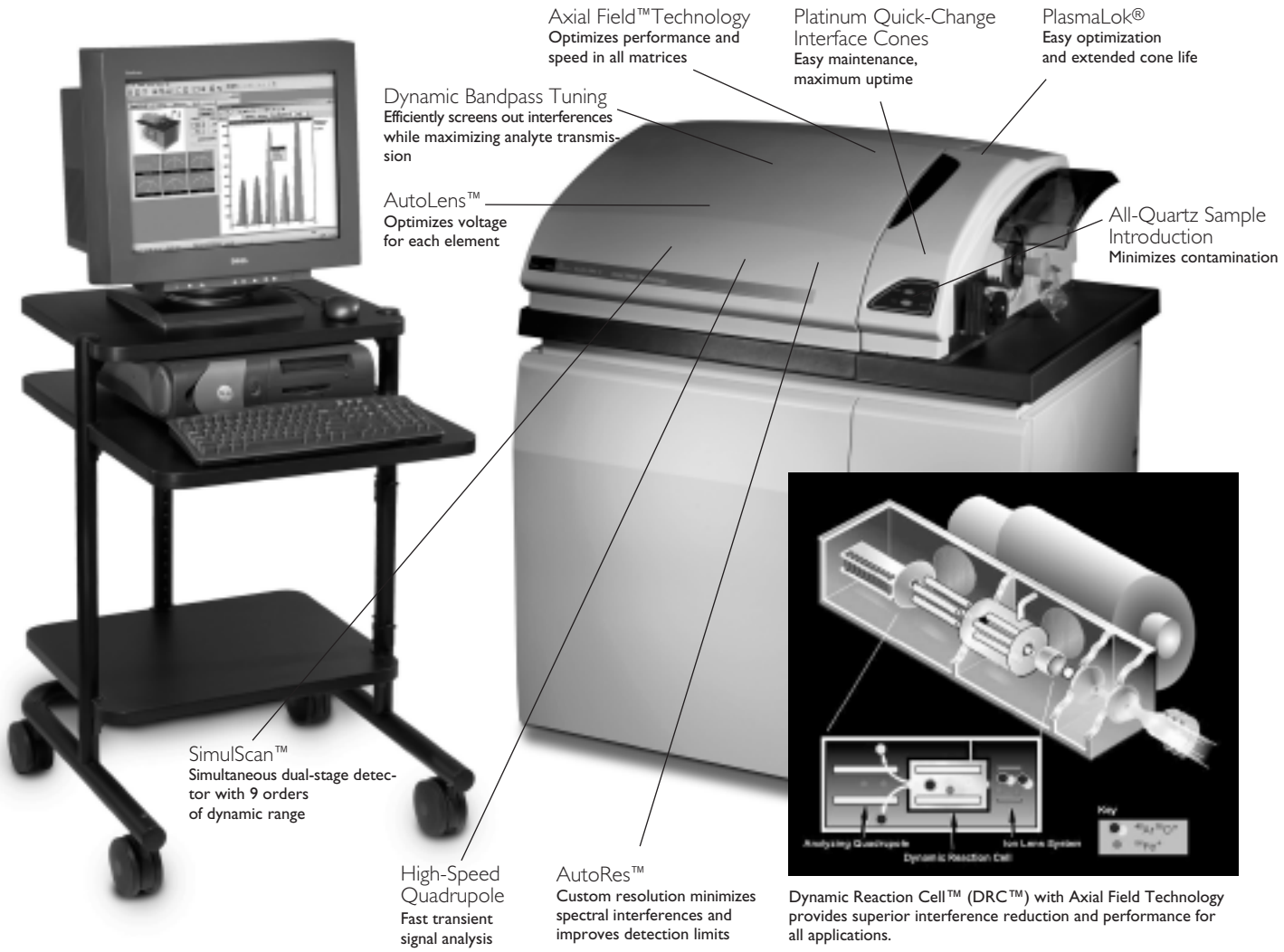

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Improved Chromium Determination in Various Food Matrices Using Dynamic Reaction Cell ICP-MS

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ABSTRACT

The application of a dynamic reaction cell inductively coupled plasma mass spectrometer (DRC ICP-MS) for interference-free Cr determination was validated for different foods. The working conditions were optimized and the method as such validated using certified reference materials and internal food samples. For the latter, reference data obtained from graphite furnace atomic absorption spectrometry (GFAAS) were used for comparison. Samples were prepared using microwave-assisted acid hydrolysis and high-pressure ashing. Both methods yielded residual carbon that leads to an over-estimation of Cr concentrations when using the ICP-MS in standard mode. The DRC however reduced this interference efficiently making accurate and precise measurements of Cr in routine samples possible. The use of the DRC was especially justified for samples that were prepared by microwave-assisted acid hydrolysis because the interference was most pronounced in those samples.

INTRODUCTION

Chromium determination in environmental samples is generally performed by graphite furnace atomic absorption spectrometry (GFAAS) because this method does not suffer from interferences. Nowadays laboratories that work on a routine basis are moving towards simultaneous techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) in order to increase their throughput by determining several elements at once. However, the application of ICP-OES for chromium determination remains limited due to the low sensitivity, while ICP-MS has disadvantages due to the poly-atomic interferences on the two most abundant isotopes-52 and -53 created by residual carbon or high chloride concentrations in the sample matrix. In the last five years, several authors have proposed to use a collision/reaction cell to decrease such polyatomic interferences (e.g., $^{37}Cl^{16}O$, $^{40}Ar^{12}C$). Neubauer and Völlkopf (1) described in detail the working conditions of a dynamic reaction cell and the usefulness of ammonia as reaction gas to decrease polyatomic interferences on chromium in carbon- and chloride-based matrices. This approach has found many applications in the semiconductor industries (2–4) or for biological samples such as urine and serum (5,6). The use of an inert gas such as He to decrease polyatomic interferences through collision has been shown recently as being a promising technique for samples with unknown matrix effects (7). For food analysis, ICP-MS in combination with an ultrasonic nebulizer has been recently described as a viable solution to decrease matrix effects and render the often low Cr concentrations quantifiable (8). However, the described method uses specially derived correction factors to correct for matrix effects, and only five different sample matrices were analyzed during validation.

Chromium is an essential trace element that is thought to play a major role in glucose tolerance and has shown evidence as an essential role in patients undergoing total parenteral nutrition. Today, chromium is also promoted as an important supplement by athletes and sports nutritionists due to indications that it can increase lean body mass and decrease percentage body fat (9). Chromium in foods can be present through accidental contamination during food production. However, up to now no Upper Intake Level has been pronounced for soluble Cr(III) salts by the U.S. Food and Nutritional Board (10) due to their low toxicity. Nevertheless, good analytical methods must be available and validated for the food industry in order to be able to check for potential contamination through contact materials, such as stainless steel, or to check for the accuracy of a supplementation. Supplementation is performed through addition of premixes, of which the composition is checked before use. Since premixes are added in small amounts to finished products, they usually consist of high concentrations of different salts, which can cause matrix effects during analyses. As a result, premixes must be significantly diluted prior to analysis.

In this paper, we describe the method validation for Cr determination in various food related products (finished products and raw materials) using an ICP-MS equipped with a Dynamic Reaction Cell™ and two different sample preparation modes. It was the purpose of this work to validate the working conditions specific to Cr determination using the dynamic reaction cell before implementing them into a multi-element method. In the scarcity of certified reference materials for several food matrices, the results were compared to

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results obtained by GFAAS as the reference method.

EXPERIMENTAL

Reagents and Standard Solutions

High-purity water (18.2 MΩ cm^{-1}) from a Milli-Q™ Plus system (Millipore, Bedford, MA, USA) and nitric acid freshly sub-distilled from conc. nitric acid (analytical grade, 65% p.a.) were used throughout.

A single-element standard solution of 1000 mg Cr L^{-1} was used for standard preparation (Merck, Certipur®). The standards matrix was 5% HNO_3. The internal standard of 5 µg L^{-1} In was prepared by dilution of a single-element standard solution of 1000 mg L^{-1} In (Merck, Certipur®) in 1% HNO_3.

Samples

Five certified reference materials (CRMs) were used as the quality control samples to monitor the digestion efficiency and the performance of the two analytical systems. These samples were IAEA 155 (Whey Powder), NIST 8415 (Whole Egg Powder), DORM-2 (Dogfish Muscle), NIST 8418 (Wheat Gluten), and NIST 8436 (Durum Wheat Flour).

For comparison of ICP-MS and GFAAS, the internal food samples were chosen from finished products (clinical nutrition, infant formulae, cereal bars, milk-based drinks) and raw materials (premixes, soy protein, and magnesium-oxide).

Instrumentation

A PerkinElmer® SCIEX ELAN® DRC™ II (PerkinElmer SCIEX, Concord, Ontario, Canada) was employed for the Cr determination in the digested food samples. The operating conditions are shown in Table I. A solution containing the internal standard (5 µg L^{-1} In) was mixed on-line with the analytical solutions using a mixing manifold connected between the peristaltic pump and the nebulizer.

For the reference method, a graphite furnace (PerkinElmer Model 4100Z atomic spectroscopy spectrometer), equipped with a THGA™ graphite tube and Zeeman background correction was used (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). A matrix modifier was applied for all samples [0.06 % $Mg(NO_3)_2$]. Details on the analytical procedure are given in Table II.

A Model MLS 1200 microwave digestion system (Milestone, Leutkirch, Germany) with Teflon® flasks and alternatively a high pressure asher (HPA-S High Pressure

TABLE I
ICP-MS Operating Conditions

Power	1275 W
Plasma Gas Flow	15 L min^{-1}
Auxiliary Flow	1.0 L min^{-1}
Spray Chamber	Peltier cooled cyclonic spray chamber cinabar (at 15°C), internal volume = 50 mL
Nebulizer Flow	0.8 L min^{-1}
Nebulizer	Micromist, micro-concentric nebulizer
Sample Uptake Rate	0.2 mL min^{-1}
Scan Mode	Peak hopping
Sweeps/Reading	20
Dwell Time	100 ms
Readings/Replicate	1
Replicates	3
Observed Masses	Cr 51.94, Cr 52.94, In 114.9
Optimized DRC Mode:	
RPa	0.05
RPq	0.65
Cell Gas	NH_3 at 0.55

TABLE II
GFAAS Operating Conditions

Analytical Wavelength		357.9 nm	
Slit Width		0.7 nm	
Graphite Tubes		THGA tubes	
Signal Measurement		Peak area	
Sample Injection Volume		20 µL	
Matrix Modifier Injection Volume		5 µL	
Furnace Program:			
Step	Temp (°C)	Ramp (s)	Hold (s)
1	110	1	20
2	130	5	30
3	1500	10	20
4	2300	0	5
5	2400	1	5

Asher, from Anton Paar through Instrumenten Gesellschaft, Switzerland) with 15-mL quartz-glass tubes was used for sample preparation.

Sample Preparation

Microwave Digestion

A 300-mg amount of sample was measured into each Teflon® vessel. After adding 2 mL HNO_3, the vessels were closed and installed in the microwave carousel. A power program was applied, as shown in Table III. After the microwave program had ended, the vessels were left to cool down for one hour. The digests were then quantitatively transferred into 15-mL Falcon PE tubes and brought to 10 mL with water. After every microwave run, the Teflon vessels were cleaned using nitric acid and applying the same microwave power program as used for sample digestion. In order to check for carryover, a preparation blank was included in each series of digestions.

High Pressure Asher (HPA) Digestion

A 300-mg amount of sample was measured into the quartz tube, and 2 mL HNO_3 was added. The tube was closed with a quartz stopper and sealed with a Teflon band. After placing the sample tubes into the stainless steel heating block, nitrogen was applied to the samples at a pressure of 65 bar and a heating program according to Table III was run. After digestion, the sample was quantitatively transferred into a Falcon PE tube (15 mL) and brought to 10–mL volume with water. Used HPA quartz tubes were cleaned after each run using an acid vapor cleaning apparatus for six hours (Trabold AG, Berne, Switzerland).

Sample Analysis

The measurement of Cr by GFAAS was conducted using standard addition for each sample. If possible, the sample digest was diluted to a concentration of around 3 µg L^{-1}. Sub-samples were spiked in order to obtain a sample concentration +3 and +6 µg L^{-1} Cr, respectively. The standard addition measurement was performed fully automated through the software of the GFAAS and its Model AS-70 autosampler (PerkinElmer) using the working conditions as described in Table II. Standard addition measurements were only accepted if the correlation coefficient r^2 was greater than 0.995 and if the digestion blank showed an absorption < 0.003 AU.

The ICP-MS DRC II was calibrated by external standards, and the samples were run in batches of 10 samples. After each batch, the accuracy of the calibration was checked by re-analysis of one standard. The standard concentrations were 0, 0.1, 0.5, 1.0, 3.0, 5.0, and 10 µg L^{-1} in 5% HNO_3.

TABLE III
Microwave and High Pressure Asher: Digestion Programs

Stage	Microwave Time (min)	Microwave Power (W)	High Pressure Asher Time (min)	High Pressure Asher Temperature (°C)
1	3	180	20	20–90
2	3	360	10	90
3	3	600	20	90–150
4	3	-	30	150–180
5	3	600	5	180–20
6	3	360		
7	3	180		
8	30	-		

RESULTS AND DISCUSSION

Before performing the analyses on the GFAAS and the ICP-MS, the limits of quantification (LOQ) for both techniques were determined by spiking a matrix-blank with a low Cr concentration. Blank-signal and spiked blank-signal were measured and evaluated as described elsewhere for another analytical method (11). The LOQs for Cr measurement by ICP-MS and GFAAS are given in Table IV.

The calibration curves of the ICP-MS in the different modes were based on seven standards (blank included) and were linear.

Accuracy of the Method

Certified Reference Materials

In a first evaluation of the use of the dynamic reaction cell for Cr measurement using the two isotopes (52 and 53), five certified reference materials (CRMs) were analyzed after HPA and microwave digestion in the standard and DRC-mode and GF-AAS. The CRMs were chosen for their representative Cr concentration range of 20 µg kg^{-1} to 34 mg kg^{-1}. Table V lists the measured concentrations in the different modes of digestion and the different analytical conditions. The figures show clearly that measurement in standard mode leads to an

TABLE IV
Limit of Quantification for Cr Measurement by ICP-MS Standard Mode, DRC Mode and GFAAS
(Concentrations in µg kg^{-1})

Std Mode	DRC Mode		GFAAS
Cr-53	Cr-52	Cr-53	
3	3	4	20

overestimation of the chromium concentrations for all three NIST samples and for IAEA 155, which were all analyzed with a dilution factor of about 100. For the high Cr concentrations found in DORM-2, a dilution factor of 7000 was applied, which considerably reduced the effect of residual carbon and led to similar results for all digestion and analytical conditions.

In the case of the NIST and IAEA CRMs, the comparison between the HPA and MW showed that the residual carbon effect was more pronounced in the MW-digested samples. This was due to the lower pressure and temperature conditions applied through MW digestion. Although the HPA was run under higher pressure and temperature than the MW, the HPA was still not able to completely reduce the residual carbon effect.

It was also observed that the IAEA CRM showed higher Cr concentrations on isotope 53 than on isotope 52 in standard mode. This is explained by the presence of high chloride concentrations in this CRM (7000 mg kg^{-1}), which led to more pronounced interferences on isotope 53 through $^{37}Cl^{16}O$. This interference was also efficiently reduced through the DRC mode.

For the analyses of internal food samples, the standard mode was only used for isotope 53 in order to track significant interferences through carbon or chloride.

The figures also show very good agreement between the GFAAS data and the certified reference data. GFAAS was therefore used in the following as the reference method in order to evaluate the method performance on internal food samples.

Internal Food Samples

In order to check the accuracy of the method on internal samples, a comparison between GFAAS and ICP-MS DRC II (alternative method) was carried out; the results are given in Table VI. The Cr concentration range in the internal food samples was similar to the CRMs. For several samples, the preparation had to be adapted because high standard deviations were observed within triplicate analyses. This was especially true for raw materials. Samples such as premixes and the MgO were prediluted in acidified water (5-g sample in 500 mL 1% HNO_3). In the case of completely dissolvable premixes (trace element premixes), the obtained solutions were filtered and directly analyzed. Vitamin premixes and MgO were sub-sampled (1 g) from the suspensions and further digested using HPA or MW.

Relatively good agreement between GFAAS and the different ICP-MS modes was found for the samples that were prepared using the HPA. Some minor differences between ICP-MS in standard mode (isotope 53) and GFAAS were found for samples with an organic matrix and with low Cr levels (e.g., soy protein extract, infant formula). This was even more pronounced in the samples that were prepared using MW digestion for sample preparation, such as in the soy protein extract where the Cr concentrations (measured in standard mode) were 3–4 times higher than the concentrations obtained from DRC mode or GFAAS.

TABLE V
Chromium Concentrations Measured in Five Different CRMs Digested by HPA and MW
(Analyses were performed by ICP-MS in standard and DRC mode and by GFAAS as the reference method. Measured concentrations that were within the certified concentrations range are shown in bold font.)
Results are means ± standard deviation and are given in µg kg^{-1}.

Sample Prep.	Sample Name	Certified Value	Standard Mode		DRC Mode		GFAAS
			Cr-52	Cr-53	Cr-52	Cr-53	
HPA	NIST-8436	23±9	95±14	**23±2**	**20±1**	**21±2**	**24±3**
	NIST-8418	53±13	416±21	99±5	**49±3**	**49±5**	**53±13**
	NIST-8415	370±180	1069±242	**481±13**	**336±7**	**337±8**	**331±9**
	IAEA-155	585±75	850±20	904±37	**547±16**	**549±17**	**593±31**
	DORM-2	34700±5500	**31272±1000**	**31975±1536**	**30645±771**	**30674±1253**	**32924±1304**
MW	NIST-8436	23±9	334±2	69±6	**21±3**	**20±2**	**22±4**
	NIST-8418	53±13	1038±128	263±41	**46±1**	**45±1**	**43±1**
	NIST-8415	370±180	2303±94	571±23	**337±4**	**332±10**	**304±16**
	IAEA-155	585±75	1261±49	1380±45	**582±20**	**583±27**	**566±26**
	DORM-2	34700±5500	**31733±1255**	**32952±2411**	**33552±604**	**33385±709**	**33525±2773**

Precision

For the evaluation of the precision of the method, six samples were subjected to duplicate analyses on eight different days (duplicate analyses were chosen as a measure of repeatability and mean values over eight days were used as a measure of intermediate reproducibility). Each analysis included sampling and sample preparation by either HPA or MW. Three samples (vitamin/mineral premix, mineral premix, and magnesium oxide) were prepared by dissolving 5 g of product in 500 mL 1% HNO_3. From these solutions, about 1 g was subsampled and digested by HPA or MW. Three samples (milk-based drink, sport nutritional bar, and whey powder) were digested directly by HPA or MW with a sampling of 0.3 g for the dry products and 1 g for the liquid product. Robust statistics, which is less sensitive to outliers was used for the statistical analysis (12). Repeatability was determined by calculating the robust standard deviation of the eight differences between duplicate measurements and expressed as the relative standard deviation [RSD(r)] in % (see Table VII). The intermediate reproducibility was calculated as robust standard deviation of the eight average values from the duplicate measurements and expressed as relative standard deviation [RSD(iR)] in % (see Table VIII).

The RSD(r) was low in the DRC mode for both Cr isotopes, with about 4–6% average RSD(r) depending on the selected isotope and digestion mode. Cr measurement in standard mode showed higher RSD(r), which is explained by more variation of the signal due to different concentrations of residual carbon in the replicates. Also, the reference method (GFAAS) showed lower precision over the whole concentration range of the analyzed samples.

In terms of intermediate reproducibility, the precision was similar in the DRC mode for both Cr isotopes and the reference method. With 9%, the standard deviation of intermediate reproducibility [RSD(iR)] was about two times higher than RSD(r), which is still acceptable for trace element determination. The intermediate reproducibility on Cr in standard mode was higher than in DRC mode (15%).

TABLE VI
Chromium Concentration Measured in 10 Internal Food Matrices Digested by HPA and MW
(Results are means of three replicates ± standard deviation and are given in µg kg^{-1}.)

Sample Prep.	Sample Name	Std. Mode	DRC Mode		GFAAS
		Cr-53	Cr-52	Cr-53	
HPA	Soy protein extract	143±10	80±8	80±7	70±11
	Sports nutritional bar	471±36	460±3	446±11	465±40
	Vitamin/mineral premix 1	864±160	1010±120	998±156	1003±123
	Vitamin/mineral premix 2	1616±179	1547±232	1575±242	1722±285
	Magnesium oxide	3260±97	2934±143	2989±141	2825±130
	Infant formula	74±15	27±1	27±1	43±14
	Milk-based drink	63±2	54±2	54±2	51±4
	Mineral premix	48147±2778	48613±4660	49719±5265	47906±3775
	Sport nutritional bar	1193±184	1162±165	1320±148	1118±48
	Clinical nutrition product	181±13	181±3	182±5	175±10
MW	Soy protein extract	222±5	55±7	54±7	72±3
	Sports nutritional bar	437±61	453±11	452±11	435±37
	Vitamin/mineral premix 1	833±84	970±56	943±43	973±47
	Vitamin/mineral premix 2	2345±513	1749±450	1768±462	1738±428
	Magnesium oxide	3257±525	2252±284	2168±316	2283±365
	Infant formula	246±21	31±5	31±4	27±3
	Milk-based drink	120±7	49±2	48±2	47±14
	Mineral premix	51237±1153	44101±2385	44698±2049	48614±506
	Sport nutritional bar	946±248	950±200	992±249	946±248
	Clinical nutrition product	202±20	166±46	162±43	158±31

CONCLUSION

A thorough validation of an analytical method for Cr determination in foodstuff based on an ICP-MS equipped with a Dynamic Reaction Cell was performed. The chosen analytical conditions delivered accurate and precise Cr concentrations compared to reference values from certified reference materials and also compared to a reference method (GFAAS). Use of the dynamic reaction cell efficiently reduced the effect of residual carbon, which acts as interference especially as shown in samples with low Cr content. Highest impact of the residual carbon interference was found in samples that were prepared using microwave-assisted acid hydrolysis. The use of a reaction cell applies especially to such samples that have been insufficiently hydrolyzed.

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TABLE VII
Relative Standard Deviation of the Repeatability [RSD(r)] Expressed in % and Based on Duplicate Analyses

Sample Prep.	Sample Name	Conc. (µg kg^{-1})	RSD(r) in % Std. Mode Cr-53	DRC Mode Cr-52	DRC Mode Cr-53	GFAAS
HPA	Milk-based drink	48	6	5	6	13
	Sport nutritional bar	500	11	8	8	6
	Whey powder IAEA 155	590	5	3	3	8
	Vit./Min. premix	1600	3	3	6	10
	Mineral premix	48000	7	3	4	7
	MgO	2600	8	3	4	8
MW	Milk-based drink	48	9	6	5	2
	Sport nutritional bar	500	12	5	5	4
	Whey powder IAEA 155	590	8	4	5	5
	Vit/Min. premix	1600	7	5	4	9
	Mineral premix	48000	9	5	6	5
	MgO	2600	2	6	9	4

TABLE VIII
Relative Standard Deviation of the Intermediate Reproducibility [RSD(iR)] Expressed in %

Sample Prep.	Sample Name	Conc. (µg kg^{-1})	RSD(iR) in % Std. Mode Cr-53	DRC Mode Cr-52	DRC Mode Cr-53	GFAAS
HPA	Milk-based drink	48	17	10	9	13
	Sport nutritional bar	500	11	8	8	10
	Whey powder IAEA 155	590	19	7	6	10
	Vit./Min. premix	1600	17	10	14	12
	Mineral premix	48000	12	9	8	9
	MgO	2600	14	8	10	10
MW	Milk-based drink	48	14	7	7	9
	Sport nutritional bar	500	16	11	8	8
	Whey powder IAEA 155	590	8	6	5	6
	Vit/Min. premix	1600	19	12	12	14
	Mineral premix	48000	11	5	6	5
	MgO	2600	20	8	15	8

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Sample Storage Conditions and Holding Times for the Determination of Total Iodine in Natural Water Samples by ICP-MS

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ABSTRACT

The determination of total soluble iodine concentration in fresh water by inductively coupled plasma mass spectrometry (ICP-MS) is simple and easy because no complicated pretreatment is needed; however, not all analysts have easy access to this instrumentation because it is expensive and has high running costs. In this study, sample storage conditions and holding times were examined for total soluble iodine measurement in standard and three river water samples by ICP-MS to provide more favorable circumstances for users.

When standard solutions were stored at room temperature, the determined iodine at day 21 decreased by ~ 20% in the samples without adding an alkaline reagent, such as tetramethyl ammonium hydroxide (TMAH), probably due to I_2 release from the solution. However, with the addition of a small amount of TMAH, iodine was retained in the solution and no decrease was observed. However, when the samples were stored at 5°C, it was not necessary to add an alkaline reagent; for example, measured total iodine concentrations did not change for six months. Besides, measured total iodine concentrations in river water samples stored at 5°C did not change for almost one year. The concentrations of total iodine in the three Japanese rivers (10 samples per each river) were all measured, and the concentration ranged from 0.33 to 3.87 μg L^{-1}, with an average of 1.16 μg L^{-1}.

INTRODUCTION

Iodine is an essential element for humans, but becomes toxic when certain limits are exceeded. For examples, iodine toxicity can result from an intake of 2.0 mg of iodine per day (1), and iodinated trihalomethanes have usually been associated with odor and taste problems in drinking water at low concentrations (2,3). However, 0.15–0.2 mg iodine per day is necessary for adults to avoid iodine deficiency (4). Therefore, it is important to know the exact iodine concentration in the environment, especially the total iodine intake from drinking water from a public health point of view. In fact, since the concentration of iodine in fresh water is much lower than in seawater (5–7), not much total iodine data in fresh water environments have been reported. Moreover, the recent trend has been to measure iodine species (5,7,8) because measurements of the total concentration of iodine were said not to provide any information about its mobility and bioavailability. However, the amount of iodine distribution in fresh water systems should be known.

To determine total iodine concentrations, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are commonly used. The ICP-MS detection limits are 2–3 orders of magnitude lower than those of ICP-OES (9–12), so that ICP-MS is very attractive for the determination of total soluble iodine in fresh water. However, the instrument is expensive and the running costs are high. Also, where there are many users for one instrument, it is not always available for immediate use, which causes a problem since the prevailing thought is that iodine should be measured immediately after sampling. Thus, not everyone has easy access to this instrument for iodine determination. In this study, we examined measurement conditions for total soluble iodine determination in river water that would be more favorable to use, especially in terms of sample storage conditions and holding times.

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EXPERIMENTAL

Instrumentation

A Model Agilent 7500a ICP-MS (Yokogawa Analytical Systems, Japan) was used for this study and the operating conditions listed in Table I.

Since iodine has only one stable isotope, m/z=127 was scanned for iodine determination. Cesium (m/z=133, 100% abundance) was used as the internal standard during iodine counting. Under the listed conditions, only 3 min were needed for one sample which includes aspirating the sample solution (20 s fast rinsing and 50 s normal rinsing) to change the solution, to stabilize the measurement conditions, and washing with deionized water (40 s, fast rinsing); which resulted in the measurement of 20 samples per hour. Only 2-mL sample volumes were needed for iodine determination. The typical

detection limit in solutions, calculated as three times the standard deviation of the blank, was between 0.01–0.05 µg L^{-1}.

For memory effect tests, we measured I-127 and Cs-133 for 4.5 s and 0.5 s, respectively, and their counts were taken every 10 s. After taking the background count with deionized water, 1 mg L^{-1} iodine (KI) solution was introduced, then the washing reagent of 0, 0.125, 0.25, 0.5, or 1.25% TMAH (0, 1/200, 1/100, 1/50, or 1/20 of the TMAH reagent).

Reagents

Super-pure grade 25% tetramethyl ammonium hydroxide (TMAH) and 68% nitric acid (TAMAPURE-AA-100, Tama Chemicals Co. Ltd., Japan), and special grade 28% ammonia solution (Wako Pure Chemicals Co. Ltd., Japan) were used. Since there is no iodine standard solution for ICP-MS or AAS, we used 0.1N KI and 0.1N KIO_3 (Kanto Chemicals Co. Ltd., Japan) to prepare 100-mg L^{-1} iodine solutions. From these solutions, the standard solutions for ICP-MS were prepared. Water (>18 MΩ), which was treated using a Milli-Q™ water system (Millipore Corporation, Bedford, MA, USA), was used throughout the study.

Table I
ICP-MS Operating Conditions

RF power	1380 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate	1.2 L min^{-1}
Solution uptake rate	0.3 mL min^{-1}
Sampling cone aperture (Ni)	1 mm
Skimmer aperture (Ni)	0.4 mm
Nebulizer	Babington-type
Oxide generation rate ($^{140}Ce^{16}O^{+}/^{140}Ce^{+}$)	<0.3 %
Dimer generation rate (Ce^{+2}/Ce)	<1.5 %
Sampling points per mass	3
Total counting time at 127	7.5 s
Sweeps per replicate	100
Number of replicates	5
Number of samples/h	20

River Samples

Sampling was carried out from the Shou, Kuzuryu, and Oota Rivers in 2004. Only 2–3 days were spent collecting the samples from any one river, because the river conditions are affected by weather and the season. Ten samples per river were collected from the upper stream to the river mouth. At a sampling site, water was collected in a thoroughly washed polypropylene bottle, and the electrical conductivity and pH were measured. All sample bottles were sent to our Institute's laboratory under cool conditions (5°C). In the laboratory, the samples were passed through a 0.45-µm Millipore filter and kept at 5°C.

RESULTS AND DISCUSSION

Memory Effects

For metallic element determinations by ICP-MS, a higher concentration of nitric acid solution is commonly used to reduce memory effects rapidly and effectively after each sample measurement. For instance, when a sample solution is acidified to 1–2% HNO_3, the washing solution should be about 3–5% HNO_3. For iodine determinations, it is necessary to use an alkaline media for this purpose. TMAH is a known strong alkali, and super-pure grade TMAH is commercially available; therefore, TMAH was selected for iodine determination. There are many reports published using TMAH for iodine determination by ICP-MS (12–16). However, it is not clear what concentration is effective for reducing iodine memory effects. We used 0–1.25% TMAH solutions as the washing reagents after introduction of 1 mg L^{-1} iodine solution. The results are shown in Figure 1. When deionized water was applied, the background count for iodine returned to the original count within 10 samplings (100 s normal rinsing); however, when TMAH solutions were used, the background counts were higher than the count for deionized water.

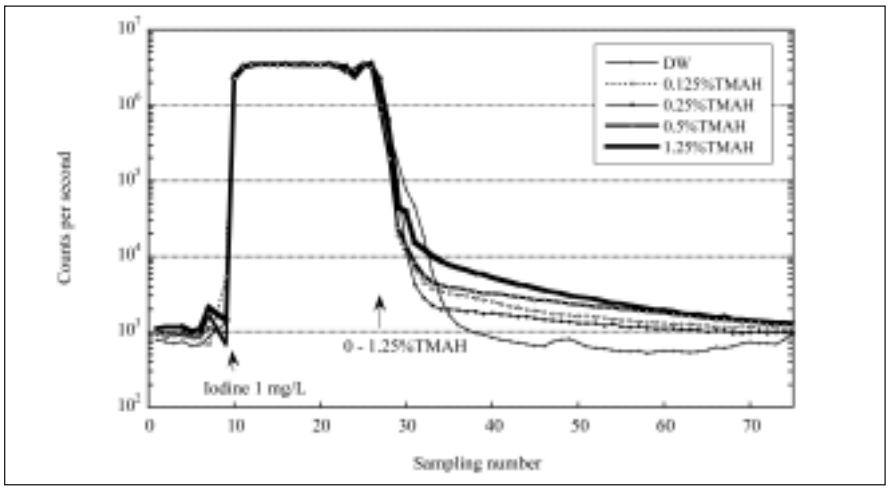

Fig. 1. Effect of TMAH concentrations as washing reagent on I-127 counts by ICP-MS. After 1 mg L^{-1} iodine measurement, 0, 0.125, 0.25, 0.5 or 1.25% TMAH (TAMAPURE-AA-100) was introduced for 600 s (10 s for one sampling).

Introduction of 0.125, 0.25, and 0.5% TMAH solutions provided faster reduction of the I-127 counts in comparison with deionized water. It was found that of these solutions, 0.25% TMAH (100-fold dilution of the original TMAH) was most effective in reducing the background counts rapidly, although the counts did not reach a stable level and continued to decrease over time. Thus, when samples without added TMAH are measured, deionized water is appropriate as the washing reagent. However, in order to remove the iodine retained in the tubing more effectively, 0.25% TMAH was applied. Higher TMAH concentrations were not effective in removing iodine from the interface.

Although application of deionized water or 0.25% TMAH gave smaller memory effects in this study, some reports have used HNO_3 solution rinses between sample runs (13,14). For instance, the sequence of using a 1% HNO_3 rinse, deionized water rinse, and then sample aspiration was reported in Reference 14. Their application of the HNO_3 solution as the washing reagent was intended to remove metallic elements from the instrument tubing. However, it is also known that addition of HNO_3 to the sample solution is not a good idea for iodine determination because iodine is easily oxidized and generates I_2 gas. Thus, I_2 gas would be continuously produced from the sample solution when HNO_3 is introduced immediately after the sample measurement and a high memory effect for I-127 determination would result.

In the present study, we applied 3% HNO_3 as the washing reagent, and the results are shown in Figure 2. Clearly, the introduction of HNO_3 solution could cause an increase in background. It is most likely that due to the reaction of iodine with the oxidant (HNO_3) in the spray chamber, I_2 gas was generated so that a long memory effect was observed. We had thought that the memory effect might decrease if the spray chamber size were decreased; thus, further work to study this effect should be carried out.

These results show that the introduction of an oxidizing reagent during iodine measurements results in a big memory effect problem. It is, therefore, better to use 0–0.25% TMAH solution as the washing reagent. Additionally, in order to decrease the background level, around 60 s for normal rinsing or 30–40 s for fast rinsing are required.

Counting Response of I and Cs Under Increasing TMAH Concentrations

During ICP-MS analysis, an internal standard is usually used to monitor the change in counting efficiency. For iodine determination, Cs is used (12–14). However, we were not certain whether or not there was a counting response difference between iodine and Cs at different TMAH concentrations. Thus, we prepared both 20 μg L^{-1} of iodine and 20 μg L^{-1} of Cs in 0–1.25% TMAH solutions (direct Cs addition). The counting responses of I-127 and Cs-133 were monitored by ICP-MS. The iodine and Cs countings at each TMAH concentration were compared with those of a 0% TMAH solution and the results are shown in Figure 3. It is clear that an increase in TMAH concentration did not affect iodine counting, although a slight count increase was observed at 0.125% TMAH.

On the other hand, with Cs the counting response decreased as the TMAH concentration increased. There are two reasons to explain these results:
(a) One reason was the Cs sorption on the bottle surfaces and tubes and so we changed the introduction method of Cs. The Cs solution was added to the sample solution through another introduction line while being pumped (pumping Cs addition). The results are shown in Figure 4. No difference was observed between direct addition and pumping addition. Therefore, a Cs count reduction would not occur by eliminating the Cs sorption on the bottle surfaces and tubes.
(b) The other possible reason would be the sample solution condition. Since TMAH is an organic alkaline reagent, the density of the

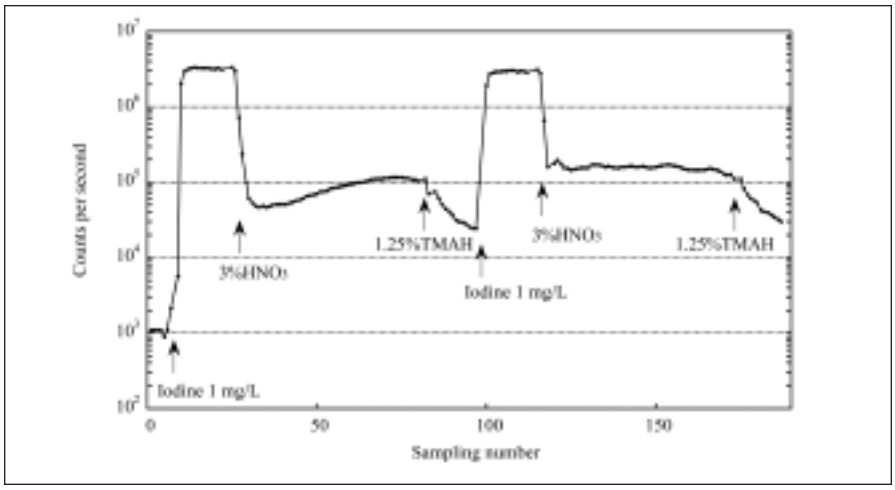

Fig. 2. Effects of washing reagents on I-127 counts by ICP-MS. After 1 mg L^{-1} iodine measurement, 3% HNO_3 was introduced for 600 s (10 s for one sampling) followed by introduction of 1.25 % TMAH for 150 s. These steps were repeated twice.

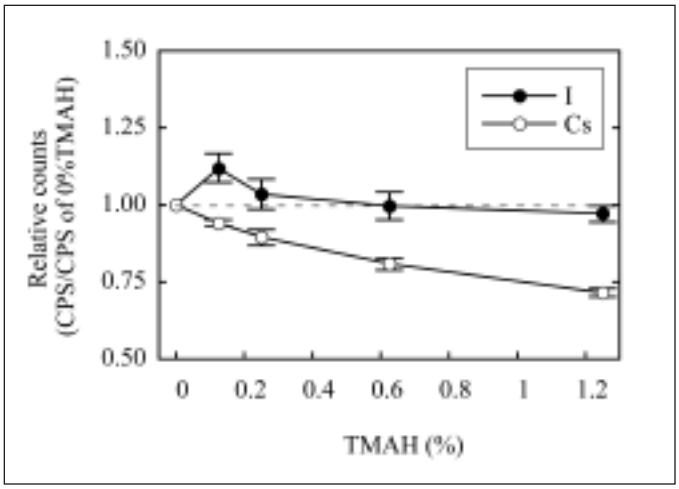

Fig. 3. Effects of 0–1.25 % of TMAH concentrations on I-127 and Cs-133 counts by ICP-MS.

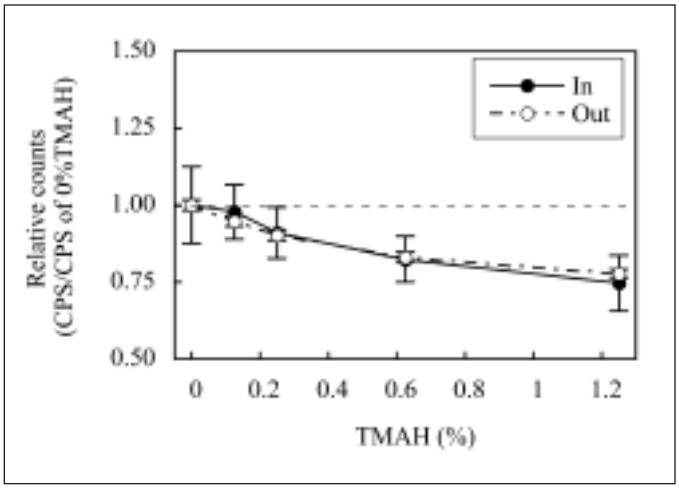

Fig. 4. Relative count of Cs in 0.125–1.25% TMAH compared to the Cs count in 0% TMAH solution. In: Cs added to the sample solution, and Out: Cs solution added by pumping.

solution affects the Cs fate until ionization. During sample introduction into the ICP-MS instrument, Cs introduction to torch and/or ionization in the plasma was probably somehow affected, although we have not yet been able to clarify the mechanism.

In order to use Cs as an internal standard, it is necessary to adjust the TMAH concentration or maintain the TMAH concentration lower than 0.125% (1/200 of 25% TMAH) for sample and standard solutions because the reactions of iodine and Cs are different. Concerning the Cs internal standard addition methods (i.e., direct addition vs. pumping addition), no intensity differences were observed. However, the iodine and Cs intensities were affected by the TMAH concentration. Clearly, direct Cs addition to samples is not required and its elimination in the sample preparation process will also save time.

Effects of Storage Conditions on Total Iodine Measurement Using Standard Solutions

We prepared 20 μg L^{-1} KI standard solutions in 0–1.25% TMAH and observed a concentration change when kept under room temperature (20–23˚C) for 21 days. The determined concentrations were compared with the first-day results (relative concentration, C/C_0) and are shown in Figure 5. Without addition of TMAH, the iodine concentration determined at day 21 decreased by 20%, probably due to I_2 release from the solution. However, with the addition of a small amount of TMAH, iodine was retained in the solution and no decrease was observed.

Then we examined whether addition of TMAH results in better iodine stability. However, addition of alkaline reagents to environmental sample solutions may lead to precipitation during storage. When water samples are

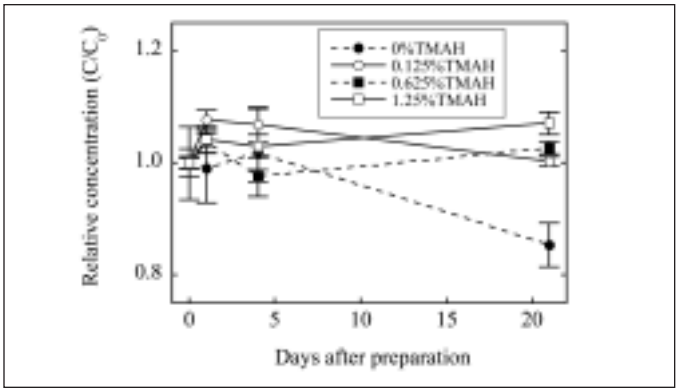

Fig. 5. Time dependence on relative concentrations of I-127 in 0–1.25% TMAH solutions stored at room temperature.

stored at room temperature without addition of alkaline reagents, total soluble iodine should be measured within seven days.

As a next step, we changed the storing temperature and stored the standard samples at 5˚C. In this experiment, standard samples were prepared from KI and KIO_3. In river water, I^-, IO_3^- and soluble organic iodine may be present. Since the ICP can ionize inorganic and organic iodine similarly if organic matter concentration is low, total iodine determination does not change due to changes in chemical form. It is expected that organic iodine will be stable since I^- and IO_3^- reach equilibrium conditions, but the solution may possibly release iodine as I_2.

To understand total soluble iodine determination stability by ICP-MS under neutral and alkaline solution conditions during storage, we prepared standard solutions from KI and KIO_3 in deionized water, 0.03 and 0.15% ammo-

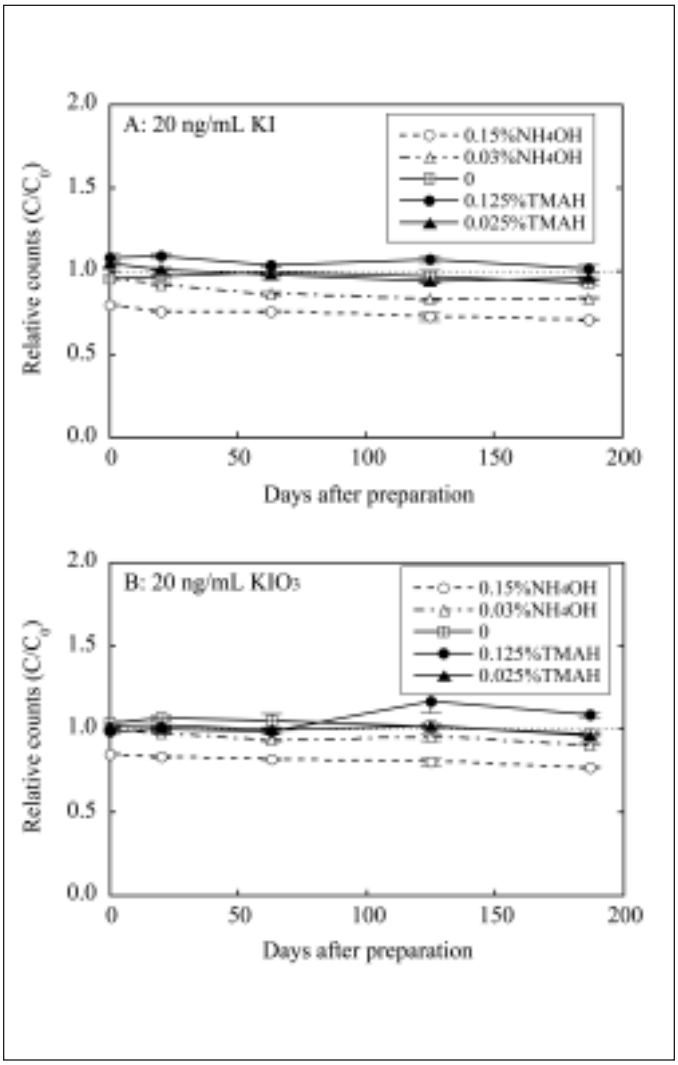

Fig. 6. Time-dependence on the concentrations of I-127 in 0.03 and 0.15% NH_4OH, DW, and 0.025 and 0.125% TMAH solutions stored at 5˚C. A: Iodine concentration was adjusted to 20 µg L^{-1} using KI solution, B: Iodine concentration was adjusted to 20 µg L^{-1} using KIO_3 solution.

nium solution, and 0.025 and 0.125% TMAH solutions, respectively, by adjusting the iodine concentration to 20 µg L^{-1}. The concentrations measured at a certain time were compared with the initial concentration. Since the TMAH concentration was lower than 0.125%, Cs was used as the internal standard for counting correction.

Figure 6 shows the relative iodine concentrations in the solutions stored at 5˚C for 6 months. For both I^- and IO_3^-, the relative iodine concentration was the lowest in 0.15% ammonium solution; in 0.125% TMAH it was slightly higher than the initial concentration. For KI solutions, ammonium addition should provide lower concentrations, and the measured concentration decreased all the time. However, with and without addition of TMAH, the determined values were the same as at the initial condition for a period of six months. A similar trend was found for KIO_3 solutions. Thus, addition of a small portion of TMAH (less than 0.5 mL to a 100-mL sample solution) offered the best condition for total iodine determination. Without addition of TMAH, the filtrated sample could also be used for total iodine measurement for sample solutions stored at 5˚C up to a period of at least six months.

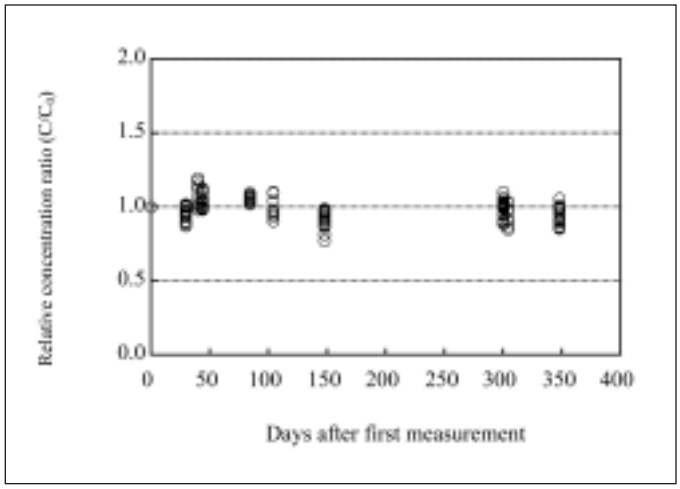

Fig. 7. Time-dependence on the concentrations of I-127 in three Japanese rivers, collected in 2004. Each river had 10 sampling points. Samples were passed through 0.45-µm membrane filters, and I-127 measurement was carried out within 2 weeks after sampling. Cs-133, an internal standard, was added by pumping.

Long-term Storage Effects on Total Iodine Measurements in River Water Samples

For actual environmental samples and to avoid precipitation generation during storage, we did not add any reagents during storage. The pH values of these river samples ranged from 6.2 to 7.9, which is within range of Japanese river waters (17). The electrical conductivity (EC) ranged from 0.03 to 0.11 mS cm^{-1}. Figure 7 plots relative concentrations (data obtained at a certain period of time compared with the first measurement) versus time. Considering the time needed for sample collection, sample transfer, and sample pretreatment, it is difficult to make the first measurement within one week from collection; therefore, the first measurement was done within two weeks from collection of each sample. As mentioned above, the total iodine data for the first measurement should be valid and correct. Each data point in Figure 7 represents the results of at least 10 samples. During a storage period of about one year, the determined total iodine did not change. From the results, we concluded that river water samples can be stored at 5˚C without addition of reagents.

The iodine concentration data are listed in Table II. The average concentrations of total iodine in the Shou, Kuzuryu, and Oota Rivers were 0.56, 0.95, and 1.97 μg L^{-1}, respectively. The concentrations were about 30–100 times lower than for seawater (about 0.07 mg L^{-1}) (7), and were almost the same as previously reported values (5,6). Unfortunately, there is no reference material for iodine in river water because standard water samples had added HNO_3 or HCl to prevent adsorption of the analyte to the bottle wall. However, Tsukada et al. (18) reported that the iodine data obtained by radiochemical neutron activation analysis and ICP-MS agreed well, thus we assume that the present data should be correct.

The major source of iodine should be sea spray; however, the EC of the Oota River was lower than of other rivers. For further explanation of the total iodine distribution and the fate of iodine in river waters, it is necessary to obtain more data, including speciation. However, the method used in this study is simple and the ICP-MS provides a low enough detection limit for I-127, usually 0.01–0.05 μg L^{-1}. Under the identified storage conditions, total soluble iodine can be easily determined by ICP-MS.

Table II
Total Iodine Concentration in Three Japanese River Waters Collected in 2004

River Name	District(s)	Length (km)	Sampling Points	pH	Electric Conductivity (mS cm^{-1})	Average Total Iodine Conc. (μg L^{-1})
Shou	Toyama, Gifu	115	10	6.8–7.7	0.03–0.11	0.56 ± 0.14
Kuzuryu	Fukui	116	10	6.6–7.9	0.03–0.11	0.95 ± 0.50
Oota	Hiroshima	103	10	6.2–7.0	0.04–0.06	1.97 ± 0.78

CONCLUSION

Sample storage conditions for total soluble iodine measurement in river waters by ICP-MS were examined. For total iodine determination, filtered water samples could be stored for almost one year at 5°C without addition of an alkaline reagent such as TMAH. For room temperature storage, addition of a small amount of alkaline reagent could keep iodine in the solution. It should, however, be noted that precipitation might occur by addition of an alkaline reagent. Under the sample storage conditions described, total iodine in water samples can be easily determined by ICP-MS at any time (within one year's time is preferable).

In order to correct the ICP-MS counting response, Cs can be used; however, it was necessary to adjust the TMAH concentration for samples and standard solutions. No washing with HNO_3 solution is recommended since this increases the background count and causes memory effects.

ACKNOWLEDGMENT

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Direct Determination of Lead in Compost by Slurry Sampling Electrothermal AAS

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ABSTRACT

Lead concentrations in compost samples were determined by slurry sampling electrothermal atomic absorption spectrometry. The compost samples were suspended at concentrations of 0.02-0.1 % (w/v) in 5% (v/v) nitric acid and 0.004% (v/v) Triton X-100. Palladium was used as the chemical modifier to improve recovery. The procedure was validated by the analysis of a certified reference compost material CP-1 and compared with conventional microwave acid digestion. External calibration with aqueous standards was used. Repeatability and reproducibility for the compost slurries was 4.0% and 7.4%, respectively. The characteristic mass was 9.7 pg and the detection limit 9 μg g^{-1} for slurries prepared from 10-mg samples suspended in 50-mL diluent and injecting a 10-μL amount into the graphite furnace.

INTRODUCTION

Compost is used in agriculture to maintain and improve the soil structure and plant nutrition (1). However, the presence of heavy metals in composts, especially in those obtained from urban wastes, can produce adverse effects on animal and human health as they become incorporated into the food chain from soil, ground water, and plants (2). Thus, the content of heavy metals is one of the criteria used to establish quality standards for compost. These standards are legal or voluntary regulations related to quality assurance and certification systems adopted in a number of countries (3).

The determination of heavy metals in compost is routinely performed by ICP-AES (4–6), ICP-MS (7), or AAS (8,9) after acid wet digestion or dry ashing. However, there is no general agreement with respect to the most suitable method (5–8, 10) for the determination of the element and with regard to the origin of the material. Within the last several years, slurry sampling has been employed for electrothermal atomic absorption spectrometry (ETAAS) analysis to simplify sample preparation procedures and to avoid sample contamination. This methodology has been applied to the determination of lead in soils (11–14), sediments (13–18), and sewage sludge (19). Even though these matrices bear some resemblance to composts, compost material is more heterogeneous and has an organic content up to around 40%, with particles of different nature and size. In the case of lead and for composts obtained from urban solid residues, the source of this element includes metals, ceramics, glasses, and plastics (20). The different European compost standards for lead concentration range from 45 to 800 mg kg^{-1}, depending on the country (3). In order to obtain the Eco-label, the Office of the European Communities has established 100 mg kg^{-1} total lead as the maximum allowable concentration for soil improvers (21).

The aim of this work was to study the performance of slurry sampling ETAAS applied to the direct determination of lead in compost as well as to evaluate the different sources of imprecision related to this determination.

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EXPERIMENTAL

Instrumentation

A PerkinElmer Model AAnalyst™ 300 atomic absorption spectrometer, equipped with a Model HGA®-800 electrothermal atomizer, AS-72 autosampler, and USS-100 ultrasonic probe, was used for all atomic absorption measurements (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). Lead absorption was measured at the 283.3- and 368.3–nm wavelengths. The spectral bandwidth was set at 0.7 nm and the hollow cathode lamp current at 5-10 mA, depending on the wavelength used. Pyrolytically coated graphite tubes (Part No. B3001254) with pyrolytic platforms (Part No. B3001256) were used for the experiments. Transient signals were evaluated by their peak areas (integrated absorbance). Deuterium background correction was also used.

Reagents and Samples

All reagents used in this work were of analytical reagent grade. Standard stock solutions of lead (1000 mg L^{-1}) were obtained from Sigma-Aldrich (Steinheim, Germany). Palladium used as the chemical modifier was prepared from a 10,000-mg L^{-1} stock solution (Merck, Darmstadt, Germany). Ultrapure water was obtained using a Milli-Q™ water system (Millipore, Molsheim, France).

The compost samples of urban solid residues (USRC-2) were obtained from a composting plant of Tecmed, S.A., Spain.

The CP-1 compost reference material was obtained from SCP Science, Baie d'Urfé, Canada.

Slurry Preparation and Introduction

The USRC-2 compost samples of urban solid residues (250 g) were ground for 30 minutes in a Model Pulverisette 9 vibrating rotary cup mill (Fritsch, Idar-Oberstein, Germany), made of agate. After grinding the samples, the particle size of 95% of the original material was below 250 µm.

The slurries were prepared by weighing the test portions of the material (10–600 mg) into precleaned polyethylene test tubes and suspending in 50 mL of 0.004% (v/v) Triton® X-100 (Sigma-Aldrich, Steinheim, Germany) and 5% (v/v) HNO_3 (Merck Suprapur®, Darmstadt, Germany). Measurements were performed using a Mettler Toledo AG245 balance (Mettler Toledo, Columbus, OH, USA), with a precision of ±0.01 mg. The tubes were placed in an ultrasonic bath (Selecta, Barcelona, Spain) for 15 minutes, then 2-mL aliquots were removed and placed in the autosampler vials, then ultrasonicated for 10 s at 50 W, and finally 20 µL of the homogenized slurry was injected into the furnace. Alternatively, 25-mg sample portions were weighed directly into the autosampler vials and suspended in 2 mL of the above-cited solution.

Determination of Analyte Partitioning

In order to determine the percentage of lead extracted into the liquid phase of the slurry (the analyte partitioning between the solid and the liquid phases), the homogenized slurry was first analyzed following the procedure described above. Then the slurry was centrifuged for 30 minutes at 3000 rpm (Megafuge 1.0, Heraeus, Hanau, Germany) and the supernatant analyzed by ETAAS.

Wet Digestion

Lead determinations were also performed after wet digestion of the compost samples. Sample portions of 0.1 g were accurately weighed into PTFE decomposition vessels and 3 mL of concentrated HNO_3 (Merck), 1 mL of H_2O_2 30% (v/v) (Merck), and 1 mL of concentrated HF (Merck) were added. The program used in the Multiwave™ microwave oven (Anton Paar, Graz, Austria) consisted of three steps: 700 W for 6 minutes, 1000 W for 15 minutes, and 15 minutes for cooling. The solution obtained was transferred to a volumetric flask and diluted to 25 mL with ultrapure water. The solutions were analyzed by ETAAS.

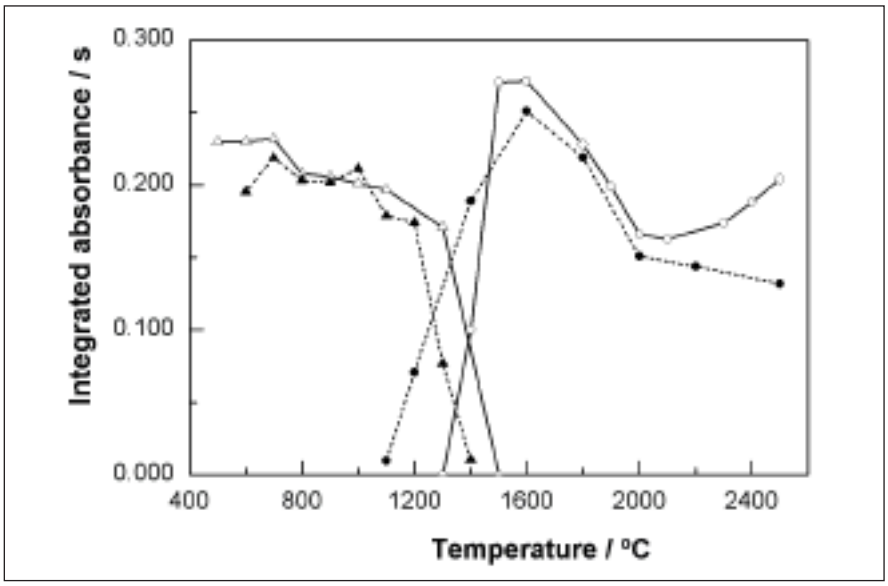

Fig. 1. Pyrolysis and atomization curves of lead from aqueous solution (–) and compost slurry (---).

RESULTS AND DISCUSSION

Optimization of the Furnace Programs

The pyrolysis and atomization temperatures were optimized using both aqueous solutions and slurried samples. The pyrolysis/atomization curves in the absence of chemical modifiers are shown in Figure 1. It can be seen that a maximum pyrolysis temperature of 900–1000ºC can be achieved for both aqueous solutions and slurries. A pyrolysis temperature of 700ºC was used for this study in order to avoid the rapid deterioration of the tubes. Optimum atomization temperatures used by other authors range from 1700–2100ºC (12), and an atomization temperature of 1800ºC was selected for our study.

Under the conditions described above, low recoveries were observed for the slurried samples, as will be shown below. Hinds and Jackson (11) reported similar effects when analyzing a soil enriched with humic acids (18% C) and found it to be due to the presence of organic carbon. These authors proposed the use of Pd-Mg chemical modifier (11) as well as the use of a fast temperature program and omitting the pyrolysis step (12). Both options worked well for the original soil, although some interference effects persisted when the soil was enriched with organic carbon (recoveries improved from 60% up to 85%).

In order to use palladium as the chemical modifier, we also studied the pyrolysis and atomization temperatures. The curves for both the aqueous solutions and the slurried samples in the presence of palla-

dium (15 µg per injection) are shown in Figure 2. The pyrolysis and atomization temperature selected was 1100 and 2200ºC, respectively. Lower atomization temperatures were not selected because a significant broadening of the transient signals was observed. Table I summarizes the furnace programs used.

Analytical Performance

The figures of merit for the determination of lead are listed in Table II. The characteristic masses, defined as the mass of analyte corresponding to 0.0044 integrated absorbance units, are in agreement with the values previously reported at the different wavelengths studied (22). When measurements were performed at the resonance wavelength of 283.3 nm, a linear range up to 1 ng was obtained, which can be extended up to 100 ng when the non-resonance wavelength of 368.3 nm is used. The limits of detection (following the three sigma criterion) were higher when using the palladium modifier and are due to the blanks obtained.

Repeatability represents the random error associated with analyte determination in the slurry and was calculated using the relative standard deviation for 10 successive injections of the slurry. The average relative standard deviation for 10 slurries was 4.0%. If repeatability from the ETAAS measurements of an aqueous standard of lead is around 1–2%, the other contribution to slurry repeatability comes from the measurement of lead in the solid particles, including their removel from the suspension, which can contribute up to 2% (23,24).

Reproducibility, which reflects the heterogeneity of the analyzed material at the mg level, was calculated from the relative standard deviation of the analysis of 10 different slurries. By using the median, a RSD of 7.4% was obtained.

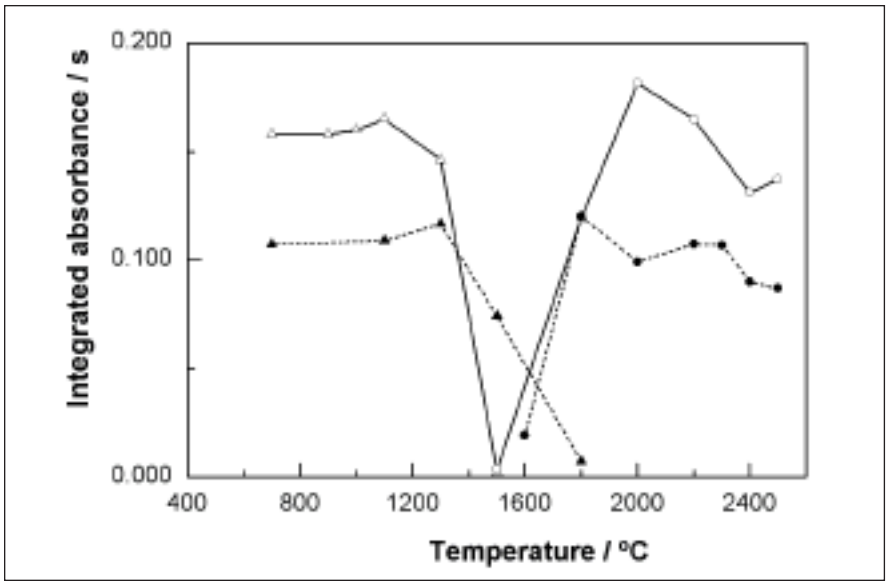

Fig. 2. Pyrolysis and atomization curves of lead from aqueous solution (–) and compost slurry (––). Chemical modifier: 15 µg of Pd.

Table I
Optimized Temperature Programs for the Determination of Lead in Compost

Step	Temp. (ºC)	Ramp Time (s)	Hold Time (s)	Ar Flow Rate (mL min^{-1})
Drying	200	1	60	250
Pyrolysis	700 [a] 1100 [b]	1	30	250
Atomization	1800 [a] 2200 [b]	0	5	0
Cleaning	2600	1	5	250

[a] Without chemical modifier. [b] With Pd (15 µg).

Table II
Figures of Merit for the Determination of Lead in Compost at Different Wavelengths

Wavelength (nm)	Chemical Modifier	Characteristic Mass (pg)	Linear Range (ng)	LOD[a] (µg g^{-1})
283.3	–	8.7	1	5.1
283.3	Pd	9.7	1	9.2
368.3	Pd	2050	100	1140

[a] Slurry preparation: 10 mg in 50 mL, furnace injection volume: 10 µL.

Analysis of Compost Samples

Compost samples of USRC2 urban solid residues and CP-1 compost reference material were analyzed following the optimized slurry procedure and the different temperature programs described above. Slurries for the USRC2 and CP-1 were prepared from 10 mg and 50 mg of sample and injecting 10 µL and 20 µL of slurry into the graphite furnace, respectively. The results, compared with those obtained from the samples dissolved by microwave-assisted digestion, are shown in Table III.

Recovery experiments were performed by spiking the samples with different amounts of lead. In the absence of chemical modifiers, recoveries lower than 80% were obtained for both the reference material and the real sample. The use of a fast temperature program, omitting the pyrolysis step and including a cool-down step (10 s at 50ºC), as suggested by Hinds et al. (12), did not improve the recovery. By applying the calibration by standard additions, the results were found to be comparable with those obtained by wet digestion. The use of palladium resulted in recoveries of around 100% for both samples, showing that aqueous standards can be used for calibration. After applying the corresponding Student's *t*-tests, no significant differences were observed for the results obtained for the slurry and the wet digestion procedures, as well as for the certified values of the reference material.

When the slurry concentration was increased to 1.2%, measured at the non-resonance wavelength of 368.3 nm for the USRC-2 compost sample, the interference effect of the matrix could not be removed even when palladium was increased to 50 µg, as shown in Table III. However, this wavelength can be useful when higher concentrations have to be measured (more than 1–2 mg g^{-1}) at low slurry concentrations.

Table III
Results for the Determination of Lead in Compost

Sample	Chemical Modifier	Wavelength (nm)	Slurry		Microwave Digestion	Certified Value
			Conc. (µg g^{-1})	Recovery (%)	Conc. (µg g^{-1})	Conc. (µg g^{-1})
CP-1	–	283.3	29.6±1.4 [a]	70		
	Pd (15 µg)	283.3	30.0±1.3 [b]	100	31.8±1.4	33±2
USRC-2	–	283.3	267±18 [a]	76		
	–	283.3	288±28 [a,c]	72		
	Pd (15 µg)	283.3	259±20 [b]	103	300±18	
	Pd (50 µg)	368.3	244±12 [a]	68		

[a] Standard additions calibration.
[b] Calibration with aqueous standards.
[c] Fast temperature furnace program.

Sources of Imprecision: Heterogeneity and Partitioning of the Analyte

The precision associated with the analysis of the sample by slurry sample introduction into the ETAAS depends on the heterogeneity of the sample and the analyte determination itself, which is related to instrument precision and distribution of the analyte between the liquid and the solid phases (25).

Although a significant analyte extraction is not necesary in slurry sampling ETAAS (26), it can improve precision and accuracy of the analysis. A solution of 5% nitric acid containing 0.004% of Triton® X-100 has been proposed as a general purpose diluent for slurry preparations (23). The surfactant serves as a wetting agent and avoids agglomeration of the particles, and the acid facilitates the extraction of the analyte to the liquid phase. This medium provided a 91% extraction of lead in the USRC2 compost sample, whereas with 0.1% nitric acid the extraction was limited to 56%.

The contributions to the precision of the analysis can be expressed as follows (27):

$$\sigma^2_{anal} = \sigma^2_{det} + m\,\sigma^2_{het} \qquad (1)$$

where σ^2_{anal} is the total variance associated with the analysis of the test portions, σ^2_{het} is the variance associated with the heterogeneity of the test sample, σ^2_{det} is the variance associated with the analyte determination, and m is the number of replicated measurements per test portion. These contributions were estimated from a one-factor analysis of variance and equation (1). Thus, 10 test portions of 10 mg each were withdrawn from the compost sample, and 10 replicate measurements were performed from each of the 10 slurries prepared. Outliers (around 6% of data) were discarded by applying the Dixon test before statistical calculations. Table IV shows the results of the one-factor analysis of variance performed, expressed as relative standard deviations (%RSD). An analogous experiment was performed where 25-mg test samples were suspended directly in 2 mL of diluent in the autosampler cups. Similar distribution of RSDs were obtained for both cases which suggests that the

Table IV
Contribution of Test Sample Heterogeneity and Analyte Determination to the total RSD of the Analysis

Test Sample (mg)	Total Volume (mL)	Wavelength (nm)	RSD_{het} (%)	RSD_{det} (%)	RSD_{anal} (%)
10	50	283.3	6.3	4.5	7.8
25	2	368.3	6.9	5.3	8.5
600	50	368.3	4.0	5.9	6.9

slurry preparation procedure was not a significant source of variability, even though a 2-mL aliquot has to be withdrawn when large volumes are used to prepare the slurry.

When the test portions were increased by more than one order of magnitude (up to 600 mg), the contribution of the sample heterogeneity was slightly lower than from the analyte determination. However, the differences between RSD values shown in Table IV cannot be considered statistically significant after applying the corresponding F-tests. These results show that the contribution of the determination to the total RSD is similar in the three experiments (4.5–6.0%) and of the same order as the heterogeneity of the sample (4–7%, depending on the mass used). Moreover, the total RSDs were not significantly affected by the amount of sample (7–9%). This behavior is justified by the high extraction of lead from the sample, which implies that only around 10% of lead is atomized from solid particles, minimizing its potential contribution to the imprecision due to the non-uniform distribution of the analyte in the sample.

CONCLUSION

Slurry sampling ETAAS can be successfully applied to the determination of lead in composts. The proposed method is simpler than those based on acid digestion of the sample, saves time, avoids the use of hazardous acid mixtures, and reduces the risk of contamination. The maximum allowable concentration of lead in compost, as proposed in the different European regulations regarding compost standards, can be determined with the slurry concentrations studied (0.02–0.1%). The interference effect produced by the matrix at these slurry concentrations can be easily managed by using palladium as the chemical modifier, allowing the use of direct calibration with aqueous standards. The precision of slurry sampling is comparable to conventional aqueous sampling. Using 5% nitric acid as the diluent, a high percentage of lead is extracted into the liquid phase, thus reducing imprecision due to the removal and atomization of particles from the slurry.

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Equilibrium Sorption Study for the Preconcentration, Removal, or Recovery of Nickel Ion From Aqueous Solution on Immobilized Silica Gel Followed by AAS Determination

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ABSTRACT

The potential use of a solid phase sorbent prepared via immobilization of salicylaldoxime on a silica gel surface for the purpose of preconcentration, removal, or recovery of Ni(II) from the aqueous phase has been investigated. The efficiency of the solid phase thus synthesized was evaluated by an equilibrium sorption study of Ni(II) in both the static and dynamic modes. The process is dependent on length of shaking period, agitation speed, adsorbent dose, pH, temperature, and flow rate of the feed solution. The adsorption data were fitted to the Langmuir adsorption isotherm model. The negative-free energy change indicates the process to be favorable.

The process was found effective for the removal and recovery of nickel ion from samples of various origins such as synthetics, industrial waste, and alloy. A 90% recovery and a 40-fold preconcentration factor were obtained for Ni(II) solutions of different concentrations up to 200 mg dm^{-3}. Merit of the process lies in its ability to determine trace amounts of nickel from a large sample volume following preconcentration.

At optimized conditions, the process is selective and can be used in the presence of other metal cations. The analytical data for the nickel content in the alloy sample NBS SRM-94C using the proposed method are comparable to certified value. The process is efficient, selective for nickel ion, and can be used without separating other constituents present in the sample matrix.

INTRODUCTION

Rapid industrialization together with too much use of fertilizers and pesticides in agricultural fields has created an enormous degradation of the environment. Toxic pollutants, particularly heavy metal ions, are released into the atmosphere, water streams, and soils and are subsequently absorbed by all living bodies such as plants, fish, and animals including human beings through the activities of breathing, eating, and drinking.

Trace amounts of nickel are present in plants and animals and small quantities in seawater, petroleum, and coal. Common nickel compounds present in large amounts produce toxic effects in humans and animals. Ni(II) binds to nucleic acids and produces significant detrimental genetic effects. It is known that occupational exposure to Ni(II) predisposes to lung and causes nasal cancer (1). Epidemiological studies show that nickel refinery workers in Britain have a five-fold increase in risk to nasal cancer compared to people in other occupations. Renal cancer has also been reported among Canadian and Norwegian workers employed in the electrolytic refining of nickel (2). Nickel dermatitis (3) is reported to be one of the most common forms of allergic contact dermatitis. In addition, nickel carbonyl is extremely toxic. The illness begins with headache, nausea, vomiting, and epigastria or chest pain, followed by cough, hyperpnoea, cyanosis, gastrointestinal symptoms, and weakness. The symptoms may be accompanied by fever and leucocytes; in more severe situations, it progresses to pneumonia, respiratory failure, and eventually cerebral edema and death. Autopsy studies show the largest concentration of Ni(II) in kidneys, but lesser amounts in liver and the brain. As per recommendations from the World Health Organization (4), the maximum nickel concentration in drinking water is $1.0.10^{-1}$ mg dm^{-3}.

In India, about 47% of Ni(II) is used in the production of steel and 21% for the production of other alloys. Ni(II) is also employed in a wide variety of commodities such as automobiles, batteries, coins, jewelry, surgical implants, and kitchen appliances. Other uses of nickel are as catalyst (as nickel oxide) in ceramics, storage batteries (Ni–Cd batteries), as nickel hydroxides in the dyeing process for coloring glass, in electronic components (as nickel carbonate), in food processing equipment, and in certain fungicides. Thus, nickel plating effluents that often contain more than 50.0 mg dm^{-3} of Ni(II) (5) have to be treated for the removal or separation of Ni(II) prior to discharge. At the same time, samples containing lower Ni(II) concentrations in large volume need enrichment or preconcentration for its precise determination.

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Solvent extraction, one of the most popular techniques for the separation or removal of metals, has limited application in concentrating trace amounts of ions present in large sample volumes. Adsorption processes offer a potential alternative for this purpose. Among the different types of adsorbents reported, active carbon (6), ion exchange resins (7), and various waste materials such as fly ash (8), rice husk ash (9), and waste Fe(III)/Cr(III) hydroxide (10) have been applied for the removal or separation of metal ions. Kantipuly (11) reviewed the application of chelating polymeric resins for the removal and separation of metal ions from industrial and other natural water systems. Modified granular activated carbon and modified clays are also used for metal removal in water treatment (12,13).

Recently, the solid phase extraction (SPE) technique has found wide application due to its versatile use, simple and cost-effective as well as fast procedure. SPE is based on the utilization of a major constituent as the supporting phase, with different ligand/chelating agents bonded through the functional groups either physically or chemically. Silica gel is found to act as a successful support for organo functional ligands since it does not swell or strain, has good mechanical strength, and can undergo heat treatment (14). The solid phases thus synthesized are stable, easy to prepare, and can be used selectively for the preconcentration of different metals. Preconcentration of metal ions with silica gel modified physically or bonded chemically has been applied successfully to various samples of different origins (15–30). Use of coating materials such as surfactants, poly electrolytes, etc., in conjunction with the immobilized silica phase (31–34) has also been reported. Investigations on the direct and simultaneous determination as well as preconcentration of Ni(II) via SPE have been reported recently (35–39).

In this study, the preconcentration, removal, and recovery of Ni(II) from the aqueous phase onto the surface of salicylaldoxime immobilized silica gel, the synthetic sorbent, following SPE, is investigated. Nickel ion concentration in the aqueous phase is determined using atomic absorption spectrometric analysis.

EXPERIMENTAL

Instrumentation

The IR spectra of the sorbent were registered with an automatic PerkinElmer Model L120-000A IR photometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The samples were prepared as thin films between KBr windows.

Atomic absorption measurement of Ni(II) was recorded on a Varian Model AA1407 atomic absorption spectrometer, equipped with a standard burner with an air-acetylene flame and using the 232.0-nm wavelength. A standard hollow cathode lamp was used as the line source with a slit width of 0.2 nm and a lamp current of 4.0 mA.

A Model 324 Systronics pH meter with glass electrode was used for pH measurements. The thermal analysis of the synthetic adsorbent was performed with a Shimadzu Model DT30 thermal analyzer to determine thermal stability. The column was a glass tube (160 x 6 mm) with a coarse sintered glass disc and a tap at the bottom.

Reagents and Standard Solutions

All chemicals were of analytical reagent grade. Silica gel H 4267 of particle size 60 µm, specific surface area 420 $m^2\ g^{-1}$ and pore size of 1200A, was obtained from Sigma. A nickel stock solution of 2.0 mg cm^{-3} nickel was prepared by dissolving nickel chloride in doubly distilled water. The pH of the experimental solution in the range of 3.5–6.0 was maintained with an acetate buffer by mixing acetic acid and sodium acetate. A pH below 3.5 was maintained by using HCl, while a pH above 6.0 was maintained using a NaOH solution.

Preparation of Immobilized Silica Gel as Synthetic Sorbent

Due to its high chelating tendency for metal ions (40) via -N, -O donors, the ligand salicylaldoxime was chosen for immobilization on the silica gel surface. The synthetic sorbent was prepared via impregnation of salicylaldoxime on silica gel as described elsewhere (41).

Preparation of Stock Solution From Alloy Sample

A 0.5-g amount of an alloy sample was fused with 10.0 cm^3 of water and 4.0 cm^3 of concentrated sulfuric acid. The extracted solution was then boiled with 2.5 cm^3 of concentrated nitric acid. The solution was cooled, filtered, and digested with 0.5 g acidified (sulfuric acid and phosphoric acid) potassium persulfate in the presence of silver nitrate. A stock solution of 500.0 cm^3 volume was made up after filtration and dilution with deionized water.

Adsorption Procedure

A batch experiment was performed in order to obtain rate, equilibrium, and isotherm data. The flask containing 20 cm^3 of Ni(II) solution (20–200 mg dm^{-3}) at the required pH was mixed with the synthetic sorbent (1.0 g) in a mechanical mixer until equilibrium was attained. The amount of Ni(II) in the supernatant was determined by atomic absorption spectroscopic measurement. The amount of Ni(II) adsorbed (q_e) per gram of synthetic sorbent (mg g^{-1}) was determined by the following equation:

$$q_e = (X–Y)/Z \qquad (1)$$

where X is the amount of Ni(II) added (mg), Y the amount of Ni(II) remaining in the supernatant (mg), Z the mass of the synthetic sorbent (g).

A column experiment was performed for retention and subsequent elution of the metal. A Ni(II) solution at a definite pH (between 2.0 to 8.0) was percolated at a fixed flow rate of 5.0 mL min^{-1} through the column. After washing the column with deionized water, an elution solution of definite composition was passed through at a flow rate 3.0 cm^3 min^{-1}. The metal ion concentration in the eluate, after dilution to the desired volume, was determined by AAS. Wet digestion of the samples with HNO_3 and H_2SO_4 was performed prior to determining the nickel concentrations by AAS and following the standard procedure (42).

RESULTS AND DISCUSSION

Characterization of Synthetic Sorbent

The synthetic sorbent was characterized following the elemental and spectral analyses. The stability of the sorbent towards heat and the inorganic acids was also determined. The results indicate that the salicylaldoxime ligand is immobilized as such without any structural change on the silica gel. Loading of the ligand was found to be 27±2 mg g^{-1} of silica gel. The sorbent is resistant to HNO_3 (4.5 mol dm^{-3}) and $HClO_4$ (2.6 mol dm^{-3}) and heats up to 60°C (43).

Batch Experiment

Role of Parameters Influencing the Retention of Nickel(II)

Effect of Initial Ni(II) Concentration and Mixing Time

It was observed that adsorption of Ni(II) on the synthetic sorbent in a batch process is dependent on the initial concentration and the mixing period (Figure 1). It was observed that the uptake rate of Ni(II) increases with a lapse in time and reaches equilibrium in 85 minutes for each initial concentration. The percent uptake decreases from 93.0 to 53.6% as the initial concentration increases from 20 to 200 mg dm^{-3}. It might be assumed that with an increase in Ni(II) concentration, the available sorption sites to metal ion load become fewer and effect a lower adsorption (30). The results further indicate that the saturation or equilibrium adsorption time is entirely independent of initial Ni(II) concentration (85 minutes in each case), while the extent of uptake is highly dependent on initial or added Ni(II) concentration.

Effect of Agitation Speed

Figure 2 shows the influence of agitation speed on the percent uptake of Ni(II) ions. As the agitation rate varies from 100 to 400 rpm for a fixed initial Ni(II) concentration (e.g., 100 mg dm^{-3}), the uptake of Ni(II) increases from 50.0 to 93.0%. With an increase in agitation rate, it may be assumed that the resistance to mass transfer in the bulk solution decreases and results in an increased driving force effecting increased metal retention.

Effect of Amount of Sorbent

The amount or dose of sorbent was varied from 0.1 to 1.5 g for 20 cm^3 Ni(II) solution (200 mg dm^{-3}) in order to study its effect on the percent uptake of Ni(II). The percent uptake increases with an increase up to 0.8 g and remains unaltered afterwards (Figure 3). A 1.0-g amount was maintained for all subsequent experiments.

Effect of pH

The adsorption behavior of Ni(II) on the sorbent at various pH values is shown in Figure 4. It was found that Ni(II) adsorbs quantitatively at pH 3.5. However, a control study with the untreated silica gel requires a much higher pH of 7.5.

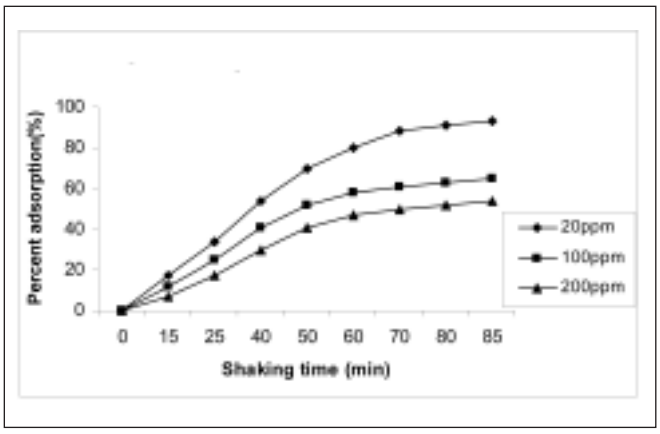

Fig. 1. Role of shaking time and initial nickel concentration on adsorption.

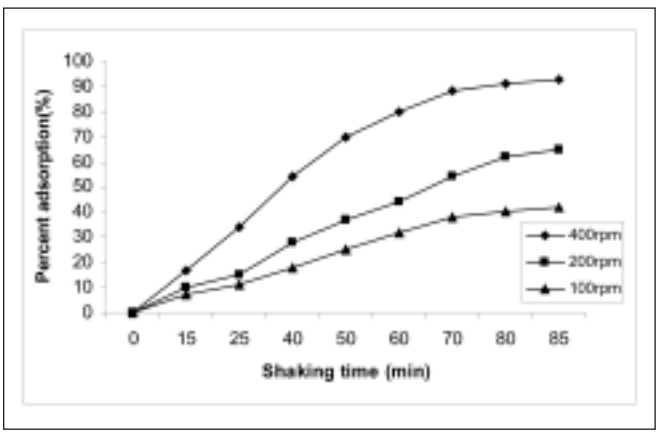

Fig. 2. Effect of agitation speed on adsorption.

Effect of Temperature

Temperature has an influence on the extent of metal retention on the sorbent. Within the studied range of 298–318 K it was found that metal ion retention on the sorbent increases with an increase in temperature (Figure 5). This may be due to an increased equilibrium constant at higher temperatures of the system.

Effect of Electrolytes, Foreign Ions, Complexing Ligands

The effect of different ions and salts towards retention of Ni(II) on the sorbent was ascertained from their levels of tolerance. Electrolytes such as sodium chloride, sodium nitrate, potassium nitrate, and potassium chloride have no influence on the retention process and were found to have highest tolerance (studied up to 1.0 g). Complexing agents such as EDTA, thiocyanate, and cyanide show tolerance levels of 5, 200, and 10 µg, respectively; however, beyond these levels, the extent of nickel retention decreases.

Fluoride and iodide ions are found to have lower tolerances of 150 and 200 µg, respectively, and hence their presence influences the extent of Ni(II) retention. On the other hand, acetate and phosphate ions do not influence the extent of Ni(II) retention since they have higher tolerances (at least up to 1 g for each). Alkali metals, alkaline earth metals, and ammonium salts do not retain on the said sorbents. The heavy metal ions Cu(II), Zn(II), and Fe(III) were found to retain on the adsorbent, but at much different pH values of the solution. Only Co(II) ion adsorbs simultaneously with Ni(II) ion in the studied pH range. Thus, even though selective separation of Ni(II) from Cu(II), Zn(II) and Fe(III) is expected, use of some organic modifiers would probably be effective in separating Co(II) and Ni(II). The separation of metals from bisolute compositions will be reported in future communications.

Adsorption Isotherm

The ability of the sorbent to extract Ni(II) from an aqueous solution at pH 4.2 was evaluated by measuring the sorption isotherm (Figure 6). The shape of the curve provides an indication of whether the adsorption is favorable or unfavorable. The L-type nature of the curve obtained in the present

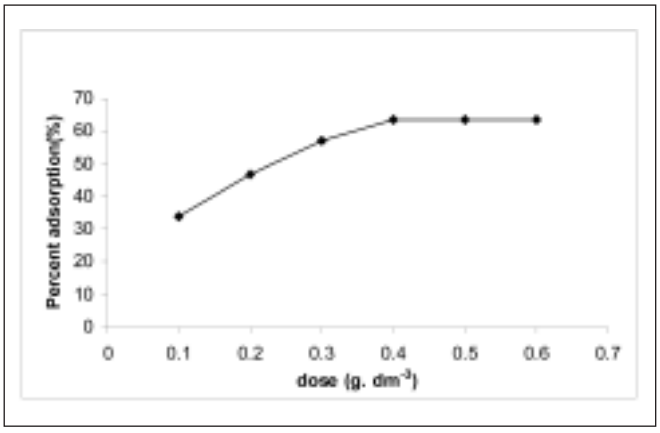

Fig. 3. Role of dose of adorbent on adsorption.

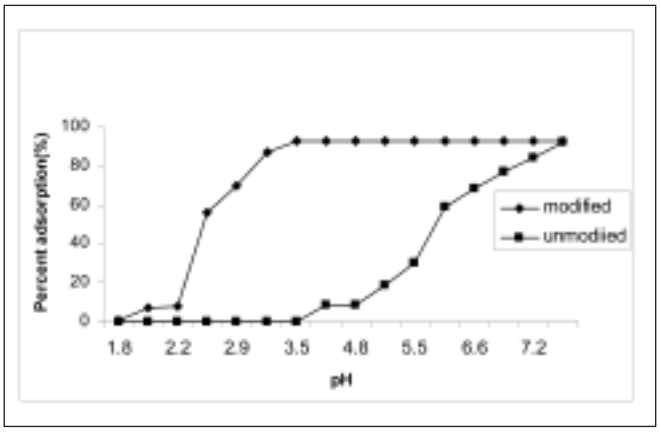

Fig. 4. Effect of pH on adsorption.

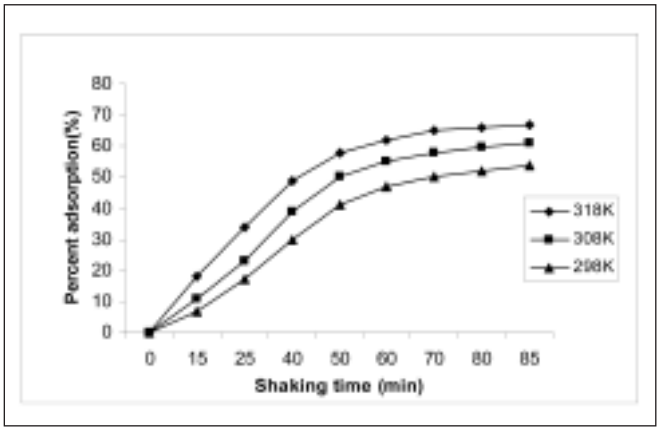

Fig. 5. Effect of temperature on adsorption.

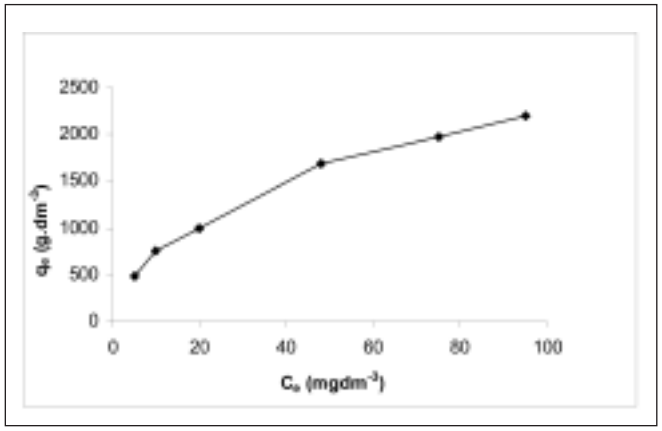

Fig. 6. Plot of adsoprtion isotherm.

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system indicates favorable adsorption with a strong tendency for monolayer formation. Data treatment revealed that the sorption data conformed to the Langmuir isotherm model, which is valid for mono-layer adsorption onto the surface containing a finite number of identical sites and is represented as:

$$1 / q_e = 1 / QbC_e + 1 / Q \quad (2)$$

where C_e (mg dm^{-3}) and q_e (mg g^{-1}) are the corresponding concentration and amount of Ni(II) adsorbed at equilibrium. Q and b are Langmuir constants and related to the adsorption capacity and energy of adsorption, respectively. The plot of $1/q_e$ versus $1/C_e$ at 298 K (Figure 7) yields Q (2.28 mg g^{-1}) and b (0.0916 dm^3 mg^{-1}) from the slope and intercept through linear regression. The high value of the regression coefficient (0.9825) indicates the validity of the Langmuir model. The adsorption capacity of the sorbent for Ni(II) corresponds to 4.0×10^{-2} mmol g^{-1}.

Evaluation of Equilibrium, Kinetic and Thermodynamic Constants

Application of the present sorbent for recovery of Ni(II) from large volumes of water demands the process to be favorable both kinetically and thermodynamically. The kinetic feasibility of the process is evaluated from $t_{1/2}$ value, defined as the time required for 50% of metal retention. The lower $t_{1/2}$ value for all the studied temperatures (Table I) indicates that the process is kinetically feasible. The free energy change (ΔG^0) of the process was calculated from the equilibrium constant (Kc) value following equations (3) and (4),

$$Kc = C_{Ac}/C_e \quad (3)$$

$$\Delta G^0 = -RT\ln K_c \quad (4)$$

where, C_e and C_{Ac} are the equilibrium concentration (mg dm^{-3}) of Ni(II) in solution and on the sorbent, respectively, R is the universal gas constant, and T is the absolute temperature. It was found that K_c increases with temperature. The negative value of ΔG^0 at all studied temperatures (Table I) indicates the thermodynamic feasibility of the process as well as its spontaneous nature.

Column Experiment

Effect of Flow Rate and Volume of Sample Solution

The effect of flow rate of the feed solution through the column on the retention behavior of Ni(II) was studied over the range of 1.0–10.0 cm^3 min^{-1}. The retention was quantitative and reproducible regardless of any change up to a flow rate of 6.5 cm^3 min^{-1} (Figure 8). Again, with a fixed amount of sorbent and for a fixed quantity of Ni(II), no change in retention was observed up to a volume of 1000 cm^3. The present study was conducted with a 20-mg dm^3 Ni(II) solution and the flow rate was maintained at 5.0 cm^3 min^{-1}.

Elution of Loaded Ni(II) From the Column

Elution of the retained Ni(II) was performed for the purpose of recovery or preconcentration of Ni(II) ion with different concentrations of HNO_3 or $HClO_4$. Elution

TABLE I
Evaluation of Equilibrium, Kinetic, and Thermodynamic Constants

Sample	K_c			$t_{1/2}$ (min)			$-\Delta G^0$ (kCalmol^{-1})		
Ni(II) Solution	298	308	318	298	308	318	298	308	318
		(K)			(K)			(K)	
	23.1	24.4	31.3	34	35	32	1.87	1.97	2.19

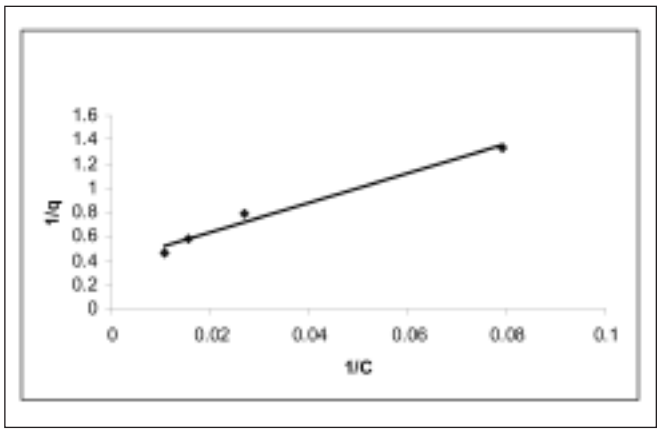

Fig. 7. Langmuir isotherm plot.

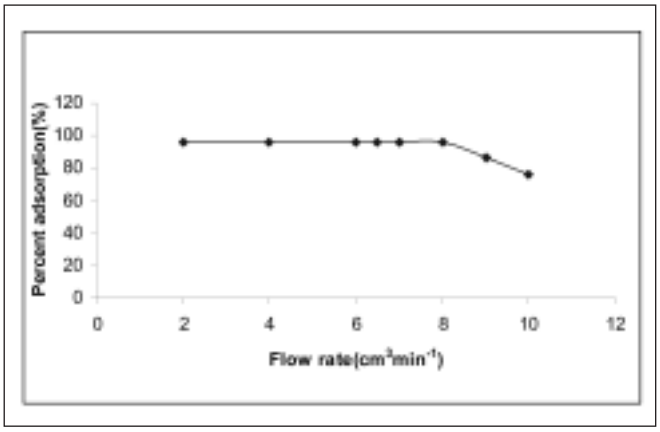

Fig. 8. Effect of flow rate on adsorption.

was effective with HNO_3 (1.0 mol dm^{-3}) and $HClO_4$ ($1.0.10^{-3}$ mol dm^{-3}) with 97.0% recovery of the retained Ni(II) ion.

Precision and Validation of Proposed Method

Precision of the proposed method was evaluated from the standard deviation (s.d.) value of replicate analyses and validation of the process was determined from spiked samples. A 1.0-mg dm^{-3} stock nickel solution was divided into 10 equal portions (100 cm^3 each). The nickel concentration in the first five portions was determined individually following the proposed method and the mean was calculated. Solutions of different Ni(II) concentrations (50.0 mg dm^{-3}) were spiked with each of the remaining five portions of the stock standard. Recovery of the Ni(II) in the samples was found to be 92.0–92.5% with a standard deviation of less than 0.06 at the 95% confidence level for five replicate analyses (Table II). The lower limit of detection of Ni(II) by the said process was found to be 1.5 μg dm^{-3} with the upper limit of Ni(II) concentration studied up to 200 mg dm^{-3}.

Effectiveness and Utility of Proposed Method

The effectiveness of the proposed method was judged using synthetic samples of Ni(II) solution of different concentrations up to 200 mg dm^{-3} and with some standard alloy sample (Table III). The utility of the synthetic sorbent as well as the feasibility of the process was tested with the effluent obtained from a typical electroplating industry. The preconcentration factor (P.F.) with subsequent recovery of Ni(II) (Table III) indicates a high degree (92%) of removal and recovery of Ni(II) from aqueous samples.

TABLE II
Recovery of Ni(II) From Spiked Sample

Sample No.	Concentration of Ni(II) Solution (mg dm^{-3}) Mean	Spiked	Found	Recovery (%)
1	1.0	0.0	0.92 ± 0.04	92.0
2	1.0	0.5	1.38 ± 0.04	92.0
3	1.0	1.0	1.84 ± 0.05	92.5
4	1.0	5.0	5.53 ± 0.06	92.2
5	1.0	10.0	10.16 ± 0.05	92.4
6	1.0	20.0	19.32 ± 0.04	92.0

n = 5; Standard deviation < 0.06; 95% confidence level.

TABLE III
Removal, Recovery and Preconcentration of Ni(II) Ion From Industrial and Alloy Samples

Type of Sample	Characteristics of Sample	Composition of Sample	Removal[a]/ Recovery[b] (%)	P.F
Industrial Effluent	Electroplating Waste	CN^-: 0.2; NH_4^+–N: 50; Cd^{2+}: 18.01; Pb^{2+}: 11.2; Zn^{2+}: 4.0; Cu^{+2}: 10.0; Cd^{+2}: 14.0; Ni^{+2}: 62.2; pH: 7.9; S.S: 100 (in mg dm^{-3}, except for pH)	92.3[a] (s.d.=0.37)	50
Alloy	NBS SRM-94C	Mn: 0.014; Sn: 0.006; Al: 4.13; Cd: 0.002; Fe: 0.018; Pb: 0.006; Mg: 0.042; Ni: 0.006. (in %)	90.0[b] (s.d =0.42)	40

(n = 5).

CONCLUSION

The present investigation shows that salicylaldoxime immobilized silica gel can be employed as an effective sorbent for removal and recovery of Ni(II) from water and waste. The removal was found to depend on time of contact, initial concentration, agitation speed, temperature, as well as pH of the medium in the batch method and influence of the flow rate in the column method. The equilibrium data fit the Langmuir adsorption isotherm model very well. The process is highly favorable from both a thermodynamic and kinetic point of view.

The efficiency of the prepared sorbent was tested with spiked samples ranging from 1 to 20 mg dm^{-3}. A >92% recovery of nickel with a standard deviation of <0.06 was obtained. The removal and preconcentration data for a typical electroplating waste were found to be 92.3% and 50, respectively, with a standard deviation of 0.37.

High recovery (>90.0%) of nickel with a preconcentration factor of 40 and a low standard deviation of 0.42 was obtained for some alloy samples. The content of nickel determined via preconcentration and following the proposed method is comparable with that of certified value for the standard alloy sample NBS SRM-94C. The

process was found to be selective at the optimized conditions for nickel ion and hence does not require separation of other constituents present in the matrix.

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Determination of Antimony in Seawater by Graphite Furnace Atomic Absorption Spectrometry With Zeeman-Effect Background Correction and Using Ammonium Nitrate as the Matrix Modifier

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ABSTRACT

An ETAAS method was developed for the determination of antimony (Sb) in seawater using ammonium nitrate as the matrix modifier plus Zeeman-effect background correction. The concentration selected for the modifier was 35.2 µg/mL, and the temperature program selected for the graphite furnace for a spiked sample was 1200ºC and 1900ºC for mineralization and atomization, respectively. The use of the standard additions method was mandatory due to the matrix effects observed.

The LOD and LOQ achieved were 2.7 and 9.0 µg/L, respectively; 9.6 pg was the mean characteristic mass obtained within the linear range of concentrations (0–20 µg/L Sb). The method was applied to spiked coastal seawater samples from the Mediterranean Sea.

INTRODUCTION

Among the major components of seawater are Cl^-, Na^+, Mg^{2+}, SO_4^{2-}, Ca^{2+}, and K^+ (1,2). The concentration levels of these components are almost constant in the sea, whereas the concentrations of trace components (such as antimony) usually show local variations, even at their lowest levels of concentration (3).

Though the literature concerning the concentration of antimony (Sb) in seawater is rather scarce, it is usually claimed to be below 1 µg/L (4,5), which causes problems related to matrix interferences and detection capability of the technique utilized. Moreover, given the importance of not only determining the total concentration of an element but also its speciation, it can be stated that the antimony species reported to be present in seawater are Sb(V) and Sb(III), as well as the two methylated acids: Methylstibonic acid [$H_3CSbO(OH)_2$] and dimethylstibinic acid [$(H_3C)_2SbO(OH)$] (5). However, Sb(V) (as hexahydroxyantimonate anion) is the predominant species (4), approximately in 20-fold excess in relation to Sb(III) (6).

Even though antimony is recognized worldwide as a non-essential yet toxic element for humans, the lack of legal regulations concerning maximum admissible levels of this substance in seawater (or at least in coastal seawater) must be highlighted. This absence becomes more relevant when one considers that the origin of the increase in antimony levels in seawater is usually anthropogenic. Therefore, the interest in developing methodologies aimed at determining this analyte in seawater needs no further explanation, even as a prior step to subsequent speciation analysis.

Over the past 20 years, literature published regarding the determination of antimony in seawater discusses the use of the following techniques: Advantage has been taken of the ability of antimony to form hydrides, combined with detection by hydride generation atomic absorption spectrometry (HG–AAS) (7,8) or hydride generation inductively coupled plasma mass spectrometry (HG–ICP-MS) (9,10). Anodic stripping voltammetry (11,12) and electrothermal atomic absorption spectrometry (ETAAS) have been applied as well (4,13,14). Moreover, in these works, the ETAAS determination of antimony in spiked seawater samples or reference materials is performed using the graphite furnace as the atomizer (GFAAS), whereas for nickel, nitric acid (4) or colloidal palladium (14) is the matrix modifier used.

In the determination of trace elements in seawater, the sample matrix (mainly sodium chloride) represents a major problem since it produces high background signals and non-spectral interferences (15). Therefore, several modifiers have been proposed in order to prevent the effects of this type of matrix, and ammonium nitrate is one of them. The behavior of this modifier in the presence of sodium chloride consists of the following reactions (16):

$$NaCl + NH_4NO_3 \rightarrow NaNO_3 + NH_4Cl$$

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

$$2\ NaNO_2 \rightarrow Na_2O + NO + NO_2$$

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This process involves the complete removal of the matrix at about 1100ºC, which can then be selected as the ashing temperature. If at such a temperature antimony losses do not take place, the use of ammonium nitrate would represent a clear advantage over the 700ºC temperature proposed by Smichowski et al. (13) or the 800ºC recommended by Sturgeon et al. (4).

The investigations described in this work propose the use of ammonium nitrate as the matrix modifier for ETAAS determination of antimony in seawater samples. The measurement conditions are evaluated as well as the analytical figures of merit. The method proposed is applied to spiked seawater samples obtained from the dock and beach area of Castellón de la Plana (a coastal Spanish city by the Mediterranean Sea).

EXPERIMENTAL

Instrumentation

The measurements were performed using a SpectrAA-600 atomic absorption spectrophotometer (Varian, Inc., Mulgrave, Victoria, Australia), equipped with a programmable sample dispenser, a Zeeman-effect background corrector, and a GTA 100 graphite furnace. The graphite tubes were pyrolytically coated and forked pyrolytic graphite platforms were used throughout.

Reagents and Standard Solutions

An ammonium nitrate solution of 352.0 µg/mL was prepared by dissolving 0.0352 g of NH_4NO_3 (p.a., Merck, Darmstadt, Germany) in ultrapure water and bringing the solution up to 100-mL volume.

Antimony(V) stock standard solution (1003.1 µg/mL) was prepared by dissolving 0.2166 g of potassium hexahydroxyantimonate (99.99%, p.a., Aldrich Chemical, Milwaukee, WI, USA) in ultrapure water and diluting to 100-mL volume. The working solutions were prepared from this solution.

Argon 5.0 was used for the atomizer, 99.999% purity (Praxair, Madrid, Spain).

Nitric acid (69.8 %) was used for trace metal analysis, ACS grade (J.T. Baker, Phillipsburg, NJ, USA).

Ultrapure water, resistivity 18 MΩ cm, was obtained with a Milli-Q™ water purification system (Millipore, Bedford, MA, USA).

Sampling Procedure

As proposed elsewhere (15), each sample was collected in a clean, dry 100-mL polyethylene (PE) bottle, then immediately acidified with 100 µL of concentrated nitric acid (resulting in a pH of <1.6) to avoid adsorption of trace elements to the PE walls. The samples were kept in a refrigerator until measurement.

Procedure for Antimony Determination in Seawater

The sample (prepared as described) was first warmed to room temperature, then 500 µL was mixed with ammonium nitrate solution at a concentration of 35.2 µg/mL in the final 1-mL solution (made up to volume with ultrapure water). The resulting solution was subjected to analysis by GFAAS using the conditions listed in Table I. Concentration of the analyte must be obtained by applying the standard additions method.

Cleaning of Material, Personal Care, and Waste Management

Contamination of the material (glassware and plastic ware) was prevented by washing and keeping it for at least 48 h in a 10% (v/v) HNO_3 solution. Afterwards, it was carefully rinsed several times with ultrapure water and left to dry before use.

Personal care devices (such as protective gloves, glasses, and gas masks) were used throughout when needed, given the toxicity of antimony compounds to man. The chemical wastes generated by this work were stored in appropriate containers and subsequently collected by the Service of Dangerous Waste Management of the University of Santiago de Compostela.

TABLE I
Measurement Conditions Obtained for Sb(V) for Standard and Spiked Sample Using NH_4NO_3 as Matrix Modifier

Step	Temp. (ºC)	Ramp (s)	Hold (s)
Dry 1	100	5	30
Dry 2	120	5	30
Mineralization	600[a] / 1200[b]	10[a] / 5[b]	5[a] / 25[b]
Atomization	1800[a] / 1900[b]	0	3 (read)
Clean	2100[a] / 2400[b]	1	1

Hollow Cathode Lamp	Sb
Lamp Current	10 mA
Wavelength	217.6 nm
Slit	0.2 nm
Measurements	Peak area
Integration Time	3 s, without delay
Background Corrector	Zeeman-effect
Ar Gas Flow	3.0 L/min; gas-stop during atomization
Volume Injected	20 µL

[a] Aqueous standard; [b] Spiked sample.

RESULTS AND DISCUSSION

Study of Temperature Program

The best temperatures and times for each step of the graphite furnace program were obtained both for an aqueous standard and the sample using NH_4NO_3 as the matrix modifier.

For the standard, an aqueous solution containing 25.1 µg/L Sb(V) and 70.4 µg/mL NH_4NO_3 was tested. Figure 1 shows that analyte loss was observed as the ashing temperature increased over the range studied. However, 600ºC was the 'compromise' ashing temperature selected, because the absorbance values recorded were slightly more precise at that temperature than at 500ºC, and because temperatures lower than 500ºC were considered not high enough for suitable matrix removal. For the atomization step, 1800ºC was the temperature chosen. In addition, as shown in Figure 1, the background absorption values were negligible.

For sample analysis, preliminary experiments showed the necessity to spike the samples, given the low antimony levels present. Thus, for a 1-mL solution containing 500 µL of sample, a Sb(V) spike of 25.1 µg/L with 70.4 µg/mL NH_4NO_3 was tested. Figure 2 shows that 1200ºC seems to be the best mineralization temperature in view of the high decrease in background signal for that temperature in comparison to the corresponding value recorded for 1100ºC. However, selection of the atomization temperature (1900ºC) was arrived at not only on the basis of the absorbance and background values, but also on the shape of the signals registered.

In addition, every other temperature (as well as the ramp and hold times of every step of the temperature program) was studied, both for the aqueous standard and the spiked sample. These steps resulted in the temperature programs listed in Table I.

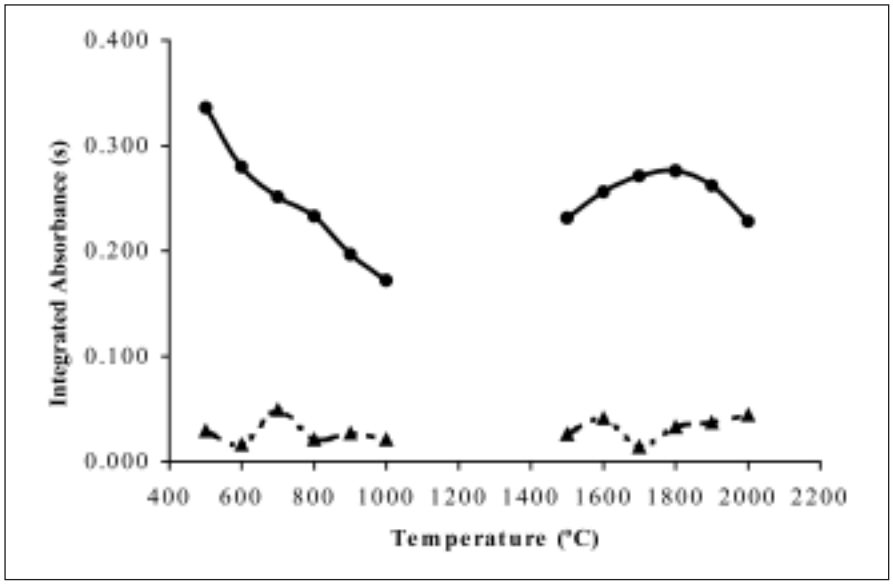

Fig. 1. Mineralization and atomization curves for an aqueous Sb(V) standard, using NH_4NO_3 as matrix modifier.
Solid line: atomic absorption; dotted line: background absorption.

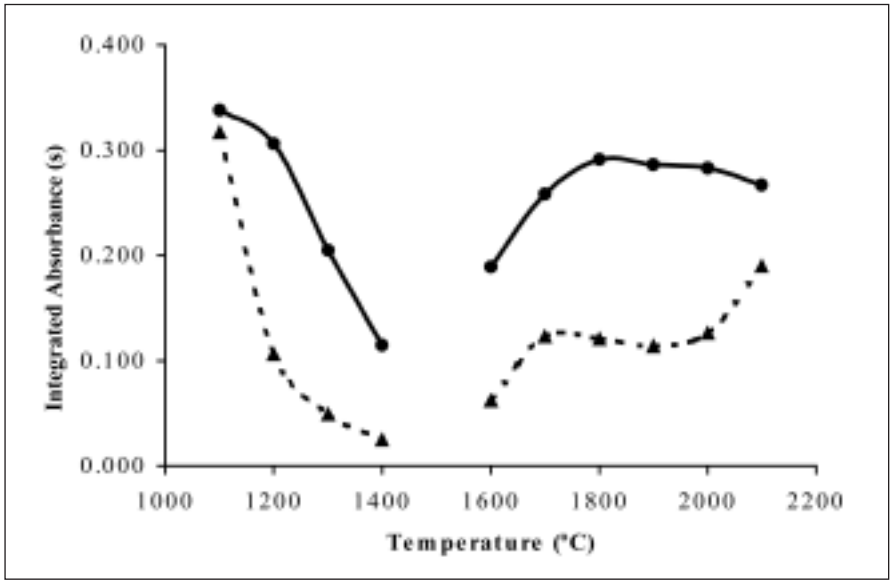

Fig. 2. Mineralization and atomization curves for a Sb(V)-spiked seawater sample, using NH_4NO_3 as matrix modifier.
Solid line: atomic absorption; Dotted line: background absorption.

Study of Amount of Matrix Modifier

The most adequate amount of matrix modifier (NH_4NO_3) to be used for standard and spiked samples was investigated. Accordingly, a series of standard solutions containing 25.1 µg/L Sb(V) and concentrations of NH_4NO_3 between 0.0 and 158.4 µg/mL were analyzed; the results are shown in Figure 3. In view of these results, it seems that the variation of the concentration of the modifier does not imply a reduction or a significant variation in the background signal. Therefore, a NH_4NO_3 concentration level of 70.4 µg/mL was not necessary (as was used in the studies described above) and it was decided to add NH_4NO_3 only up to the 35.2-µg/mL concentration level.

An analogous experiment was carried out on a series of 1-mL solutions each containing 500 µL of sample, a 25.1-µg/L Sb(V) spike, and NH_4NO_3 at a level of concentration between 0.0 and 158.4 µg/mL. The outcome of these measurements is shown in Figure 4 which, when compared to Figure 3, shows higher background signals and also lacks a variation of those signals concomitant with the variation in the concentration of the modifier. Again, 35.2 µg/mL NH_4NO_3 was chosen as a high enough concentration given that its use enabled higher ashing temperatures than those recommended for other modifiers, as pointed out in the Introduction section.

Moreover, since the absorbance values recorded in these studies for both the standard and the spiked samples and for both modifier concentrations (35.2 and 70.4 µg/mL) were quite similar, it was concluded that the studies performed to obtain the temperature programs listed were valid, despite the fact that they were performed with a different modifier concentration than the concentration finally selected (35.2 µg/mL).

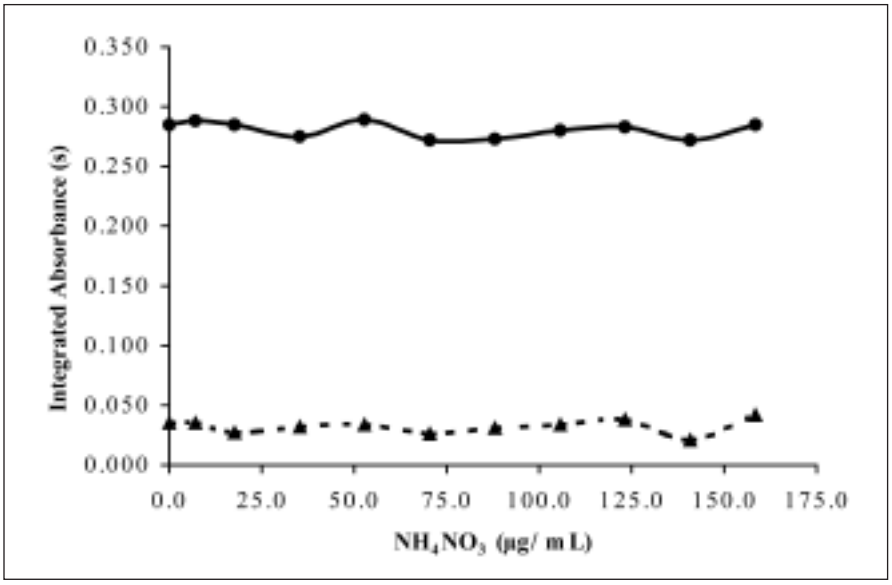

Fig. 3. Effect of concentration of NH_4NO_3 modifier on the measurements for an aqueous Sb(V) standard.
Solid line: atomic absorption; Dotted line: background absorption.

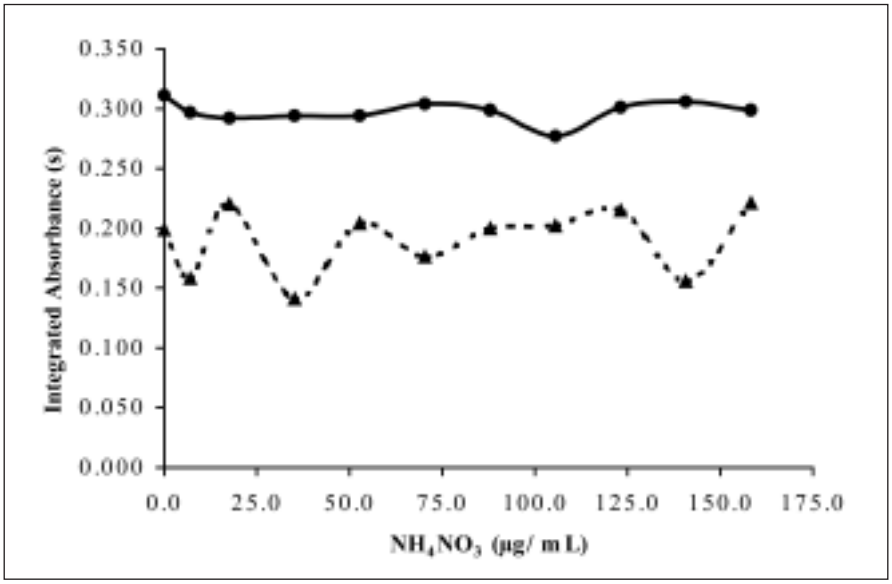

Fig. 4. Effect of concentration of NH_4NO_3 modifier on the measurements for Sb(V)-spiked seawater sample.
Solid line: atomic absorption; Dotted line: background absorption.

In view of the results obtained in this modifier study, the feasibility of eliminating the use of a modifier was also investigated. The background absorption recorded in the absence of a modifier was higher than when present. Thus, it was found more practical to add a small quantity of modifier in order to develop a method applicable to samples with a more complex matrix than the samples used for analysis in this work.

Analytical Figures of Merit

Linear Range of Concentrations

With the goal of finding the linear range of concentration and to check whether there was a matrix effect, an aqueous standards calibration was performed and the standard additions method applied to a sample. After carrying out the corresponding measurements, using the temperature programs and the modifier concentrations described above, the lines that fitted the data were calculated as follows:

Standard calibration:
$A = -2.20 \cdot 10^{-3} + 1.25 \cdot 10^{-2}\ C$

Standard additions:
$A = -5.40 \cdot 10^{-3} + 9.02 \cdot 10^{-3}\ C$

where A is integrated absorbance, C is the Sb(V) concentration in µg/L.

In view of this, the matrix effect is confirmed, which means that quantitative measurements must be performed using the standard additions method. Anyway, the response is linear (i.e., straight) up to at least 20 µg/L Sb(V), both for standards and samples.

Precision

A study of repeatability of the measurements at different levels of concentration was performed using a spiked sample. Four series of solutions were prepared. Each series consisted of ten 1-mL solutions each containing the same amount of sample (500 µL) and modifier (35.2 µg/mL NH_4NO_3) as well as an Sb(V) spike to give 5.0, 10.0, 15.1, and 20.1 µg/L, respectively. The corresponding GFAAS measurements (using the programs listed in Table I) produced the results in Table II, which are quite acceptable (the mean RSD of the measurements was 4.1%).

Accuracy

Since a certified reference material was not available, the accuracy of the method proposed was evaluated by means of analytical recovery. The results achieved (see Table III) are fairly good and imply a mean analytical recovery within the linear range of concentrations of 100.3%.

Sensitivity

Defined as the slope of the standard additions line, the sensitivity of the method was $9.02 \cdot 10^{-3}$ µg/L Sb(V). Moreover, the values of the limits of detection (LOD) and quantification (LOQ), as well as the characteristic mass (m0), were calculated and defined as follows (17,18):

$$LOD = \frac{3 \cdot s}{b} \qquad LOQ = \frac{10 \cdot s}{b}$$

$$m_0 = \frac{0.0044 \cdot V \cdot C}{A - A_b}$$

where s is the standard deviation of the blank; b is the slope of the standard additions line, V is the volume injected into the atomizer, C is the concentration of analyte, and A and A_b are the integrated absorbance values recorded for the standard and the blank, respectively, for each level of concentration studied.

Accordingly, the LOD and LOQ, respectively, were 1.3 µg/L Sb(V) (2.7 µg/L, referred to sample,) and 4.5 µg/L Sb(V) (9.0 µg/L, referred to sample). Finally, the mean m_0 within the linear range of concentration was 9.6 pg Sb(V). Therefore, the sensitivity of the method is guaranteed.

Application

The method developed was applied to seawater samples collected from the dock and beach area of Castellón de la Plana (on the Mediterranean Coast of Spain, near Valencia). However, the levels of antimony found were below the LOD of our method, and therefore the samples analyzed can be said to contain less than 2.7 µg/L of antimony.

CONCLUSION

The use of ammonium nitrate as the chemical modifier has proved to be advantageous in the determination of antimony in seawater by ETAAS, since it allows a higher ashing temperature and a lower atomization temperature than other modifiers proposed in the literature for this type of sample. It also provides a suitable removal of the

TABLE II
Repeatability of Measurements at Different Levels of Concentration of Sb(V) for Spiked Sample

Sb(V) Added (µg/L)	No. of Measurements	Mean Integrated Absorbance (s)	RSD (%)
5.0	10	0.044	5.2
10.0	10	0.082	7.4
15.1	10	0.122	2.4
20.1	10	0.156	1.3

TABLE III
Analytical Recoveries Obtained for Sample

Sb(V) Concentration (µg/L) Added	Found	Analytical Recovery (%)
5.0	5.1	102.0
10.0	10.0	100.0
15.1	15.0	99.3
20.1	20.1	100.0

matrix, which is one of the difficulties usually encountered when analyzing such complex samples as seawater.

In addition, the analytical characteristics of the method developed in this work clearly show that it enables reliable (i.e., precise, accurate, and sensitive) determinations, although the levels found in the samples analyzed lie below the LOD obtained.

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Inorganic Mercury Determination in Whole Blood Using On-line Microwave Digestion With Flow Injection Mercury System (FIMS)

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ABSTRACT

The ability to accurately determine inorganic mercury relative to total or organic mercury is essential for studies of human health effects and biomonitoring. This paper describes a flow injection mercury system (FIMS) with on-line microwave digestion for the determination of inorganic mercury in whole blood.

Recovery of inorganic mercury in diluted bovine and human whole blood was compared with the results of on-line microwave digestion and without microwave digestion. The results suggest that on-line microwave digestion was necessary for the full recovery of inorganic mercury from human whole blood but was not necessary from bovine whole blood.

The limit of detection, based on three standard deviations of a base blood material, was calculated to be 0.35 µg/L (n=793). The relative standard deviation was 17% at 1 µg/L of mercury in diluted whole blood (n=20) and 14% at 2 µg/L (n=20). Throughput was approximately 17 samples per hour for two readings. Calibration was linear up to 150 µg/L.

INTRODUCTION

The determination of inorganic mercury in whole blood is essential for examining human exposure to mercury from dietary (mainly methyl) versus environmental sources (inorganic or elemental). Exposure to inorganic mercury can occur through inhalation of mercury vapor, which can affect the lungs and the nervous system, and through ingestion of inorganic mercury, which can affect the kidneys (1).

Flow injection cold vapor atomic absorption spectrometry (FI-CVAAS) is an effective tool for analyzing mercury, where on-line sample pretreatment minimizes possible contamination, mobility, and evaporation of mercury, while allowing high throughput (2–5). In this analytical technique, mercury is oxidized into an ionic form (Hg^{2+}), which is then reduced to mercury vapor and measured by absorbance at 253.7 nm. When on-line microwave digestion is used, blood flows first through a 10-meter microwave coil (in knitted form) before the ionic mercury is reduced to vapor.

This method is based on a method designed by Guo and Baasner (2) for the analysis of total mercury in whole blood, which was modified in our study for measuring inorganic mercury in whole blood. Similar to their method, on-line microwave digestion was also used in this work. However, instead of a strong oxidizing solution (bromate/bromide) for diluting the sample, blood was diluted with a Triton® X-100 solution (a mixture of 0.12% [v/v] Triton X–100 and ≥18 $M\Omega.cm^{-1}$ ultrapure water) and instead of sodium borohydride (which is a strong reductant), stannous chloride was used, which is a weaker reductant.

Although on-line microwave digestion (combined with the FIMS) is described in the literature only for the determination of total mercury in whole blood (2–5), we demonstrate here that it can also be used to optimize the release of inorganic mercury from blood proteins without transforming the organic species into inorganic mercury, which is the reducible form.

Because an analytical system without on-line microwave is simpler and faster than one with on-line microwave, we compared its ability to recover inorganic mercury from whole blood with a system containing on-line microwave. Both human whole blood and bovine whole blood were compared using the two systems.

EXPERIMENTAL

Instrumentation

A PerkinElmer FIMS™–400 atomic absorption (AA) spectrometer was used, consisting of a flow injection mercury system and an AS–91 autosampler (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The FIMS is fully controlled from a personal computer using AA WinLab™ software (6). The instrumental parameters are listed in Tables I and II. In addition, a Maxidigest MX 350

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microwave digester (Prolabo, Paris, France) was used, in which the sample flows into a knitted digestion coil (3D–Digester loop, 10 m long). A 500-µL sample coil was used to inject the diluted blood sample.

Because excess blood foam in the gas-liquid separator (PerkinElmer) might flood the filter and the quartz cell leading to the detector, a modified 10-mL glass volumetric pipette (KIMAX Class A, glass volumetric pipette which was cut 3 cm at each side of the expanded area) was added onto the gas-liquid separator. This specific design reduces the surface tension as the blood flows through the gas-liquid separator, thus preventing blood foam from traveling toward the filter and the detector (Figure 1, Foaming Control Expansion Chamber). Such minimization of blood foam also reduces the amount of antifoam added to the reductant ($SnCl_2$), thus decreasing the possibility for clogging the manifold's mixing blocks and tubing.

Reagents and Standard Solutions

All reagents were prepared with analytical reagent grade chemicals and high-purity water with a resistance of ≥18 MΩ.cm^{-1} (NANOpure DIamond Ultrapure Water System, Barnstead International, Bedford, MA, USA).

Reducing Solution:
A 2.5% (w/v) stannous chloride (SnCl2) solution was prepared daily by dissolving 25g of stannous chloride suitable for mercury determination (J.T Baker Chemical Co., Phillipsburg, NJ, USA) in 5% (v/v) HCl, adding 1 mL silicon antifoaming agent (Dow Corning DB–110A, Atlanta, GA, USA), and diluting to 1-L volume with 5% HCl.

TABLE I
FIMS and FIAS Parameters (FIMS-400)

Parameter	Setting
Wavelength	253.7 nm
Slit Width	0.7 nm
Technique	AA
Signal Measurement	Peak Height
Smoothing Point	9
Microwave Power Level	20%
Read Time	35 s
Read Delay	0

TABLE II
Flow Injection Program: Inorganic Mercury Measurements

Step	Time (s)	Pump 1 Speed (rpm)	Pump 2 Speed (rpm)	Valve Position	Read Step
Prefill	4	100	90	Fill	
1	7	100	90	Fill	
2	40	0	90	Inject	
3	35	0	90	Inject	X
4	1	0	90	Fill	

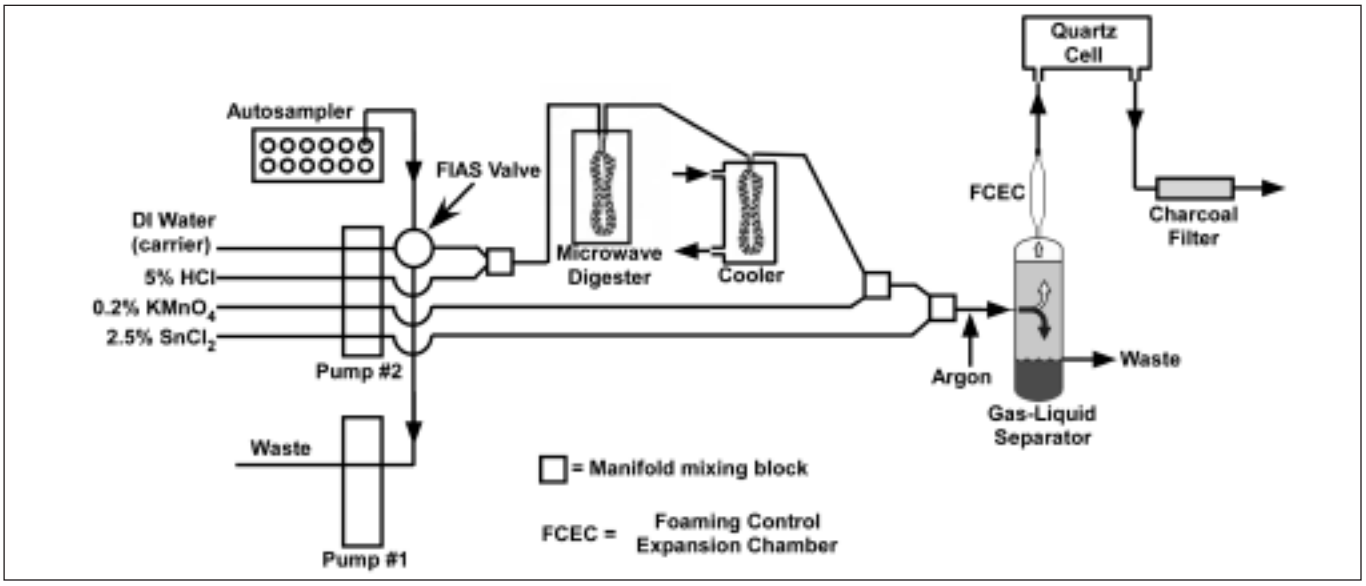

Fig. 1. Schematic diagram of the FIMS-400 with on-line microwave digestion

Oxidizing Reagent:
A 0.2% (w/v) potassium permanganate solution (J.T. Baker Chemical Co., Phillipsburg, NJ, USA) was prepared weekly by dissolving 2.0 g of potassium permanganate in ultrapure water and diluting to 1-L volume with ultrapure water (stored in dark bottles).

Hydrochloric Acid Solution:
A 5% (v/v) hydrochloric acid solution (J.T. Baker Chemical Co.) was prepared daily by mixing 50 ml of concentrated hydrochloric acid solution with ultrapure water and diluting to 1-L volume with ultrapure water.

Triton Solution:
A 0.12% (v/v) Triton solution was prepared monthly by dissolving 0.6 mL of concentrated Triton X–100 (J.T. Baker Chemical Co.) in 500 mL ultrapure water and diluting to 1-L volume with ultrapure water.

Carrier Solution:
Ultrapure water was prepared daily.

Mercury Stock Solutions

(a) Inorganic mercury ($HgCl_2$ – NIST SRM 3133, 10 mg/mL):
A 25-µg/L working standard was prepared every 6 months by diluting the stock solution with 10% HCl.

(b) Methylmercury (CH_3HgCl):
A 100-µg/L working standard was prepared every 6 months by diluting 50 µL of 1000 mg/L methylmercury (II) chloride (Alfa Products, Danvers, MA, USA) in 50 mL ultrapure water.

Quality Control Materials

Three types of quality control materials were used to evaluate the method:

(a) Reference material NIST SRM 966–2 (National Institute of Standards and Technology, Gaithersburg, MD, USA, Standard Reference Material) composed of bovine whole blood spiked with both inorganic and methylmercury stock solutions.

(b) Quality control material from the Centre de Toxicologie du Quebec (Quebec, Canada) composed of human whole blood spiked with inorganic mercury.

(c) Human whole blood (Tennessee Blood Services, Memphis, TN, USA) and bovine whole blood (Baxter Healthcare Co., Deerfield, IL, USA) spiked in our lab with combinations of inorganic and methylmercury stock solutions.

Calibration

Bovine whole blood with undetected levels of mercury and spiked with different amounts of inorganic mercury was used for preparing a calibration curve. 0 µL, 10 µL, 20 µL, 40 µL, and 80 µL of the 25-µg/L working standard were dispensed into 15-mL conical tubes containing 200 µL of bovine blood diluted with 2.0 mL of the Triton solution, which correlates to mercury concentration levels of 0, 1.25, 5.0, 10.0, and 20.0 µg/L, respectively (calculated based on 11 times dilution factor of the sample, where 200 µL of blood is mixed with 2 mL of the Triton solution). A matrix-matched calibration curve was used.

Sample Preparation and Measurement

After whole blood samples are diluted off-line by a factor of 11 (200 µL of blood mixed with 2 mL of the Triton solution), blood flows from the autosampler into a valve containing a 500–µL loop (volume of blood injected), and mixes with 5% (v/v) HCl solution in the first mixing block of the manifold. This blood-acid mixture flows into the microwave through the digestion coil and upon returning to the manifold, reacts with the oxidizing reagent ($KMn0_4$) in the second mixing block and with the reducing solution ($SnCl_2$) in the third mixing block, where mercury vapor is formed. In the fourth mixing block, argon gas is introduced, carrying the mercury vapor through a gas-liquid separator and a quartz cell into the spectrometer for detection at peak height. Table III lists the functions of Pump 1 and Pump 2.

Table III
Pump Tubing

Solution	Color Code	I.D. (mm)	Flow Rate (mL/min)
Pump 1			
Sample	yellow/blue	1.52	9–11
Pump 2			
Carrier Solution:	yellow/blue	1.52	9–11
HCl	red/red	1.14	5–6
$KMnO_4$	red/red	1.14	5–6
$SnCl_2$	red/red	1.14	5–6
Cooling:			
Water	black/white	3.18	32–35
Waste	violet/violet (two tubings)	2.06	35–40

RESULTS AND DISCUSSION

Recoveries of inorganic mercury from human blood spiked with different combinations of inorganic and organic (methyl) mercury averaged 105% (90%–115%) in a system containing on-line microwave digestion, and 61% (53%–71%) in a system without microwave digestion (Table IV). Since organic mercury is usually the predominant species in human blood (mostly methyl), combinations of organic and inorganic mercury were spiked with higher proportions of organic mercury in order to simulate actual patient samples. Recoveries of inorganic mercury from the Quebec whole blood reference materials (composed of human blood) averaged 99.8% (81%–115%) with on-line microwave digestion, and 59% (32%–92%) recovery without microwave digestion (Table V).

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TABLE IV
Recovery of Inorganic Mercury from Human Whole Blood Spiked With Combinations of Inorganic and Methylmercury

Mercury Spiked (µg/L)		Inorganic Target Values (µg/L)	Inorganic Measured Mean Values (µg/L)		% Recovery	
Organic	Inorganic		With Microwave (n=5)	Without Microwave (n=5)	With Microwave	Without Microwave
4	1	1	1.08 (0.83–1.4)	0.67 (0.52–0.78)	108	67
15	15	15	17.0 (13.2–19.6)	8.2 (7.0–9.2)	113	55
12	3	3	3.1 (2.5–3.8)	1.6 (1.3–1.9)	103	53
10	5	5	4.8 (4.4–5.3)	2.7 (2.2–3.3)	96	54
10	10	10	11.5 (10.9–12.1)	5.6 (3.8–7.6)	115	56
1	1	1	0.95 (0.82–1.1)	0.56 (0.42–0.7)	95	56
15	4	4	4.2 (3.6–5.3)	2.8 (2.1–4.0)	104	70
5	1	1	1.15 (0.95–1.3)	0.71 (0.6–0.9)	115	71
8	2	2	2.2 (1.8–3.0)	1.1 (0.75–1.3)	110	55
2	2	2	1.8 (1.2–2.6)	1.4 (0.75–2.1)	90	70
			Average % Recovery:		**105**	**61**

Recovery of inorganic mercury from human blood without microwave digestion corresponded to about 60% (Tables IV and V), suggesting that microwave digestion was responsible for about 40% of the recovery. We did not use a stronger acid (on-line) to mix with the blood (which might have helped to increase the recovery of inorganic mercury without microwave digestion) because it would have caused frequent clogging in the sampling valve, manifold, and tubing due to precipitates formed by denatured blood proteins (4), and would have also increased the possibility of converting organic mercury to inorganic mercury.

With bovine blood as the matrix, recoveries of the samples spiked with inorganic and organic mercury (Table VI) averaged 104% (93%–117%) using microwave digestion compared to 101% (89%–117%) without microwave digestion. Figures 2, 3, and 4 show the concentration of inorganic mercury in human and bovine blood obtained with and without a microwave digestion step.

With on-line microwave digestion, human blood spiked with only organic (methyl) mercury resulted in 0% recovery of inorganic mercury up to 20 µg/L of sample, and 3% - 4% recovery for samples between 20 and 40 µg/L (Table VII). According to the Third National Report on Human Exposure to Environmental Chemicals (1), 95% of the total number of U.S. population measured for total blood mercury [National Health and Nutrition Evaluation Survey (NHANES) 1999–2002] corresponded to less than 7.1 µg/L and the geometric mean to less than 1 µg/L (levels that are consistent with those of other countries), suggesting that this slight conversion of organic mercury into inorganic mercury is not likely to affect epidemiological measurements.

The limit of detection (LOD), based on three standard deviations of a base blood material with a 500-µL sample loop, n=793) was 0.35 µg/L with on-line microwave digestion, and 0.40 µg/L (n=40) without microwave digestion. The relative standard deviation (RSD) (n=20) using on-line microwave digestion was 17% at 1 µg/L of blood and 14% at 2 µg/L, while without microwave digestion, the RSD (n=20) was 13% at 1 µg/L of blood and 14% at 2 µg/L. (Precision values were established using low and medium bench control materials, which are composed of bovine blood spiked in our lab with both inorganic and organic mercury. The results were calculated using data from seven days of analyses.)

The calibration curve was linear up to 150 µg/L for both systems. Throughput for a system with on-line microwave digestion, based on two readings per sample, was about 3.5 minutes per sample (about 17 samples per hours), and about 1.5 minutes per sample in a system without microwave digestion.

TABLE V
Recovery of Inorganic Mercury from Whole Blood Samples Obtained From the Centre de Toxicologie du Quebec (CTQ)[a]

CTQ ID	Inorganic Target Values (μg/L)	Inorganic Measured Mean Values (μg/L)		% Recovery	
		With Microwave (n=4)	Without Microwave (n=4)	With Microwave	Without Microwave
M-02-18	6 (3.8–8.2)	6.1 (5.2–7.2)	4.2 (3.5–4.5)	101	70
M-02-12	23 (17.4–28.6)	22.7 (21.0–23.9)	8.1 (7.5–9.1)	104	35
M-02-15	18.4 (13.8–23)	16.1 (14.7–16.9)	5.8 (4.6–6.9)	91	32
M-02-17	23 (17.4–28.6)	23.1 (19.7–24.9)	9.1 (6.2–10.7)	86	40
M-04-07	9.4 (6.6–12.2)	9.8 (9.6–10.1)	6.0 (3.3–8.0)	106	64
M-04-09	54 (42.2–65.8)	58.1 (54.9–60.1)	49.6 (34.2–65.7)	102	92
M-04-11	7.6 (5–10)	8.6 (6.5–12.4)	4.7 (4.4–5.2)	113	62
M-04-02	23 (13–33)	18.6 (16.3–25.2)	11.4 (9.9–13.2)	81	50
M-04-18	32 (26–39.4)	31.8 (25.7–36.7)	20.4 (17.1–22.8)	99	64
M-04-15	24 (18.2–29.8)	27.6 (23.8–33.0)	19.9 (18.1–21.9)	115	83
		Average % Recovery:		**99.8**	**59.2**

[a] Human blood containing inorganic mercury only.

Recovery of inorganic mercury without microwave digestion was satisfactory for bovine blood, but not for human blood. With on-line microwave digestion, however, recovery of inorganic blood mercury was satisfactory both for bovine and human blood, suggesting that elevated temperatures help with the process of releasing inorganic mercury from blood proteins.

CONCLUSION

The FIMS flow injection mercury system, combined with on-line microwave digestion, is an accurate, precise, and fast tool for the recovery of inorganic mercury in both human and bovine whole blood samples. Without microwave digestion, however, satisfactory results were obtained only for inorganic mercury determination in bovine blood, suggesting that such a system is not optimal for human studies. With the on-line microwave system, sample manipulation is minimal, the system is fully automated, and throughput is suitable for large epidemiological studies.

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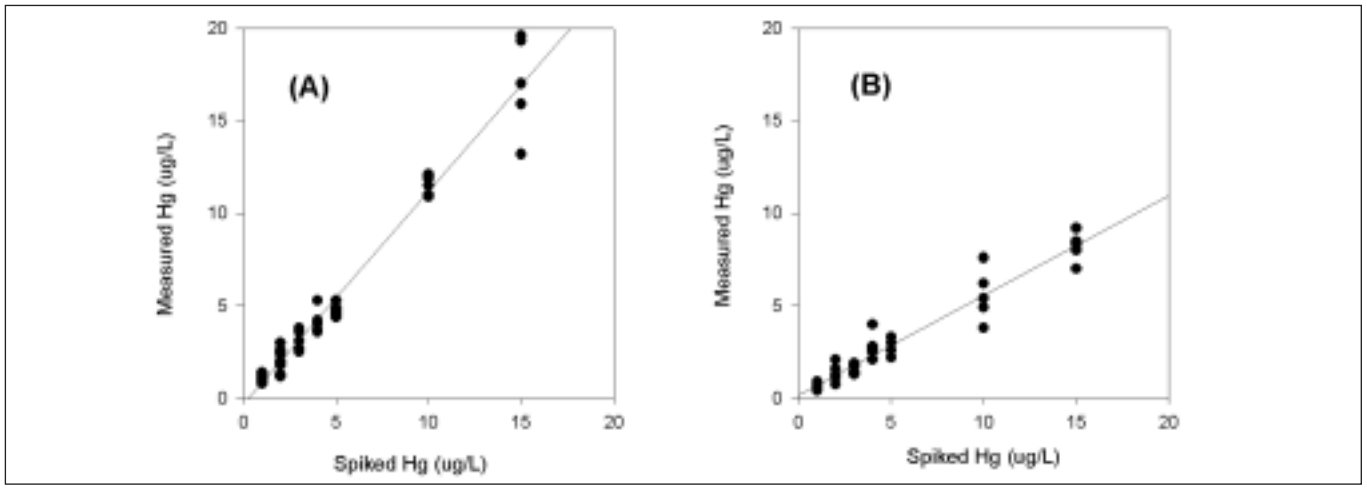

Fig. 2. Performance results of inorganic blood Hg concentrations in human blood spiked with combinations of inorganic and organic (methyl) Hg. (A) Microwave: slope = 1.15, r^2 =0.9694, (n=50); (B) Without microwave: slope = 0.56, r^2 = 0.9433, (n= 50)

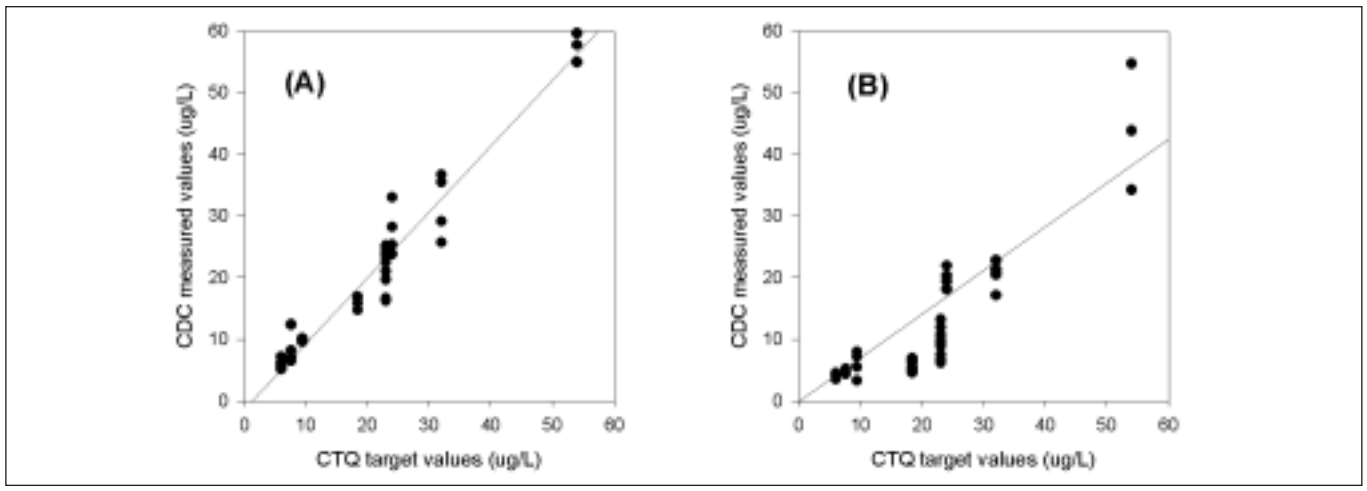

Fig. 3. Performance results of inorganic Hg concentrations on Centre de Toxicologie du Quebec whole blood samples. (A) Microwave: slope = 1.07, r^2 = 0.9480, (n=40); (B) Without microwave: slope = 0.71, r^2 = 0.7940, (n=40)

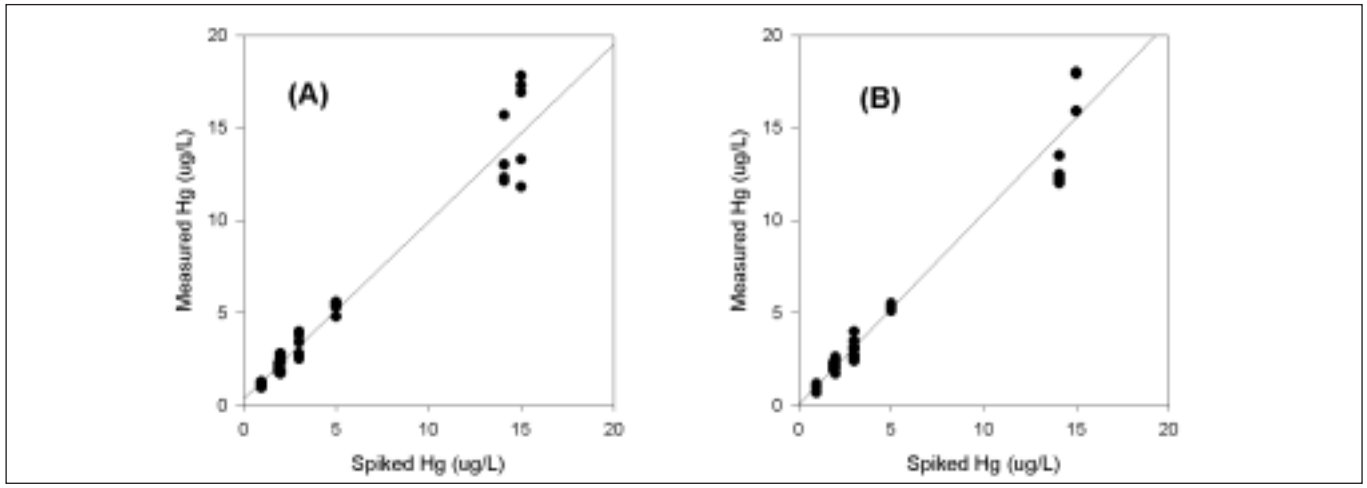

Fig. 4. Plots of inorganic Hg concentrations in bovine whole blood spiked with combinations of inorganic and methylmercury. (A) Microwave: slope = 0.96, r^2 = 0.9560, n=45; (B) Without microwave: slope = 1.03, r^2 = 0.9604, (n=45)

TABLE VI
Recovery of Inorganic Mercury From Bovine Blood Spiked With Combinations of Inorganic and Methylmercury

Mercury Spiked (µg/L)		Inorganic Target Values (µg/L)	Inorganic Measured Mean Values (µg/L)		% Recovery	
Organic	Inorganic		With Microwave (n=5)	Without Microwave (n=5)	With Microwave	Without
2	2	2	2.1 (1.7–2.8)	2.0 (1.7–2.3)	105	100
12	3	3	3.5 (2.8–3.8)	3.4 (3.0–4.0)	117	107
10	5	5	5.3 (4.8–5.6)	5.3 (5.1–5.5)	106	104
8	2	2	2.3 (1.9–2.8)	2.5 (2.2–2.6)	115	110
15	15	15	15.4 (11.8–17.8)	17.5 (15.9–18.0)	103	117
LowBenchQC[a]		1.0	1.1 (0.97–1.3)	1.0 (0.68–1.15)	111	100
MediumBenchQC[b]		2.16	2.0 (1.8–2.1)	2.0 (1.9–2.3)	93	93
HighBenchQC[c]		3.0	2.9 (2.5–4.0)	2.7 (2.4–3.2)	97	90
NIST SRM 966-2[d]		14.1±1.1-	13.1 (12.1–15.7)	12.5 (12.0–13.5)	93	89
			Average % Recovery:		**104**	**101**

[a] Bench quality control material spiked in our lab with 1 µg/L organic (methyl) and 1 µg/L inorganic Hg.

[b] Bench quality control material spiked in our lab with 8 µg/L organic (methyl) and 2 µg/L inorganic Hg.

[c] Bench quality control material spiked in our lab with 3 µg/L organic (methyl) and 3 µg/L inorganic Hg.

[d] Certified values of 14.1±1.1-µg/L for inorganic mercury and 31.4±-1.7 µg/L for total mercury (bovine blood).

TABLE VII
Recovery of Organic Mercury (MeHgCl) Spiked in Human Blood Using On-line Microwave Digestion

Spiked Organic Mercury (µg/L)	Measured Mean Value (µg/L) (n=2)	% Recovery[a]
1	0.21	0
2	0.20	0
5	0.23	0
10	0.34	0
20	0.7	3.5
40	1.8	4.5

[a] Percent recovery is indicated as zero when result is below detection limit, 0.35 µg/L.

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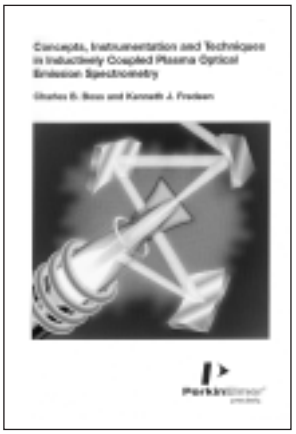

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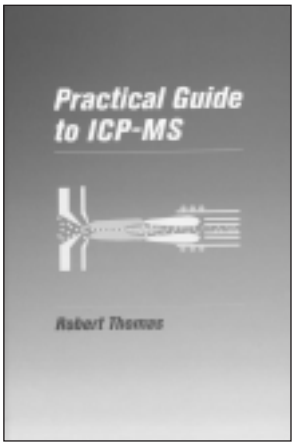

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