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On-line Sequential Determination of Cr(III) and Cr(VI) With Selective Elution of Solid Extracts Using an Alumina Column

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ABSTRACT

Many of the most recent developments in analytical and environmental chemistry involve metal speciation studies. For chromium it is possible to distinguish between the toxic hexavalent species and the non-toxic trivalent species. The purpose of this study was to develop a method for the quantification of chromium using an on-line system for the separation and preconcentration of both species. The research builds on previous publications using an alumina column and eluent solutions of ammonia for Cr(VI) and nitric acid for Cr(III). However, this approach facilitates either the determination of Cr(VI) or Cr(III), but not both from the same sample injection. Using standards containing both Cr(III) and Cr(VI) in Na_2CO_3/NaOH media at a pH of 7.5 ± 0.5, both species are retained on the column simultaneously, and are then eluted selectively and sequentially using ammonia solution and nitric acid. Similar results were obtained with samples containing Cr(VI). The optimum conditions obtained were 2M ammonia, 1.5M nitric acid, with a flow rate of 2 mL min^{-1}. Two types of samples, marine sediments and cements, were analyzed. The LODs were 0.45 $\mu g_{CrVI}\ g^{-1}$(alkaline extraction) / 0.38 $\mu g_{CrVI}\ g^{-1}$(water extraction), and 2.9 $\mu g_{CrIII}\ g^{-1}$(alkaline extraction) / 1.2 $\mu g_{CrIII}\ g^{-1}$(water extraction). Speciation recoveries were 102 ± 4% and 101 ± 5%, and the percent relative standard deviation of peak area was 7.1% and 8.7% for Cr(VI) and Cr(III), respectively. The overall recovery of the procedure of alkaline extraction/speciation for Cr(VI) was 99 ± 3% (75 $\mu g_{CrVI}\ g_{cement}^{-1}$); and linear ranges extended to 150 $\mu g\ L^{-1}$ for Cr(III) and 200 $\mu g\ L^{-1}$ for Cr(VI).

INTRODUCTION

Large volumes of Cr waste in various chemical forms are generated from industrial processes and discharged into the environment. These anthropogenic discharges of Cr result from industrial activities such as plating, tanning, paint and pigment production, chromite ore processing or cement production, where both the trivalent and the toxic and carcinogenic hexavalent compounds are used (1). Due to the different toxicity and bioavailability of the Cr species, environmental studies need to investigate the speciation of this metal (2). Several sample types have undergone study utilizing speciation analysis (3,4) with particular attention to pre-treatment techniques (5,6). Most of this work has focused on speciation in water samples, but additionally there are speciation studies based on industrial materials, soils, sediments, geological samples, sludge, clinical and biological samples, and also foods (7,8).

There are fewer analytical methods capable of identifying and quantifying chromium species in solid samples than there are for waters. Identifying one of the species in this kind of sample usually involves its selective extraction from the matrix. Different alkaline extraction procedures have been applied to extract all the chemical forms of Cr(VI) in solid samples. Hexavalent chromium has been extracted in these samples using sodium hydroxide or by Na_2CO_3/NaOH with and without heating (9). Cr(VI) determination in environmental media such as soils, sediments, and solid waste is routinely achieved following the USEPA Method: SW-846 Method 3060. The alkaline protocol (USEPA Method) has been evaluated positively for the accurate quantification of total Cr(VI) (10) and, therefore, the selective extraction is completed with the speciation of the extract. This should facilitate simultaneous speciation of both species, Cr(III) and Cr(VI), rather than the determination of only one of the chromium species in the alkaline extract of the solid samples investigated.

There are many publications describing the liquid chromatographic separation of aqueous species of Cr(VI) and Cr(III) (11). For solid samples, ion exchange may be applied following a previous alkaline extraction (12). Additionally, non-chromatographic solid

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adsorbents have been employed in flow injection systems for preconcentration prior to the speciation of chromium. Several metal oxides, e.g., ZrO_2, TiO_2, MgO, CeO_2, or Al_2O_3, have been used as selective adsorbents in preconcentration systems for aqueous solutions (13–16). Water samples containing Cr(III) and Cr(VI) were analyzed with simultaneous preconcentration using a small column of acidic or neutral activated alumina. The species were eluted with ammonia solution for Cr(VI) and with nitric acid solution for Cr(III) (17–20). For solid samples, speciation was investigated applying weak extraction methods prior to the separation of the chromium forms; here, the acid-activated aluminium oxide adsorbed Cr(VI) at pH 2–7, while the Cr(III) was not retained (21,22). Many of the above methods are based on the simple and inexpensive chromium speciation with alumina because of its high affinity for both Cr(III) and Cr(VI), but most of the studies have been for a water matrix and required pH changes to preconcentrate and separate the species. Hence, the determination was not simultaneous.

The aim of this study was to determine the speciation of chromium in extracts from solid samples. There are no previous publications describing the use of alumina for the speciation of chromium in extracts of solid samples retaining both Cr(VI) and Cr(III) simultaneously into the alumina column from the same sample injection.

Chromium speciation in marine sediment and cement samples was investigated to complete this work. Cements were studied because of health risks and its international interest. The European Commission recommends that cement should not be placed on the market or used as a substance or be a constituent of a preparation for manual activities when there is a risk of contact to the skin, and if it contains more than 2 μg g^{-1} (0.0002%) soluble Cr(VI) (23). The other samples investigated were marine sediments where speciation is used to establish toxicity and environmental consequences. Sediments are useful indicators for monitoring heavy metals pollution since these are usually present at higher levels than in waters from the same sampling site.

EXPERIMENTAL

Instrumentation

A schematic diagram of the instrumentation used is shown in Figure 1. The individual components included a Rheodyne Model 7060RV, 6 Position/6 Port standard valve (Bensheim, Germany), a Model Minipuls™-3 peristaltic pump (Gilson, Villiers le Bel, France), and a PerkinElmer® Model 3110 flame atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) with a chromium hollow cathode lamp (Cathodeon, Cambridge, UK). Other instrumentation used during sample preparation included a shell freeze system (Labconco, Kansas, USA), Centromix Selecta Model 540 centrifuge (Centromix, Abrera, Spain), Sartorius Model BP121S analytical balance (Sartorius, Goettingen, Germany), "Vibromatic" shaker from Selecta, "Agimatic" magnetic stirrer from Selecta, polytetrafluoroethylene (PTFE) column (5 cm length, 3 mm i.d.), and polyethylene (PE) tubings and connectors from Gilson and PerkinElmer. Redox potential and pH measured were with a Thermo Orion Model 720 pH meter (Thermo Orion,

Fig. 1. On-line system for preconcentration and quantification of Cr(VI) and Cr(III) of the solid extracts: Photograph and schematic.
Numbers 1, 2, and 3 correspond to the order of the pumped solutions through the system: 1(sample extract), 2(ammonia 2M), and 3(nitric acid 1.5M). V: valve; P: peristaltic pump; C: alumina column; B: air-bleed, and D: FAAS detection system.

Beverly, MA, USA) equipped with a Thermo Orion Model 8102BN glass body combination pH electrode and a Model Inlab 501 ORP electrode (Mettler Toledo, Greifensee, Switzerland).

Reagents

Reagents used included chromium standard solution of $Cr(NO_3)_3$ (Merck, Darmstadt, Germany); potassium chromate PR (Panreac, Barcelona, Spain); sodium hydroxide pellets PA (Panreac, Barcelona, Spain); sodium carbonate anhydrous extrapure (Scharlau, Barcelona, Spain); ammonia solution 25% PA (Panreac, Barcelona, Spain); nitric acid 69% (Hiperpur from Panreac, Barcelona, Spain); sulphuric acid 95-98% (J.T. Baker B.V., Deventer, Holland); and aluminium oxide 90 active neutral (activity stage I) for column chromatography (Merck, Darmstadt, Germany). Where necessary, dilution was realized with Milli-Q™ water (18 MΩ cm, Millipore Corporation, Bedford, MA, USA).

Sample Collection and Pre-treatment

Extraction and speciation procedures were applied to two types of samples: environmental and industrial.

(a) The marine sediment samples were obtained from an estuary polluted with chromium compounds. The surface sediment samples were collected from the Arousa Estuary (Northwest Spain) with a grab, operated from on board the ship R/V Mytilus. The samples were removed from the surface layer with a polyethylene spatula to avoid contamination, and then stored in a hermetically sealed polyethylene bottle at –22ºC to avoid changes in sample speciation. The bottles had previously been cleaned with 10% nitric acid for 24 hours and rinsed with Milli-Q water. The samples were lyophilized in a shell-freeze system and then sieved through a 63-µm nylon mesh before storing in polyethylene bottles. In heavy metal studies, the effect of variable grain size is reduced by the separation of the fine fraction of the sediment (24). The size-normalized data for chromium was obtained analyzing the sediment fraction of <63 µm.

(b) The cement samples used for this study were collected from four sampling points in the line production of a factory and stored in hermetically sealed polyethylene bottles at room temperature. The particle size was again <63 µm.

Alumina On-line Speciation System

The speciation and preconcentration system employed used an activated acidic alumina column that was prepared, as in previous chromium concentration works published (25), by mixing 2 g of Al_2O_3 with 3–5 mL nitric acid (6M), boiling for 5 minutes, rinsing with water, and then packing into the PTFE column. The column capacity was 0.5 g of Al_2O_3. Stock solutions and sample solutions were introduced into the system using a 6-port valve. First, sample/standard was pumped through the column, followed by the elution of Cr(VI) with ammonia, and finally by the elution of Cr(III) with nitric acid solution (Figure 1).

RESULTS AND DISCUSSION

Chromium Extraction and Speciation

Two different extraction procedures were applied to determine the total Cr(VI) and the water-soluble Cr(VI) levels. In addition, an evaluation was made as to whether or not Cr(III) was extracted simultaneously.

For the total extraction of one of the chromium species from the solid samples, the alkaline extraction procedure described in the USEPA SW-846 Method 3060 was evaluated. With this extraction, the total hexavalent species was obtained with a pH of >12, which also renders the trivalent chromium insoluble. The extractant was a mixture of Na_2CO_3 (0.28M)/NaOH (0.5M) which liberated all the chemical forms of Cr(VI) from the solid sample.

The study of water-soluble Cr(VI) in cements followed the TRGS 613 procedure (26) which involved a shaking step of the sample with Milli-Q water. Both the total Cr(VI) and the water-soluble Cr(VI) extraction methods listed in Table I completed the study of the forms of Cr(VI) in the samples. Both extracts were separated from the residual solid fraction by centrifuging at 3000 rpm for 10 minutes. Once separated, the alkaline

TABLE I
Conditions Applied to the Solid Samples to Extract Total Soluble and Insoluble Cr(VI)[a] or Water-soluble Cr(VI)[b]

Item	Alkaline Extraction[a]	Water-soluble Extraction[b]
Weight of sample with particle size of < 63 µm taken / g	2	1
Extractant Solution	Na_2CO_3(0.28M)/ NaOH(0.5M)	Milli-Q Water
Extractant Solution Volume (mL)	20	6
Extraction Temperature (°C)	90–95	Ambient
Extraction Time (min)	60	15
Extraction Conditions	Magnetic Stirring	Mechanical Shaking
Acidification	pH between 7–8	pH between 7–8

extract was diluted 50-fold with Milli-Q water and the pH adjusted to 7.5 ± 0.5 with 3M sulphuric acid. The pH working range used for the alumina column was between 6–8, and avoiding other pH values where the simultaneous retention and sequential elution of chromium species was not possible. The solution was then injected into the on-line alumina system (Figure 1). The water extract was also centrifuged and its salt composition was modified by adding an aliquot of the of Na_2CO_3/NaOH solution using the same pH working interval (7.5 ± 0.5). The volume of the saline solution added was sufficient to achieve an overall 50-fold dilution, but not the same dilution of the sample extract.

On-line Speciation Using an Activated Alumina Column

For the initial investigations, only single chromium species solutions were used. It was found that Cr(III) was not liberated by the ammonia solution, but conversely Cr(VI) was liberated with ammonia while not giving any signal during the nitric elution/cleaning step. The concentration of the extractant solution (Na_2CO_3/NaOH) was found to be critical for the working conditions of the Al_2O_3 column.

Two parallel studies (Figure 2) were carried out to investigate the working conditions of the chromium speciation in the alumina column:

(a) Na_2CO_3 (0.28M) / NaOH (0.5M) (concentration of the USEPA Method SW-846 3060 for alkaline extraction) diluted and the pHs adjusted to 7.5 ± 0.5. All pH of the extractant solutions (Na_2CO_3/NaOH) were adjusted with sulphuric acid to give a working pH between 7–8 in order to achieve relative stability of both chromium species. The original alkaline extractant was eluted at different times (25-, 50-, and 100-fold) with Milli-Q water. All dilutions were spiked with 100 µg L^{-1} of Cr(III) and 100 µg L^{-1} of Cr(VI), then injected into the on-line system.

(b) Synthetic solutions containing sodium concentrations were prepared with NaCl to achieve an equivalent sodium content in the alkaline dilutions. To study the cationic effect in chromium speciation, different sodium concentrations equivalent to the extractant solutions studied were analyzed to compare the results of Cr(III)/Cr(VI) retention and the elution in the alumina column (Figure 2). These different concentrations of the sodium solutions were prepared with NaCl at the same pH interval and the pH was adjusted where necessary with the ammonia used for the Cr(VI) elution. The sodium chloride solutions were spiked with the same chromium content of both species; but the absence of sulphates (anions that interact with alumina) in the sample solutions (NaCl) makes total preconcentration of the Cr(III) species not possible and gives a chromium signal with the sample pumping step.

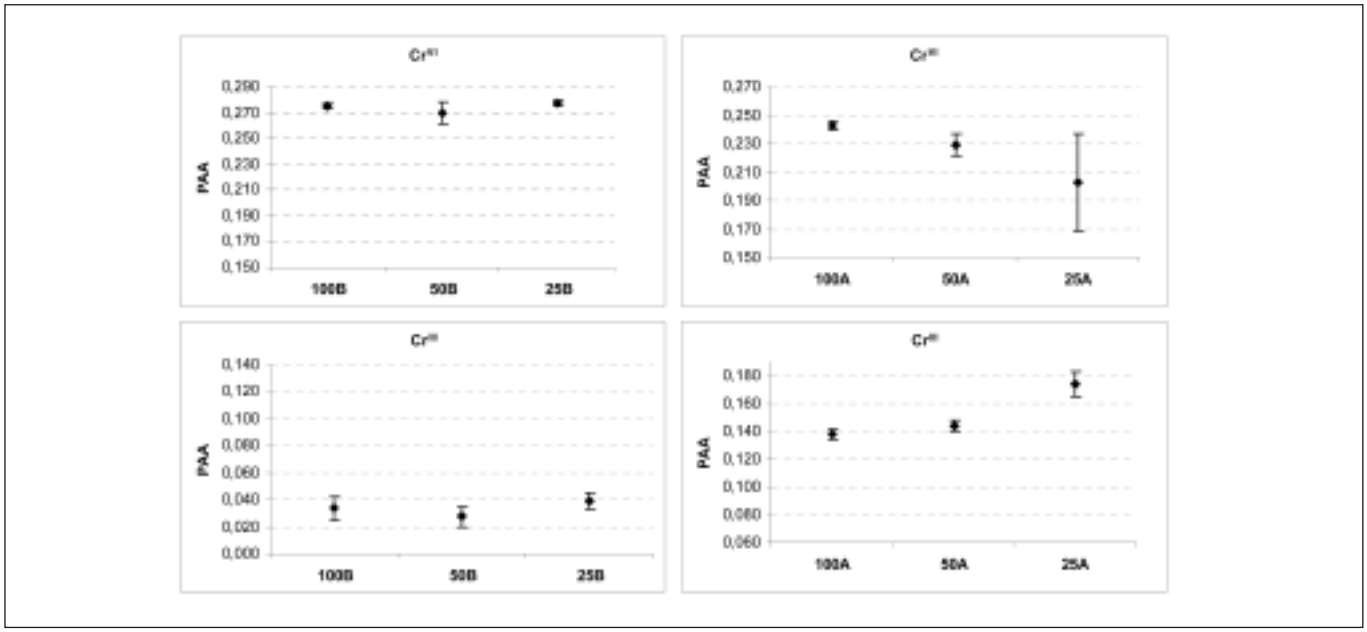

Fig. 2. Study of Na_2CO_3 (0.28M) / NaOH (0.5M) effect in the alumina column by means of peak absorbance area (PAA) of chromium species, and parallel study with the same sodium content (NaCl) in all dilutions.
A: Na_2CO_3 (0.28M) / NaOH (0.5M) solution with 100-, 50-, and 25-fold dilutions;
B: NaCl solutions with dilutions having the same concentration of sodium content in A solutions.

The results demonstrate that the sodium concentration is not enough for the speciation work. The column needed both an anionic and cationic charge and interaction with the chromium retention and speciation. Figure 2 shows that diluting the extractant only 25-fold results in the smallest absorbance peaks for Cr(VI) (corresponding to the highest sulphate concentration added) but the highest peaks for Cr(III). Although a 100-fold dilution gave better results for Cr(VI), they were poorest for Cr(III). Reversible and reproducible injections of both species were obtained using at a 50-fold water dilution of the Na_2CO_3 (0.28M) / NaOH (0.5M) solution where both species are reproducible, with reversible retention and elution.

Optimization of the Pumping Flow Rate

Peak profiles depend directly on the pumping flow rate introduced into the air-acetylene flame and the flame aspiration flow. Coupling of the column with the FAAS instrument was achieved by the simple connection of the aspiration tube of the nebulizer to the end tube of the column. Since the flow rate of the pump through the column has little effect on the aspiration flow rate, an air flow was added to compensate for this change between pump and nebulizer. The air flow was introducted with a T-connection at the end of the column. The post-column flow rate (mL min^{-1}) versus the pump speed (rpm) was studied and a linear working range was obtained up to 40 rpm (flow rate = $0.0516 \times rpm + 0.0340$; $r^2 = 0.9996$) without leaking. The higher flow rates of the system (2 mL min^{-1}) gave the best absorbance peak shapes. Pump speeds higher than 40 rpm, the last point of the linear range, led to a leaking of the aqueous solution. The changes in time elution and peak shapes are shown in Figure 3.

Optimization of Cr(III) and Cr(VI) Elution

The mentioned amphoteric properties of aluminium oxide and its interaction with metals like chromium are well known for workers who started studies of metal adsorption onto alumina at a different pH. Previously mentioned studies of chromium speciation have used ammonia and nitric acid solutions for the selective elution of chromium species. The pH was critical and in most studies the preconcentration and speciation was not simultaneous. Publications concerning chromium speciation in water using alumina columns have focused on the retention of the hexavalent chromium that is eluted using ammonia solutions at a specific pH. In this study, by changing the pH, the trivalent chromium becomes retained on the alumina and is then eluted with nitric acid. The alkaline matrix in the present study completely changed the mechanism of the adsorption properties of the alumina. A change in pH was not necessary when the alkaline saline concentration of the solutions, pumped through the alumina column, was kept constant. Both Cr(VI) and Cr(III) were retained and preconcentrated simultaneously for the same sample injection: Cr(VI) eluted first with ammonia, followed by Cr(III) with nitric acid. The nitric acid also served to clean the system.

The initial concentration of eluents during the optimizations was 1.5M for ammonia and 1M for HNO_3. The first eluent studied was ammonia. The results of the univariant optimization of the ammonia concentration for the liberation of the hexavalent chromium species are shown in Figure 4(a). With 0.5M ammonia, the peaks were broad and the analysis was more time-consuming. At higher concentrations of ammonia (2M and 3M), sharper peaks were obtained and the total liberation of the analyte was more rapid. A concentration of 2M (30–45 seconds at 2 mL min^{-1}; see Table II) was selected to avoid degradation of the alumina column arising from extreme changes in pH.

For the trivalent species, the peak shapes were better when the nitric acid concentration was higher. As with ammonia, the lowest acid concentration that yielded a well-shaped absorbance peak while eluting all of the analyte was selected. Figure 4(b) shows that a concentration of 1.5M (30–60 seconds at 2 mL min^{-1}; see Table II) was sufficient to achieve a good peak shape.

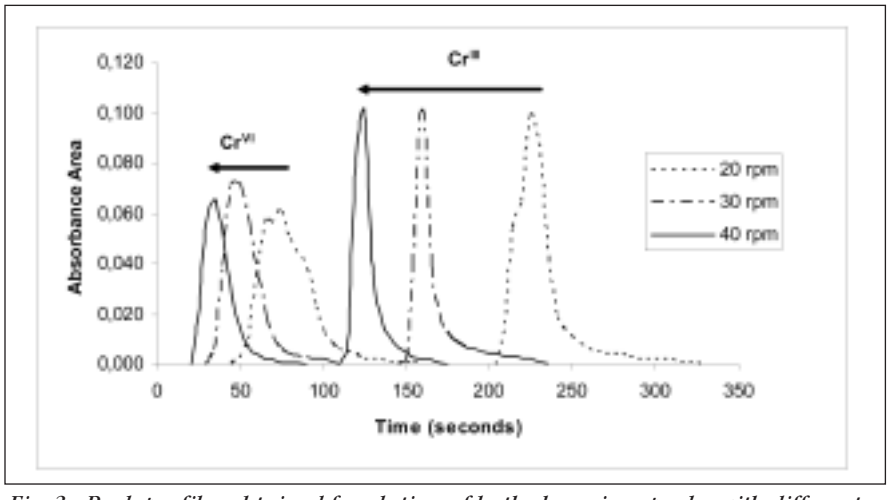

Fig. 3. Peak profiles obtained for elution of both chromium peaks with different flow rates.

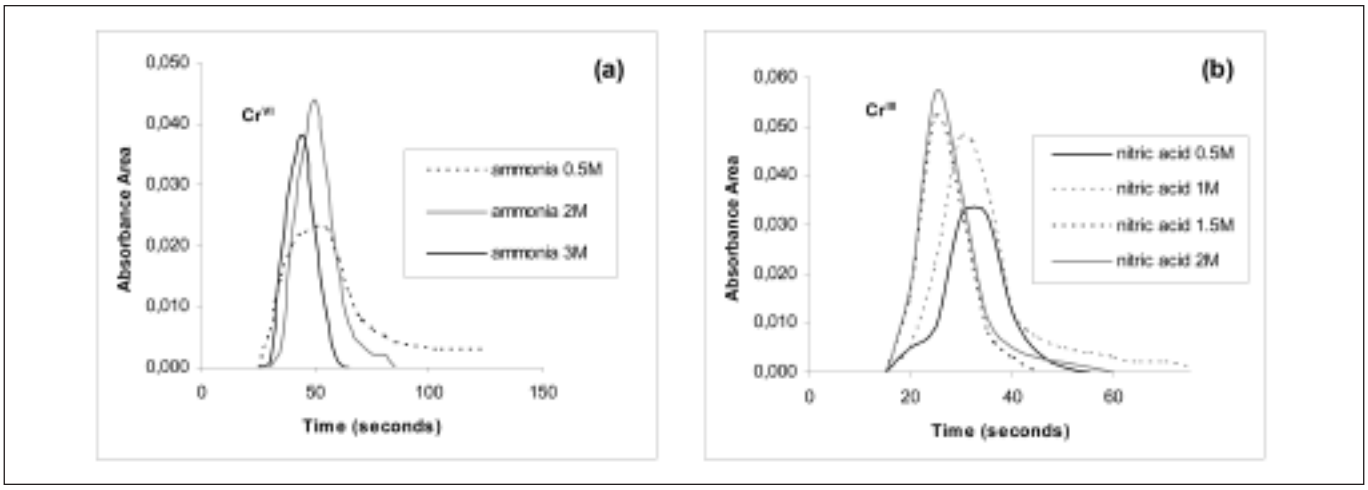

Fig. 4. (a) Peak profiles obtained for elution of Cr(VI) with different ammonia solution concentrations and (b) peak profiles obtained for elution of Cr(III) with different nitric acid concentrations. For Cr(III) elution, the ammonia concentration used was the optimum obtained [Cr(VI) with ammonia 2M].

TABLE II
Analytical Characteristics in the On-line Simultaneous Determination of Cr(III) and Cr(VI) in Alkaline and Water Extracts of Solid Samples

Item	Cr(VI)	Cr(III)
LOD (n=11) Alkaline Extract	0.45 μg g^{-1}	2.9 μg g^{-1}
LOD (n=11) Water Extract	0.38 μg g^{-1}	1.2 μg g^{-1}
LOQ (n=11) Alkaline Extract	1.52 μg g^{-1}	9.6 μg g^{-1}
LOQ (n=11) Water Extract	1.26 μg g^{-1}	3.4 μg g^{-1}
Calibration Graph	A=0.0013C–0.0001	A=0.0010C–0.0033
	R=0.9977	R=0.9997
Addition Graph	A=0.0013C–0.0366	A=0.0007C–0.0013
	R=0.9979	R=0.9972
Matrix Effect in the On-line System	No	Yes
%RSD (CV%) n = 11	7.1	8.7
Working Range	0–150 μg L^{-1}	0–200 μg L^{-1}
Time of Peak Elution	30–45 sec	30–60 sec

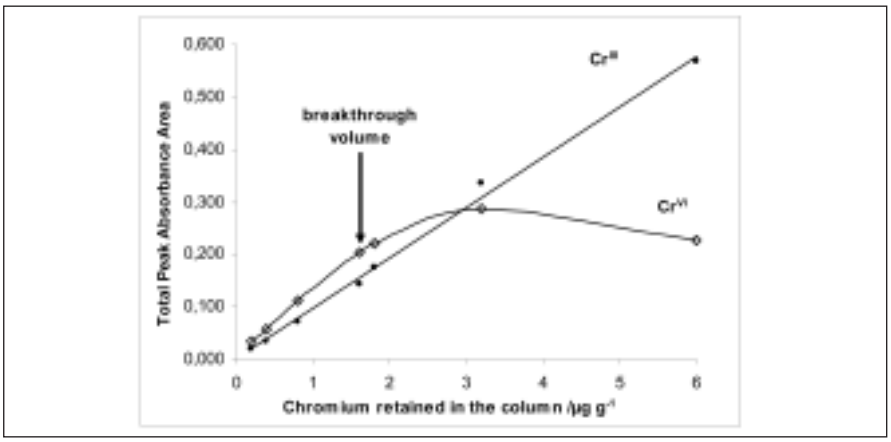

Fig. 5. Variation and lineal response of Total Absorbance Peak Area versus Cr(III/VI) concentration pumped through the alumina column and breakthrough volume of Cr(III).

Adsorption Capacity of Alumina for Cr(VI) and Cr(III)

The column (5 cm long, 3 mm i.d.) contained 0.5 g of Al_2O_3. The maximum loading of the column was studied by pumping a 100-µg L^{-1} Cr(III) / 100-µg L^{-1} Cr(VI) solution over different time periods. Total peak absorbance areas (TPAAs) obtained are shown in Figure 5 and demonstrate a linear response for Cr(VI) and Cr(III) with different concentrations. The maximum Cr(VI) that could be retained on the alumina column was 1.6 µg per g of Al_2O_3 (TPAA [Cr(VI)] = 0.1227 × C + 0.0118; r^2 = 0.9991 where C is µg of Cr(VI/III) per g of Al_2O_3). However, a linear response was still obtained with more than 6 µg of Cr(III) per g of Al_2O_3 (TPAA [Cr(III)] = 0.0964 × C – 0.0005; r^2 = 0.9958). The maximum chromium concentration selected for routine analysis using this system was therefore the last point of linear response of Cr(VI).

Analytical Characteristics

Calibration graphs were measured with a diluted and a pH-adjusted Na_2CO_3/NaOH solution. The addition graphs were obtained with a cement extract following the alkaline extraction procedure, adjusting the pH and diluting (50-fold with Milli-Q water, pH 7.5±0.5 with sulphuric acid). A comparison of the slopes of the calibration and the standard addition graphs using a *t*-test (95% significance level) (27) was made and no differences were observed for Cr(VI), but significant differences were observed for Cr(III), indicating that there was a matrix effect with Cr(III) in the column-FAAS detection system but not with Cr(VI) (Table II). This matrix effect is basically due to the different column interaction with Cr(III) of the sample and the stock solutions.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated from 11 blank injections introduced through the on-line system. The injection repeatability was calculated from 11 injections of the same solution containing 100 µg L^{-1} of each chromium species. The limit of detection is defined as 3×SD/m, where SD is the standard deviation of the measurements and m is the slope of the calibration (for the hexavalent chromium) or the slope of the standard addition (for the trivalent chromium) graphs. LOQ is defined as 10×SD/m. The injection repeatability is the closeness of agreement between independent results obtained with the same on-line preconcentration/speciation/detection method on an identical test material, under the same conditions (same operator, same apparatus, same laboratory, and after short intervals of time). Injection repeatability was evaluated by measuring the consecutive injections in the system (n=11) by means of the percent relative standard deviation (%RSD). The %RSD or CV(%) is defined as SD/X*100, where SD is the standard deviation of the peak absorbance signal of the solution injected n times, and X is the average of the peak absorbance signals obtained. The results are given in Table II.

Interferences

Alumina is an amphoteric oxide that retains both chromium species in the conditions explained in this work. Cr(III) is retained in the column because of its cationic behavior with alumina and Cr(VI) is retained like a typical anion (28). Cation sorption favors electrostatic adsorption of Cr(VI) anions but does not improve the cationic retention of Cr(III) as we concluded in the sodium chloride studies. The Cr(III) and Cr(VI) sorption in the alumina column was evaluated in the presence of different cations, interferences that could be co-eluted or could be competing with chromium species. The effect of the metals investigated demonstrates that there are no obvious interferences to be expected. Only the study gives sensible interferences with Fe(III) at 5 µg mL^{-1} and Al(III) at 0.5 µg mL^{-1}. The results are shown in Table III.

Applications

The speciation system described above was applied to the analysis of cements and marine sediment samples. The study was focussed on total Cr(VI) content and was completed with the water-soluble frac-

tion. The results are given in Table IV. No Cr(III) was detected in any of the alkaline extracts, as we expected.

The alkaline extraction procedure was also examined (Table V). To verify the efficiency of the extraction procedure, four cement samples were spiked with Cr(VI) (75 $\mu g_{CrVI}\, g_{cement}^{-1}$), followed by the extraction and speciation steps to obtain the recoveries of the overall process. The concentration of Cr(VI) spiked in the sediments were 25–50–75 $\mu g_{CrVI}\, g_{sediment}^{-1}$. The total Cr content determined was between 34 and 41 $\mu g_{Cr}\, g_{cement}^{-1}$ (determination by ETAAS of an acid digestion with aqua regia); and around 60 $\mu g_{Cr}\, g_{sediment}^{-1}$ (determination by ETAAS in slurries) (29). For the marine sediments, the sample matrix was rich in organic material. Values of pH/E_h(mV) were obtained following EPA Method 9045 (30), shaking the solid samples for 30 minutes with 0.01 mol L^{-1} $CaCl_2$, and letting the slurry stand undisturbed for about one hour to allow most of the suspended clay to settle out. The results of the redox potential (E_h/mV) were weakly reducing (31): 400–200 mV, and pH values around 7.5–8.2. Therefore, the pH/E_h values were found to be near the solid $Cr(OH)_3/CrO_4^{-2}$ interface, since the hydroxide form is the most stable.

TABLE III
Influence on Absorbance Area of Cr Species Peaks Adding Different Ions as Potential Interference

Ion	[Interference] (μg mL^{-1})	**Cr(VI)** Signal Variation(%)[a]
Al(III)	0.5	16.8
	0.25	1.0
Cd(II)	5	5.1
Cu(II)	5	1.8
Fe(III)	5	10.5
	1	–3.4
Mn(II)	5	7.8
	3	–1.0
Ni(II)	0.25	–1.0
Pb(II)	5	–1.7
Zn(II)	10	8.7
Ion	[Interference] (μg mL^{-1})	**Cr(III)** Signal Variation(%)[a]
Al(III)I	0.5	–13.5
	0.25	1.9
Cd(II)	5	8.2
Cu(II)	5	6.5
Fe(III)I	5	64.9
	1	32.8
	0.5	–10.9
	0.25	6.1
Mn(II)	5	15.3
	3	–6.3
Ni(II)	0.25	3.8
Pb(II)	5	4.6
Zn(II)	10	3.9

[a] Signal variation of Cr was obtained adding interference ions in a solution of 100 μg L^{-1} Cr(III) / 100 μg L^{-1} Cr(VI) and compared with the signal without any interference.

TABLE IV
Chromium Determination in Cement and Estuarine Sediment Samples From Arousa (μg g^{-1})

Sample	Cr(VI) (μg g^{-1}) (Alkaline Extraction)	Cr(VI) (μg g^{-1}) (Water Extraction)	Cr(III) (μg g^{-1})
Marine Sediments	<LOD	Not analyzed	<LOD
Cement 1	4.9 ± 0.8	2.11 ± 0.03	<LOD
Cement 2	3.2 ± 0.9	<LOD	<LOD
Cement 3	4.5 ± 0.8	1.9 ± 0.1	<LOD
Cement 4	1.9 ± 0.7	< LOD	<LOD

It was concluded that Cr(VI) was not stable in the sediment samples because of the reducing conditions. This lack of stability was demonstrated by spiking Cr(VI) into the sediments before the alkaline extraction, as in the cements. Recovery was found to be extremely low when the sediments were extracted using the standard method (Table V). The effects of the organic material, the pH of the water, and the general reductive nature of the sediments make it unlikely that the Cr(VI) will remain stable. However, with the cements, Cr(VI) was detected and found to be stable.

Recovery values of the speciation method were obtained with different concentrations of Cr(VI) and Cr(III) spiked into the cement extract (Table VI). The objective of this experiment was to evaluate the recovery of both the trivalent and hexavalent Cr from the alumina system at different chromium levels. The material was deliberately not spiked in these experiments because the extraction step is reportedly selective for Cr(VI).

TABLE V
Cement and Marine Sediment Samples Spiked With Potassium Chromate for Different Times Before Extraction Step[a]

Spiked Sample	Cr(VI) Spiked (μg g^{-1})	Recovery (%)
Cement 1[a]	75	105
Cement 2[a]	75	96
Cement 3[a]	75	100
Cement 4[a]	75	95
Marine Sediment[b]	25	0
Marine Sediment[b]	50	0
Marine Sediment[b]	75	0

[a] Potassium chromate was in contact with cements for 4 hours before the extraction step.
[b] Potassium chromate was in contact with marine sediments at different times up to 24 hours.

TABLE VI
Speciation Recoveries Obtained for Cement Extract Spiked at Different Cr(VI-III) Levels

Cr(VI)	
Spiked Levels	30, 60, 90, 120 μg L^{-1}
Recovery	99 ± 2%
Cr(III)	
Spiked Levels	50, 100, 150, 200 μg L^{-1}
Recovery	101 ± 6%

CONCLUSION

The on-line system described is simple to construct, rapid, and relatively inexpensive. The results agree well with those obtained in previous Cr(III) and Cr(VI) speciation studies. However, in those investigations using alumina for the speciation, changes in pH were required for the selective retention of one of the chromium species. In our present study, a simultaneous and selective procedure to speciation and preconcentration of Cr(III) and Cr(VI) in solid sample extracts is described without requiring pH changes during the retention phase. The sample extracts were pumped through the alumina column and no chromium species were lost during this step. Ammonia solution was then pumped through the column, and Cr(VI) eluted and determined by FAAS. Finally, nitric acid was used to liberate Cr(III) and to clean the system prior to a further sample injection.

Optimization of flow rate, concentration of ammonia and nitric acid, capacity of the alumina column, and salt concentration in the extracts injected in the on-line system was established. The analytical characteristics are presented and the optimized procedure was applied to real samples. Extraction of materials (cements and sediment samples) was performed using a standard USEPA method and, depending on the sample matrix, Cr(VI) was extracted and detected. Cr(VI) was detected in cement samples, but neither Cr(VI) nor Cr(III) were detected in alkaline extracts of marine sediment samples. This was attributed to the strongly reducing nature of the sediment samples in converting Cr(VI) to Cr(III).

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Flame AAS Determination of Beryllium in Water Samples After Preconcentration on Activated Carbon

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ABSTRACT

A simple, sensitive, accurate, and selective method for the determination of ultratrace levels of beryllium is modified. The method is based on preconcentration of the complexes of beryllium–acetylacetone plus morin on activated carbon at pH 8.0–10.0 using a contact time as low as 10 minutes. The adsorbed beryllium was eluted with aqua regia and measured by flame atomic absorption spectrometry (FAAS). Recoveries up to 85% were achieved.

For removing chemical interferences and applying the method to the Be determination in water samples, sensitivity and reproducibility were examined. The Be detection limit was found to be 0.012 ng mL^{-1}. The relative standard deviation (%RSD) was found to be 7% for 200 mL of 0.5 ng mL^{-1} Be and 9% for 1000 mL of 0.1 ng mL^{-1} Be using the 10 replicate enrichment procedures. The Be concentrations in the water samples were found to be in the 0.05–1.687 ng mL^{-1} range.

INTRODUCTION

Beryllium (Be) is lighter than aluminum and six times stronger than steel. Thus, Be and its alloys with other metals is a key component of materials used in the aerospace and electronic industries (1). Briefly, coal-fired power plants, industrial manufacturing, and nuclear weapons productions and disposal operations are sources that release Be to the environment. Despite the increasing use of Be, there is surprisingly little published information about Be concentrations and its transport into the environment. Although acute and chronic Be poisoning occurs mainly by inhalation of industrial gases and dusts, the determination of ultratrace amounts of Be in natural waters is of interest as it can indicate environmental pollution and could provide information of the metal uptake through these sources.

Beryllium is one of the exceedingly toxic metals including As, Cd, Cr, Pb, and Hg. The carcinogenic risks to humans from Be and Be compounds have been considered by the International Agency for Research on Cancer (IARC)-World Health Organization (WHO) since 1970 (2). In 1993, the IARC published a monograph on Be, Cd, and Hg regarding the carcinogenity of these metals to humans (3). It is now known that Be affects the cellular membranes and bioaccumulates through binding to specific regulatory proteins. The acceptable ceiling concentrations in various matrices were described as 0.01 μg m^{-3} Be for respirated air (4) and 4.0 μg L^{-1} Be for drinking waters (5). However, different national guidelines suggest that Be concentrations should not exceed 0.1 μg L^{-1} for tap water and 0.2 μg L^{-1} for surface water (6). On the other hand, Be levels in fresh waters are generally < μg L^{-1} (7). The daily average Be exposure for a U.S. citizen was estimated to be 0.00006 μg obtained through inhalation of air, 0.4 μg from drinking water, and 12 μg from food (2). Thus, it can be said that the source of daily Be intake is mostly from food. Hubert and coworkers (2) reviewed the data with regard to Be in food and drinking waters, and found that Be levels in food samples range from < 1 to about 20 μg kg^{-1}, with few exceptions (2).

Due to the allowable low levels of Be and the very low concentrations in food and environmental samples such as water and air, reliable and sensitive analytical methods are required. For this purpose, ETAAS (4,6–8), ICP-OES (7,8), and ICP-MS (9) are generally used. However, FAAS (2,10) has also been used in connection with enrichment procedures. On the other hand, suitable enrichment procedures are required for Be determination by all of the analytical methods described above (even for ICP-MS) because the Be concentrations in some natural water samples are as low as 0.001 μg L^{-1}. Among several complexing agents, acetylacetone has been commonly used in the preconcentration procedure because the overall formation constant of Be acetylacetonate, $Be(acac)_2$, is about 3.10^{14} (11–13). In our laboratory, FAAS has successfully been used for the determination of very low levels of various metals in different matrices after enrichment methods (14–22).

In this study, a preconcentration method was modified for the FAAS determination of Be at the ng L^{-1} level in different water samples including surface, ground, and commercial mineral waters.

EXPERIMENTAL

Instrumentation

An ATI UNICAM Model 929 flame atomic absorption spectrophometer (FAAS), equipped with an ATI UNICAM hollow cathode lamp, was used for the determinations (UNICAM, England). The

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optimum conditions for FAAS are given in Table I. The pH was measured with an EDT GP 353 ATC (Dover, Kent, UK) pH meter. In the enrichment procedure, magnetic stirrers and a centrifuge were used.

All Pyrex glassware was kept permanently full of 1M nitric acid when not in use. In the digestion work, *aqua regia* (one volume HNO_3 plus three volumes HCl) was used. Stock standard Be solution (1000 mg L^{-1}) was prepared by dissolving $BeSO_4$. $4H_2O$ (Merck, Darmstadt, Germany) in 2M HNO_3.

TABLE I
Operating Parameters for FAAS

Parameters	
Wavelength	234.9 nm
HCL Current	6.0 mA
Type of Flame	N_2O – C_2H_2
Background Correction	Deuterium Lamp
Slit Width	0.5 nm
Nitrous Oxide Flow Rate	4.7 L min^{-1}
Acetylene Flow Rate	4.2 L min^{-1}

Standards and Reagents

Buffer solutions in the pH range of 3.0–11.0 ± 0.2 were prepared by using 0.1M citric acid plus 0.1M HCl / 0.1M NaOH, 0.1M KH_2PO_4 plus 0.1M NaOH, and 0.2 M H_3BO_3 plus 0.1M HCl / 0.1M NaOH solutions.

A solution of 5% (v/v) acetylacetone was prepared by diluting 5.0 mL of concentrated acetylacetone to 100 mL with distilled water. A morin solution of 0.06% was prepared by dissolving 0.06 g of this reagent in 100 mL distilled water. In the enrichment procedure, a solution of 1.10^{-3}% was freshly prepared from this morin solution.

For masking of the matrix elements in the enrichment procedure, a solution of 5% EDTA was prepared by dissolving a suitable amount of EDTA in distilled water.

Activated carbon passed through a 325-mesh sieve (Taylor) was purified by treating it with concentrated HCl for 3 hours, washing with distilled water, drying at 110ºC, and treating with aqua regia for 24 hours, as described elsewhere, with the following slight modification (16). The mixture was filtred through filter paper (Advantec Toyo 5 B, white ribbon), washed with water, and dried at 110ºC. A suspension of 25 mg mL^{-1} in distilled water was prepared from this dried activated carbon.

Enrichment Procedure

In the optimization studies, 100 mL of Be solution of 2 ng mL^{-1} was used as the model solution. The solution pH was adjusted to the desired value by adding required volume of HCl (0.1M) and and NaOH (0.1M). After adding the necessary buffer solution, complexing agents such as acetylacetone, morin, and acetylacetone (2 mL) plus morin (5 mL) were separately added. Then, 5.0 mL of activated carbon suspension (25 mg mL^{-1}) was added and the pH was again adjusted to the studied pH of 9.5±0.2, if necessary. The mixture was stirred mechanically for 10 min and filtered through a filter paper (Advantec Toyo 5 B, white ribbon). The residue was dried at 105ºC for 1 hour. After transferring the residue to a glass beaker, 5 mL *aqua regia* was added, and the solution was evaporated to near dryness. The steps of the enrichment scheme are given in Figure 1.

RESULTS AND DISCUSSION

The parameters that might affect the enrichment and measurement steps in the analytical scheme were examined. These parameters were investigated by using the model Be solutions of 2 ng mL^{-1} containing matrix components at the following concentrations:

Ca^{2+} : 200 mg L^{-1},
Mg^{2+} : 100 mg L^{-1},
Fe^{3+}, Al^{3+} and Zn^{2+} : 10 mg L^{-1} each,
and Mn^{2+} : 5 mg L^{-1}.
Furthermore, 100 mL of these solutions was preconcentrated to a final volume of 2.0 mL of 2M HNO_3, and a 50-fold enrichment factor was achieved. The effect of each parameter was tested three times.

Influence of pH on Recovery

The model solutions of Be were preconcentrated using pH values ranging from 3.0–11.0 (see Figure 1). The recoveries obtained are given in Figures 2–3.

From Figure 2, it can be seen that the optimum pH for the recoveries was up to 70% in the 8.0–10.0 range by using morin (5 mL of 1.10^{-3}%) and up to 80% in the same pH range (8.0–10.0) by using acetylacetone (2 mL of 5%). Furthermore, up to 85% of the recoveries were in the pH range of 8.0–10.00 by using acetylacetone (2 mL of 5%) plus morin (5 mL of 1.10^{-3}%), resulting in a synergistic effect (Figure 3). For all subsequent studies, the pH of 9.5±0.2 was selected.

Effect of Amount of Complexing Reagent on Recoveries

The Be recoveries at the optimum pH (9.5 ± 0.2) were examined by using different volumes of 5% acetylacetone and by adding 125 mg (5 mL) of activated carbon. It can be seen in Figure 4 that the recoveries increased

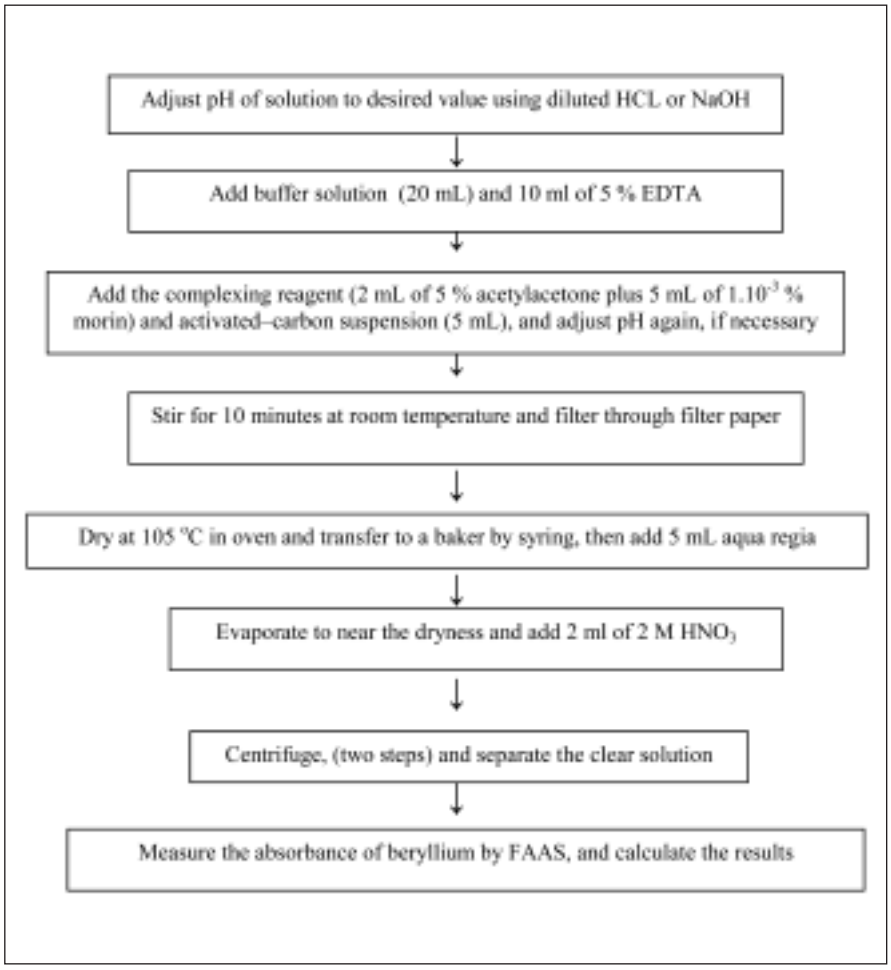

Fig. 1. Steps of analytical scheme in the enrichment procedure.

up to 80% using acetylacetone of 1 mL and did not change by adding up to 5 mL. Figure 5 shows that the recoveries increased up to 70% using morin of 4 mL (1.10^{-3}%) and did not change by increasing up to 10 mL of morin. In the last step, 5.0 mL of morin was used together with 2 mL of acetylacetone, and recoveries of 85% were achieved. Thus, morin plus acetylacetone at the volumes described above (2 mL acetylacetone + 5 mL morin) were used for subsequent studies.

Effect of Amount of Activated Carbon on Recovery

In order to determine the optimum amount of activated carbon, different amounts of this suspension were added to the model Be solutions described above, and applying all other optimum conditions (pH=9.5, and 2 mL acetylacetone plus 5 mL morin as the complexing agents). Figure 6 shows that the recoveries increased up to 85% by adding 100 mg activated carbon and did not change up to a 200-mg volume.

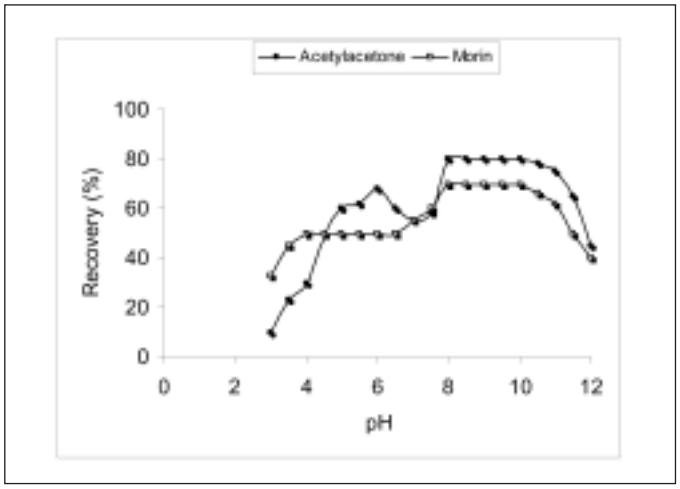

Fig. 2. Influence of pH on recovery of Be with acetylacetone and morin.

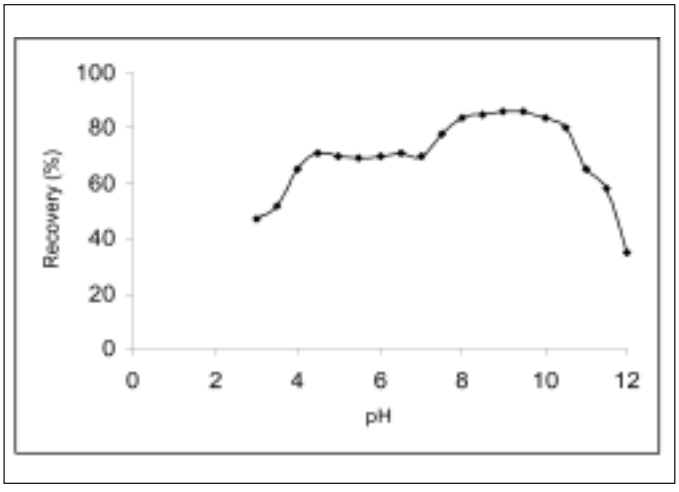

Fig. 3. Influence of pH on recovery of Be with acetylacetone plus morin.

Effect of Stirring Time on Recovery

The enrichment procedure was applied to the model Be solutions by using different stirring times at the optimum conditions described above. The results in Figure 7 showed that five minutes was sufficient for maximum recovery (85%), and the recovery did not change up to 60 minutes. A stirring time of 10 minutes was used for all further studies.

Interferences

Interferences from concomitant elements were investigated. Table II shows that some of the concomitant metals in the model Be solutions cause an important decrease in recovery (up to 65%). However, this decrease was removed by adding 10 mL of 5% EDTA solution. Consequently, the presence of 5000 mg L^{-1} Ca, 500 mg L^{-1} Mg, 100 mg L^{-1} Al, and 50 mg L^{-1} Fe did not cause a decrease in the analytical scheme. It can therefore be stated that the addition of EDTA is necessary to achieve reliable and maximum Be recovery.

Calibration Curves and Precision

The calibration curve was observed to be linear at the concentration range of 25–200 ng mL^{-1} using direct FAAS. Therefore, a 500 times enrichment factor is required at a Be concentration as low as 0.05 ng.mL^{-1} in fresh surface waters.

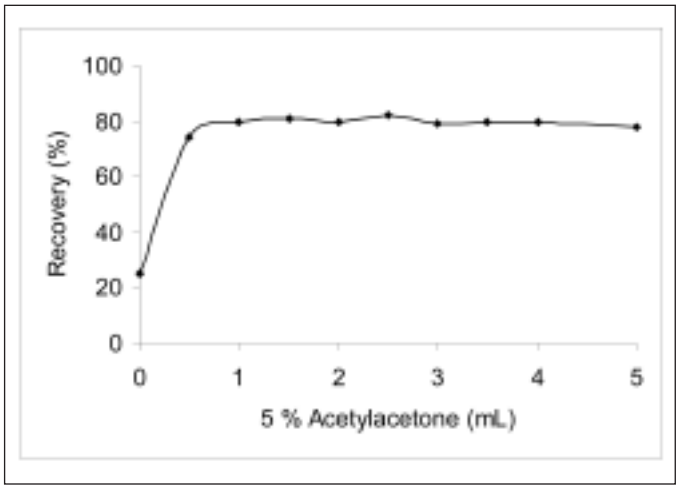

Fig. 4. Determination of optimum amount of acetylacetone (5%).

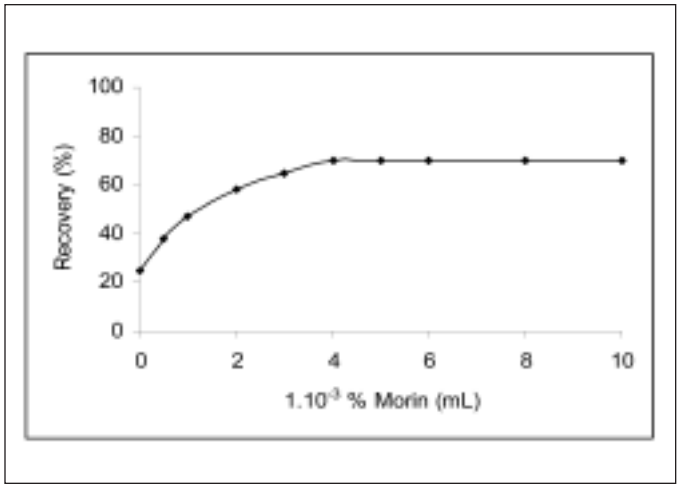

Fig. 5. Determination of optimum amount of morin (1.10^{-3}%).

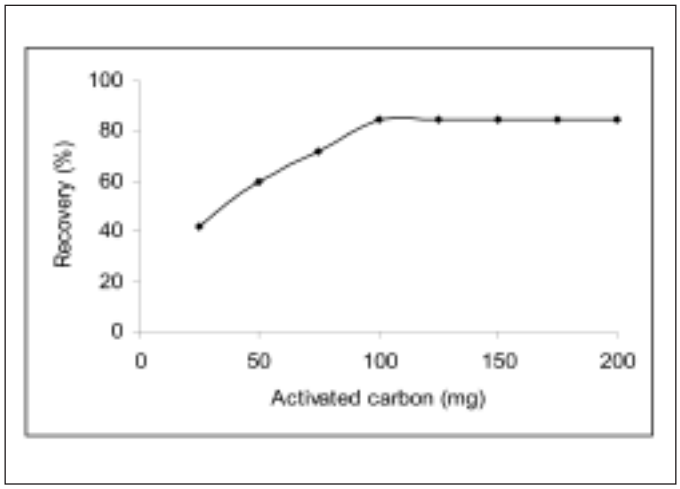

Fig. 6. Determination of optimum amount of activated carbon using acetylacetone plus morin.

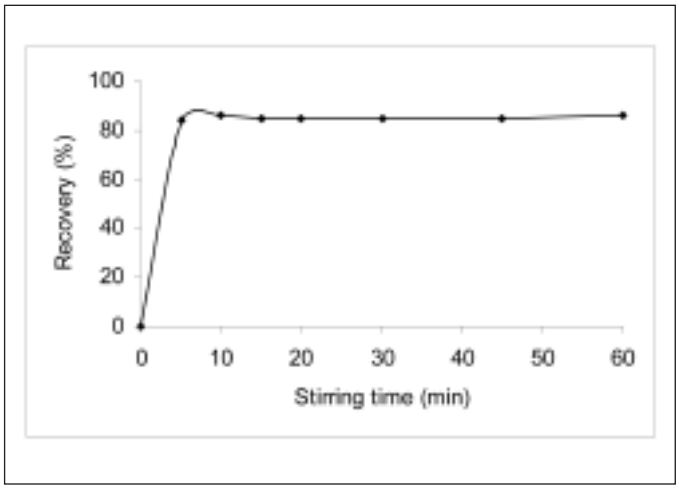

Fig. 7. Determination of the optimum stirring time using acetylacetone plus morin.

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In this study, calibration curves were obtained by using two different volumes of Be solutions (200 and 1000 mL) because these Be levels are at wide ranges in the studied natural waters (from 0.05 to 2 ng mL^{-1}). Thus, Be solutions of 1000 mL at the concentration range of 0.05–0.40 and 200 mL at the concentration range of 0.25–2.0 ng mL^{-1} were used to obtain calibration curves. The calibration curves were linear in these concentration ranges. The equations of the curves were as follows:

$y = 139x + 1.1419$
($R^2 = 0.9975$) for 1000 mL

$y = 28x + 0.7778$
($R^2 = 0.9981$) for 200 mL

The relative standard deviations (%RSD) were 9% for 1000 mL of 0.1 ng mL^{-1} and 7% for 200 mL of 0.5 ng mL^{-1} for 10 replicate enrichment procedures. The level of Be in the blank was 0.02 ng mL^{-1} with a standard deviation of 0.004. Therefore, the detection limit (LOD) defined as three times the standard deviation of the blank was 0.012 ng mL^{-1} when 1000 mL of solution was preconcentrated to a final volume of 2 mL.

Accuracy and Applications

To ensure that this method was valid, the recoveries of Be from water samples fortified with this element were obtained by using the optimized enrichment method. From the results in Table II, it can be seen that at least 80% of the Be added to the water samples was recovered. Furthermore, the slope of the calibration curve obtained with the matrix components added to the standard solution is the same as that obtained with the standard additions method (Figure 8). These results show that the calibration curve with the matrix components should be preferred to the standard additions method, because the latter method requires a high volume of water. There were no adsorption losses since the same procedure was followed using the same glassware and the same reagents.

TABLE II
Effect of Matrix Components on Recovery of Be With and Without EDTA

Conc. of Metal Ions	With 10 mL of 5% EDTA Recovery (%)	Without EDTA Recovery (%)
100 mg L^{-1}/Mg^{2+}	86	70
200 mg L^{-1}/Mg^{2+}	86	70
100 mg L^{-1}/Ca^{2+}	85	78
200 mg L^{-1}/Ca^{2+}	85	78
100 mg L^{-1}/Fe^{3+}	85	78
100 mg L^{-1}/Al^{3+}	85	74
100 mg L^{-1}/Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}	85	70
10 mg L^{-1}/Pb^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}	85?	65?
100 mg L^{-1}/Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}	85	65

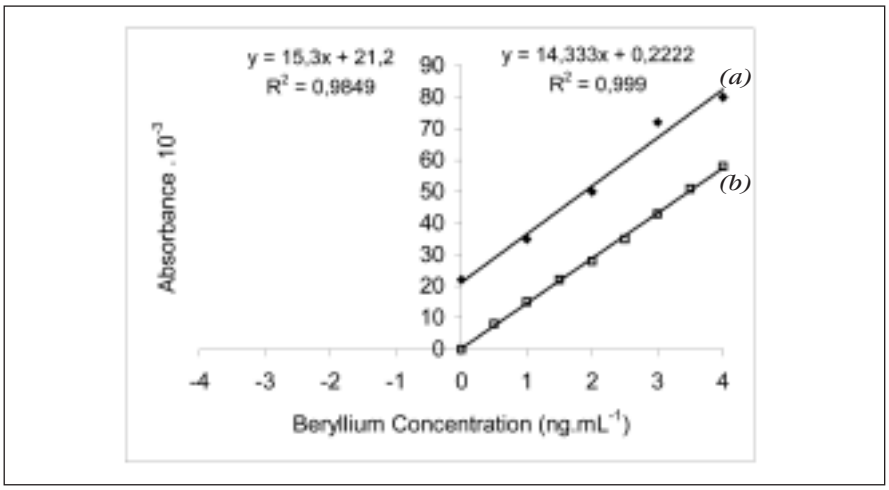

Fig. 8. The calibration curves obtained (a) with standard additions method and (b) with standards + artificial matrix by enrichment of the Be solutions of 100 mL to final volume of 2 mL.

The optimized enrichment method was applied to the determination of Be in various water samples including river, thermal, and fresh waters. The results listed in Table III are the mean values of three different portions of the same sample. The Be concentrations were found to range from 0.07–0.183 ng mL^{-1} for river waters, 0.050–0.064 ng mL^{-1} for fresh waters, and 0.815–1.687 ng mL^{-1} for thermal water samples (Table III).

These results are in agreement with the values found in the literature (2,4,6–7,15,23–25). Valencia and coworkers (25) used solid-phase spectrophotometry for the determination of Be in tap and natural waters. However, they reported serious interferences from Ca(II) and Mg(II) which are commonly found at high concentrations in water. Furthermore, Nukatsuka et al. (23), Dong et al. (26), Vin and coworkers (27), and Hayashi et al. (28) also used the spectrophotometric method for this purpose, but the interferences due to foreign ions caused serious difficulties in

TABLE III
Beryllium Concentrations Determined in Various Water Samples
(The results are the mean values ± standard deviation; n = 3.)

Sample Type	Be Concentration (ng mL^{-1})
River I	0.183 ± 0.023
River II	0.070 ± 0.008
Thermal Water I	0.815± 0.089
Thermal Water II	1.687 ± 0.141
Fresh Water I	0.064 ± 0.007
Fresh Water II	0.050 ± 0.006
Lake Hazar	<D.L.

D.L.: detection limit.

the measurement step. On the other hand, there are no serious difficulties in FAAS determinations. Hubert and coworkers (2) provide detailed information about the advantages of FAAS in comparison to other methods.

CONCLUSION

A sensitive, selective, and reliable enrichment method was modified using adsorption on activated carbon for the determination of Be in water samples. Matrix components were characterized and upper concentration levels of Ca, Mg, Al, and Fe were added to all standard Be solutions. The observed interferences from these matrix components were overcome by adding EDTA solution as the masking reagent. The sensitivity of FAAS was increased up to 500-times by using the optimized method and a detection limit of 0.012 ng mL^{-1} was achieved.

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Speciation of Cr(III) and Cr(VI) in Seawater After Separation With a Sulphate-form of Dowex-1 and ETAAS Determination

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ABSTRACT

Speciation of Cr(III) and Cr(VI) in seawater was achieved using a sulphate-form of Dowex-1. The resin adsorbs Cr(VI) selectively, eluting out Cr(III) even in the presence of associated anions such as Cl^-, NO_3^-, HCO_3^-, and SO_4^{2-}. The adsorption of Cr(VI) is near quantitative, whereas rejection of Cr(III) is ~99%. The adsorbed Cr(VI) is eluted using 2M HNO_3 and the residual Cr(III) is preconcentrated by coprecipitation with $Fe(OH)_3$ for ETAAS determination.

The method developed was applied for the speciation of Cr(III) and Cr(VI) in real seawater and three synthetic seawater samples containing 3.5% sea salt in deionized water. The detection limits for Cr(III) and Cr(VI) were 0.049 and 0.037 ng mL^{-1} with corresponding process blanks at 0.02 and 0.07 ng mL^{-1} (10-fold preconcentration), respectively.

INTRODUCTION

The determination of toxic metals in different types of waters is essential as they affect the health of man and mammals (1). The level of toxicity depends on the chemical form in which the element is present. Chromium (Cr) is one such element which exists in two oxidation states, namely Cr(III) and Cr(VI). Cr(III) is an essential trace element, whereas Cr(VI) is toxic and affects the kidneys, lungs, and liver (2,3). Cr(VI) in seawater is reported to be toxic to aquatic life (4). Release of Cr into ground waters is due to the extensive use of this metal in various industrial activities such as effluent discharge, the tanning industries, and in industrial electroplating. When Cr in water does not sediment, it will eventually reach the sea where it will remain in seawater for long periods before sedimentation (5). The toxicity of Cr(VI) is attributed to its ability to migrate across the cell membrane, thus increasing intracellular chromium concentrations (6). The different toxicity levels of Cr have led to the development of various analytical methodologies for its speciation (7– 9). Although the methodology for the speciation of Cr(III) and Cr(VI) is rather straightforward, it is difficult when the salt content of a sample is high, such as in seawaters (10). Anion exchange procedures using the Cl^- form are not suitable for the speciation of Cr in seawater due to the presence of associated anions (10,11). However, Cr speciation in seawater samples have been performed after complexation, solvent extraction, or coprecipitation (12–18). The procedures based on co-precipitation are prone to elevated process blank values due to the reagents used. The organic solvents used for solvent extraction are less preferred nowadays due to their toxicity. The main disadvantage of all of these procedures for Cr speciation is that one of the species is determined by calculating the difference between the total chromium concentration (obtained after reduction or oxidation) and its other chemical form. Such procedures lead to large inaccuracies, especially in the Cr concentration of the lesser component/species in the sample. It is therefore essential to investigate other alternatives that are simple and suitable for the routine monitoring of Cr(VI) in seawaters.

The present paper describes a simple ion exchange procedure for the separation, preconcentration, and determination of Cr(VI) in seawater samples using a sulphate-form of Dowex-1. Optimization of the conditions for quantitative separation of Cr(III) and Cr(VI), and the determination of these species by electrothermal atomic absorption spectrometry (ETAAS) is also discussed.

EXPERIMENTAL

Instrumentation

An Analytikjena Model ZEEnit 65 graphite furnace atomic absorption spectrometer (Analytikjena, Jena, Germany), equipped with an MPE 60 autosampler, was used in this study. The operating parameters are given in Table I.

Reagents

Analytical grade reagents were used throughout. Pure water (18 MΩ cm) was prepared by passing potable water through a mixed-bed ion exchanger and then through a Milli-Q™ water purification system (Millipore Corporation, Bedford, MA, USA). Dowex-1 resin

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(chloride form) was obtained from Sigma, St. Louis, MO, USA. The Cr(III) and Cr(VI) standards were prepared using AR grade Cr(III) chloride and potassium dichromate, respectively. Polypropylene bottles used for sample collection are soaked in 10% HNO_3 overnight and cleaned thoroughly to be free of acid, then rinsed with deionized water.

Preparation of Resin

Commercial Dowex-1 (10 g, chloride form, 50–100 mesh) resin was placed in a 50-mm i.d. column, equilibrated with 2M HNO_3, washed with Milli-Q water, and equilibrated with HCl. This resin was loaded with 100 mL of 10% potassium sulphate to convert it into the sulphate form, then washed to remove excess sulphate, air-dried, and used for all subsequent studies. The flow rate used was 2 mL min^{-1}.

Adsorption

A 10-mm i.d. column was prepared using 1 g of the sulphate form of Dowex-1 resin. Deionized water (100 mL) containing 3.5% sea salt and 2.5 ng mL^{-1} of Cr(III) or Cr(VI) was passed through the resin at a flow rate of 1 mL min^{-1}. The eluate was analyzed for Cr [preconcentrated in case of Cr(III)]. The above experiment was repeated at different pH levels (2–8) of the loading solution.

Elution

After adsorption, the resin was washed with 50 mL of deionized water at a pH adjusted to that of the loading solution in order to remove any salt physically trapped on the resin. The adsorbed Cr(VI) was eluted using 10 mL of different concentrations of HNO_3 (0.5–2.5M) at a flow rate of 1 mL min^{-1}. The eluate was analyzed for Cr(VI).

Preconcentration of Cr(III)

The seawater (100 mL) was passed through the column and mixed with the wash solution (50 mL), then $FeCl_3$ (10 mg as Fe) was added, and the Cr(III) present in seawater was coprecipitated using 25% ammonia solution (1 mL). The precipitate was centrifuged, dissolved in a minimum amount of HNO_3, diluted to 10 mL, and analyzed for Cr(III). The procedure was repeated after addition of Cr(III) standard (250 ng) to the seawater in order to establish the percentage recovery.

Purification of $FeCl_3$

Iron (III) chloride (1 g as Fe) was dissolved in 50 mL of 4M HCl, then 1 mL of 10 mg mL^{-1} sodium sulphite was added to reduce any Cr(VI) present to Cr(III), and the $FeCl_3$ extracted with 100 mL MIBK. The $FeCl_3$ was stripped into deionized water, evaporated to near dryness, and diluted to 100 mL with Milli-Q water. This solution was used to coprecipitate Cr(III).

Distribution Coefficient (Kd)

Adsorption of Cr(III) and Cr(VI) was carried out in batch method using 250 mg of resin at different pH levels (2–8 pH) of the loading solution [50 µg of Cr(III) or Cr(VI) in 25 mL] (see Figure 1). The distribution coefficient (Kd) of Cr(III) and Cr(VI) was computed as the amount of metal per gram of resin/amount of metal per mL of solution.

TABLE I. ETAAS Operating Parameters

HCL Current	5.0 mA		Wavelength	357.9 nm	
Temperature Program					
Type	Temp. (°C)	Rate (°C sec^{-1})	Hold (sec)	Time (sec)	Gas (Argon)
1. Drying	90	5	20	32.8	Maximum
2. Drying	105	3	20	25	Maximum
3. Drying	110	2	10	12.5	Maximum
4. Pyrolysis	700	50	15	26.8	Maximum
5. Auto Zero	700	0	6	6	Stop
6. Atomization	2400	1500	5	6.1	Stop
7. Cleanout	2450	500	4	4.1	Maximum

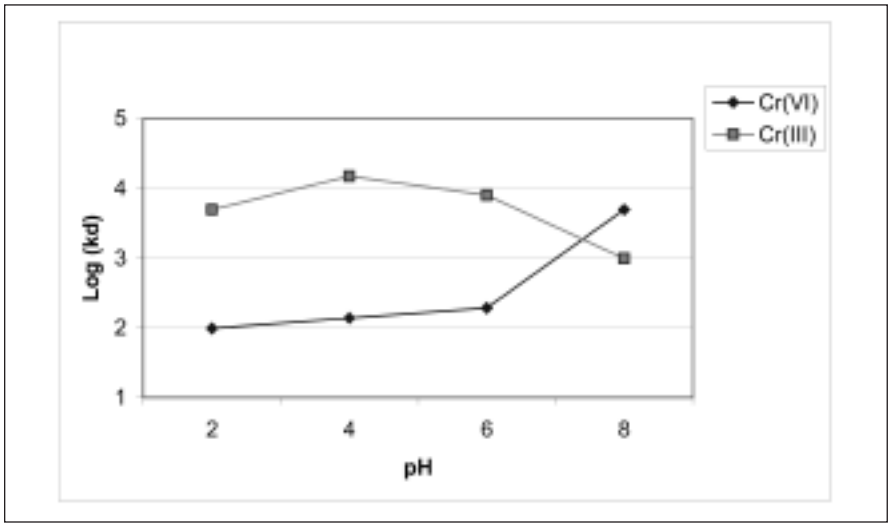

Fig. 1. Distribution coefficient (Kd) values of Cr(III) and Cr(VI) with pH.

Analytical Procedure

The pH of the seawater samples, both synthetic and real (100 mL), was adjusted to pH 4–5 with dilute HCl. At a flow rate of 1 mL min-1, the samples were passed through a glass column containing the sulphate form of Dowex-1 resin (1 g, 10 mm i.d.). After adsorption, the resin was washed with 50 mL of deionized water (with the pH adjusted to 4–5 using HCl). The eluate and the wash solution were mixed, purified $FeCl_3$ solution (10 mg as Fe) was added, and Cr(III) in the solution was coprecipitated using 25% ammonia solution (1 mL). The precipitate was centrifuged, the supernatant decanted, and the precipitate dissolved in a minimum amount of HNO_3 (1 mL) and diluted to 10 mL. The adsorbed Cr(VI) was eluted with 10 mL of 2M HNO_3 and both solutions were analyzed for Cr(III) and Cr(VI) by ETAAS. The procedure was repeated by adding 2.5 ng mL^{-1} each of Cr(III) and Cr(VI) to calculate the percentage recovery in the real seawater sample. A blank solution was also prepared by repeating the procedure above.

Validation

The method developed was validated using the following procedure for Cr(III) and Cr(VI) speciation (19):

Cr(VI): A 100-mL seawater sample was placed in a separating funnel, treated with 1 mL 5% aliquot-336 in MIBK, 0.1 mL 15M HNO_3, 5 mL of MIBK, and shaken well for 2 minutes. The extract was analyzed for Cr(VI).

Cr(III): A 100-mL seawater sample (100 mL) was placed into a Teflon bottle, 0.1 mL 15M HNO_3 and 2 mL of 0.1M sodium peroxodisulphate solution were added, and boiled for 15 minutes. After cooling, total Cr was extracted as above. The concentration of Cr(III) was computed by the difference of the concentration of total Cr and Cr(VI).

RESULTS AND DISCUSSION

The speciation of Cr(III) and Cr(VI) in seawater samples is difficult due to the high salt content. Dowex-1 resin is reported to be the best suited resin for the anion exchange separation of Cr(VI) (10). However, the anion exchange procedures, using the chloride or oxalate form of Dowex-1 for the selective adsorption of Cr(VI) fail due to poor recovery (11). A comparison of percentage recoveries of Cr(III) and Cr(VI), at a pH 2.5 and 4.5, respectively, using the chloride-form and sulphate form of Dowex-1 are shown in Table II. The sulphate-form of Dowex-1 was found to have tolerance for the salt content and is suitable for the adsorption of Cr(VI) from seawater. The conditions for the quantitative recovery of Cr(VI) and rejection of Cr(III) need to be optimized.

Optimization of Conditions

Adsorption

The effect of the pH of the loading solution on the adsorption of Cr(III) and Cr(VI) was studied by changing the pH from 2.0 to 8.0 for both Cr(III) and Cr(VI) separately. As shown in Table III, for the selective adsorption of Cr(VI) and the rejection of Cr(III) a pH of 4–5 was found to be suitable. Though there is little sorption of Cr(III), this pH was selected because of the large separation factor, close to the natural pH of seawater, the possibility of reducing Cr(VI) to Cr(III) at a lower pH in the presence of organic materials, and the ability to obtain better recovery.

TABLE II
Comparison of Recovery[a] of Cr(III) and Cr(VI) on Chloride and Sulphate Forms of Dowex-1 From Seawater

Species	pH = 2.5		pH = 4.5	
	Chloride	Sulphate	Chloride	Sulphate
Cr(III)	98.0 ± 1.3	98.2 ± 1.2	98.4 ± 1.2	98.9 ± 1.0
Cr(VI)	82.0 ± 2.0	99.0 ± 0.8	77.0 ± 3.0	99.9 ± 0.6

[a] Average of three different experiments.
Concentration of Cr(III) and Cr(VI) was 25 ng mL^{-1}.

TABLE III
Recovery[a] of Cr(III) and Cr(VI) From Seawater on Sulphate Form of Dowex-1 With pH Level

pH	% Recovery Cr(VI) on Resin	% Recovery Cr(III) in Eluate
2	96.1 ± 1.2	99.0 ± 0.8
4	99.9 ± 0.9	98.9 ± 1.0
5	99.6 ± 0.8	98.9 ± 1.1
6	98.7 ± 1.0	87.0 ± 2.3
8	95.0 ± 1.3	23.4 ± 3.4

[a] Average of three different experiments.
Concentration of Cr(III) and Cr(VI) was 25 ng mL^{-1}.

TABLE IV
Elution[a] of Cr(VI) With HNO_3 Concentration

Conc. of HNO_3 (M)	% Elution
0.5	26.0 ± 3.0
1.0	56.0 ± 2.6
1.5	94.4 ± 1.3
2.0	99.9 ± 0.6
2.5	99.9 ± 0.5

[a] Average of three different experiments. Volume of HNO_3 was 10 mL.

Elution

After near quantitative adsorption of Cr(VI), it was eluted using 10 mL of different concentrations of HNO_3 (0.5–2.5M). A 2.0M concentration of HNO_3 was found to be optimum. The results are shown in Table IV.

Preconcentration of Cr(III)

Since the concentration of Cr(III) in the samples is at the sub-ng mL^{-1} levels, pre-concentration is required prior to ETAAS determination. Preconcentration was carried by coprecipitation with iron (Fe) as hydroxide. However, the process blank of the Cr(III) solution coprecipitated with Fe is higher (14 ng of Cr in 10 mg of Fe) than the concentration of Cr(III) in the samples due to the high amounts of $FeCl_3$ used. Hence, $FeCl_3$ was purified from Cr(III) by extracting it into MIBK. Since the Cr(VI) species present in $FeCl_3$ as contaminant can also be extracted into MIBK, it was reduced to Cr(III) using sodium sulphite prior to extraction. As a result, the process blank was reduced to 0.01 ng in 10 mg of Fe.

Even though the possible mechanism for the adsorption of Cr(VI) is through anion exchange, the tolerance to high salt content/associated anions is possibly due to the presence of SO_4^{2-} as the counter ion which is doubly charged. It therefore has preference over singly charged ions such as Cl-, NO_3^-, and HCO_3^- which are usually present in sea water in large excess. The tolerance of the resin for associated anions, with respect to adsorption of Cr(VI), was found to be 20 mg mL^{-1} for Cl^-, 3 mg mL^{-1} for SO_4^{2-}, and 150 µg mL^{-1} for NO_3^- and HCO_3^-.

TABLE V
Concentration[a] of Cr (III) and Cr(VI) in Different Types of Seawater

Sample	Concentration of Cr(VI) (ng mL^{-1})			
	Present Method		Reported Method	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Seawater	<0.1	1.20 ± 0.04	<0.1	1.40 ± 0.06
Salt-I (Raw)	0.22 ± 0.06	0.45 ± 0.08	0.28 ± 0.08	0.50 ± 0.10
Salt-II (Raw)	0.17 ± 0.06	0.52 ± 0.06	0.20 ± 0.10	0.50 ± 0.10
Salt-III (Purified)	0.12 ± 0.08	0.15 ± 0.08	0.16 ± 0.10	0.16 ± 0.10

[a] Average of three different experiments.

Sampling and Sample Analysis

The seawater samples were collected from Waltair, India, and put into pre-cleaned polypropylene bottles. The synthetic samples were prepared by dissolving 3.5 g of sea salt procured from different vendors in 100 mL of deionized water. The pH of the samples was adjusted to 4–5 just before analysis. The analysis was carried out within two days after collection, though the sample can be stored for one month at natural pH (19).

Since recovery of Cr(III) and Cr(VI) is near quantitative, the procedure described was applied for their determination in real seawater and three synthetic seawater samples. The results are shown in Table V. Raw Salt-I and Raw Salt-II are seawaters prepared using raw sea salt and Purified Salt-III is seawater prepared using purified sea salt. As shown in Table V, the concentrations of Cr(III) and Cr(VI) are at the sub ng mL^{-1} levels, except for Cr(VI) in seawater which is 1.2 ng mL^{-1}. The results were compared with the solvent extraction procedure and were found to be in good agreement.

Limits of detection were computed as 3σ variation in repeated measurements (six measurements) of the process blanks and found to be 0.049 and 0.037 ng mL^{-1}, respectively, for Cr(III) and Cr(VI).

CONCLUSION

The ion exchange method was found to be suitable for the speciation of Cr(III) and Cr(VI) in seawater samples despite the presence of the associated ions such as Cl^-, NO_3^-, HCO_3^-, and SO_4^{2-}. The method is simple, with low process blank values, enables the determination of Cr(III) and Cr(VI) independently, and is suitable for the routine monitoring of Cr(VI) in seawater samples.

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Slurry Sampling Introduction With Electrothermal Vaporization for Multielement Analysis of Amber by ICP-AES

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ABSTRACT

A simple and rapid method is described for the direct multielement analysis of amber by electrothermal vaporization (ETV) inductively coupled plasma atomic emission spectrometry (ICP-AES) and using slurry sampling. Polytetrafluoroethylene (PTFE) was used as the chemical modifier to improve analyte release from the matrix and to match the vaporization behavior of the analytes from the matrix and from the aqueous standard solution for calibration. The fluorination vaporization processes and the influence factors for this method (such as particle size, vaporization temperature, ashing temperature, matrix effect and PTFE content) were investigated in detail. Under optimum operating conditions, detection limits (DL) between 1.3 ng mL^{-1} (Cu) and 131 ng mL^{-1} (Zn) were achieved and precision, expressed as the relative standard deviation (RSD), was better than 9%.

The proposed method was successfully applied to the direct determination of trace V, Cu, Al, Zn, Cd, and Pb in amber using aqueous calibration and minimum chemical pretreatment. The determined values were in good agreement with those obtained by pneumatic nebulization (PN) ICP-AES after decomposition of the same sample by dry ashing. Analysis of the standard reference material, Poplar Leaves GBW 07604, confirmed the reliability of this approach.

INTRODUCTION

Amber is the result of resin fossilization from specific plants over tens of millions of years (1). Unlike other fossils, amber is mainly organic in nature, and its chemical composition remains almost constant (2). Due to its lightness, the ability to be carved, its insulating properties, and the appeal as a gemstone, the material has attracted great interest since ancient times. In addition, it is also used as raw material for the production of medicines as well as for coatings and dyes. The trace element content in amber can give valuable information in the study of the geological, biological, and mineralogical sciences, as well with regard to human health and the environmental impact of its processing and use.

It is well known that amber, as a natural fossil, is difficult to dissolve in organic/inorganic solvents (3), and sometimes the sample size for analysis is limited. Accordingly, there is the need for a method requiring a small sample size and elimination of the dissolution step for the accurate and precise determination of trace elements in amber. Inductively coupled plasma atomic emission spectrometry (ICP-AES), as an effective multi-element analysis technique, has been widely applied to the determination of trace elements in various samples (4–7). However, most analyses by ICP-AES require the destruction of the sample matrix to obtain a solution of the analytes, which could lead to long analysis times, larger sample requirements, risk of contamination and loss of analyte, and discharge of pollutants from sample decomposition.

In recent years, the application of direct solid sampling techniques with ICP-AES, including direct sample insertion, powder insertion, slurry nebulization, laser ablation, and electrothermal vaporization (ETV) have been investigated for routine analysis (8–12). The advantages of solid sampling over conventional wet digestion or dry ashing sample preparation procedures can be summarized as follows: (a) reduced sample pretreatment; (b) less possibility of analyte loss; (c) low contamination risk; and (d) avoidance of the use of corrosive and hazardous chemicals. Of the many solid sample introduction techniques, interest in adapting electrothermal vaporization (ETV) for sample introduction into ICP-AES has increased significantly (13–16). Compared to conventional pneumatic nebulization (PN) sample introduction, ETV offers the benefits of high sampling efficiency, small sample consumption, low absolute detection limits, direct solid sample analysis, and complete or partial removal of the organic/inorganic matrix in the ashing step. Various chemical modifiers can be used in ETV-ICP-AES to promote analyte release from the matrix, and to match the vaporization behavior of the analytes from the matrix and from the aqueous standard solution for calibration (17–20). This not only solves the calibration problems resulting from direct solid sample analysis, but also significantly improves the analytical performance of the method.

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In the present work, a method was developed for the direct determination of the trace elements (V, Cu, Al, Zn, Cd, and Pb) in amber by ETV-ICP-AES using slurry sample introduction. Polytetrafluoroethylene (PTFE) was used as the chemical modifier in order to change the volatility of the analytes and to improve the analytical performance. The focal points in optimizing slurry sample analysis were slurry preparation, particle size, influences of the chemical modifier, and selection of the furnace temperature program. Accuracy and precision of the slurry method using aqueous standards for calibration were evaluated in the analysis of the standard reference material GBW 07604 Poplar Leaves and by comparing the results with a conventional dry ashing method.

EXPERIMENTAL

Instrumentation

A power 2 kW, 27±3 MHz ICP spectrometry source (Beijing Second Broadcast Equipment Factory, P.R. China) and a conventional plasma torch were used. A modified graphite furnace vaporizer was used as the vaporization device. The radiation from the plasma was focused as 1:1 straight image on the entrance slit of a WDG-500-1A monochromator (Beijing Second Optics, Beijing, P.R. China) with a reciprocal linear dispersion of 1.6 nm/mm. The evolved components were swept by a stream of carrier gas from the ETV device into the plasma excitation source through a 0.5-m long Teflon® tube (4 mm i.d.). The transient signals were detected with a R456 type photo-multiplier tube (Hamamatsu, Japan) and a home-built direct current amplifier, and recorded with a U-135 recorder (Shimadzu, Japan).

Reagents and Standard Solutions

The standard stock solutions of V, Cu, Al, Zn, Cd, and Pb (1.0 mg mL^{-1}) were prepared by dissolving the SpecPure® reagents . A 60% (m/V) PTFE emulsion (d<1 μm; viscosity, 7×10^{-3}–15×10^{-3} Pa s) was purchased from the Shanghai Institute of Organic Chemistry (Shanghai, P.R. China). A 1.0% (m/V) aqueous solution of plant glue was employed as the stabilization reagent during preparation of the slurry samples. All reagents were of analytical grade or better. Doubly distilled water was used for all experiments.

Sample Preparation

The amber samples were washed, dried, and ground in an agate mortar until they could completely pass through the different mesh-sized polyester sieves. A 10-mg portion of the sample was accurately taken into a graduated micro-test tube. Then, 0.1 mL 60% (m/V) PTFE slurry, 1% agar (m/V), 0.05% Triton® X-100 solution (v/V), and 3% HNO_3 (v/V), which was previously checked for blanks, were added and the solution diluted to 1.0 mL with doubly distilled water. The resulting mixture was dispersed with an ultrasonic vibrator for 20 min; the bottles were shaken for 1 minute prior to analysis.

Recommended Procedure

After igniting the plasma, a 10-mL volume of sample was deposited into the graphite furnace. The sample inlet hole was blocked using a graphite cone. After drying and ashing, the analyte was vaporized and carried into the plasma by a carrier gas (Ar), and the emission signals of the analytes were recorded simultaneously. The aqueous standard series containing 6% (m/V) PTFE was used for calibration.

RESULTS AND DISCUSSION

Optimization of ICP Operation Parameters

The main operating parameters of ICP, including incident power, flow rate of carrier gas, observation height and entrance/exit slit width, were optimized on the basis of signal-to-background ratios (S/B) by using standard solutions of the analytes containing 6% (m/V) PTFE. The experimental parameters selected for the optimum S/B are given in Table I.

Slurry Preparation

The accuracy and reproducibility of the determinations with a slurry sampling technique depend basi-

TABLE I
Operation Parameters for ETV-ICP-AES

Incident Power	1.0 kW
Carrier Gas (Ar) Flow Rate	0.50 L min^{-1}
Coolant Gas (Ar) Flow Rate	18 L min^{-1}
Observation Height	13 mm
Entrance Slit Width	25 μm
Exit Slit Width	25 μm
Drying Temperature	100°C, ramp 10 s, hold 20 s
Ashing Temperature	700°C, ramp 10 s, hold 30 s
Vaporization Temperature	2400°C
Vaporization Time	4 s
Clear-out Temperature	2700°C for 3 s
Sample Volume	10 μL

cally on the homogeneity and stability of the slurry. In order to optimize the slurry preparation, a number of preliminary experiments were performed. The results demonstrated that 0.1% agar (m/V) + 0.005% Triton X-100 (v/V) + 0.3% HNO_3 (v/V) and a slurry concentration of 1% were optimum with respect to sensitivity and precision. Slurry samples prepared in this way were stable within at least 90 minutes of the analysis. During this period no significant signal intensity variations of the analytes were observed.

Influence of Particle Size

Particle size is one of the most important parameters for slurry preparation. Thus, the influence of particle size was studied by measuring the relative signal intensities of the elements (V, Cu, Al, Zn, Cd, and Pb) in different slurries prepared from the same sample but with different particle sizes. The relative signal intensity is defined as the ratio of the signal intensity of the analyte in the slurry to that in the solution and expressed as percentage with PTFE as the chemical modifier. The experimental results show that when the average particle size of the sample is smaller than 105 μm (140 mesh), the relative signal intensities are higher than 91% with a relative deviation less than ±10%. However, when the average particle size of the sample is larger than 105 μm, the relative signal intensity of the analyte decreases due to the incomplete vaporization of the analytes. These results show that a particle size less than 105 μm is adequate for preparing the slurry.

Selection of Ashing Temperature

Experiments were carried out to determine the signal loss of the elements (V, Cu, Al, Zn, Cd, and Pb) during the ashing step with PTFE. As can be seen in Figure 1, the signal losses of the analytes occur above 800°C. It should be noted that for the easily volatile elements (Cd, Zn, and Pb), the tolerable ashing temperatures were greatly increased due to the formation of the more stable fluorides with higher boiling points (CdF_2:1750°C, ZnF_2: 1497°C, and PbF_2:1293°C, which is beneficial for the removal of the organic matrix in amber. For the simultaneous determination of the elements studied, the ashing temperature was set at 700°C.

Effect of Vaporization Temperature

Figure 2 shows the effects of the vaporization temperature on the signal intensities of the analytes in the presence of PTFE. As shown in Figure 2, the signal intensities of the elements increased gradually with an increase in vaporization temperature. However, the signal intensities could reach the plateau at a proper vaporization temperature (about 2400°C) in spite of the great differences in their physical and chemical properties. This is due to the formation of the more volatile fluoride with similar vaporization characteristics. In this experiment, 2400°C was selected as the vaporization temperature.

Other parameters of the ETV temperature program, such as hold and ramp times for the ashing and vaporization stage, drying and cleaning conditions, were also investigated. The optimum values are listed in Table I using PTFE as the chemical modifier.

Comparison of Vaporization Behavior

For methods based on solid and slurry sampling, in addition to the use of matrix-matched solid stan-

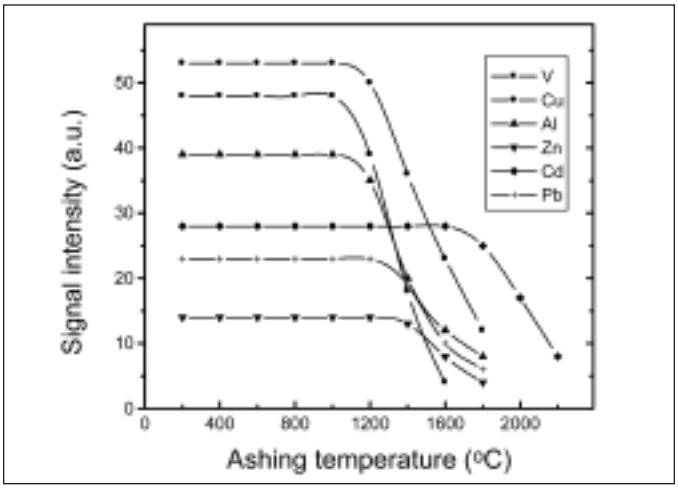

Fig. 1. Influences of asbing temperature on signal intensity with PTFE. V and Cu: 1.0 mg mL^{-1}, Al: 3.0 mg mL^{-1}; Zn, Cd, and Pb: 20 mg mL^{-1}.

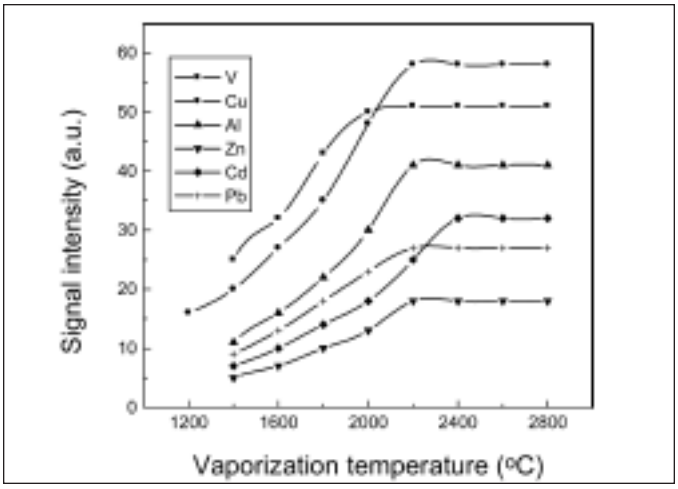

Fig. 2. Signal intensity versus vaporization temperature with PTFE. V and Cu: 1.0 mg mL^{-1}, Al: 3.0 mg mL^{-1}; Zn, Cd, and Pb: 20 mg mL^{-1}.

dards, calibration can be performed using aqueous standard solutions. However, the question is whether the calibration is as accurate as required? To answer this question, V was selected as a representative element to investigate its vaporization behaviors in both the slurry and the solution with and without PTFE. Figure 3 shows that in the absence of PTFE, the signal intensity of V in the slurry and solution was very weak, and the residue signals were almost the same as the original ones. But in the presence of PTFE, sharper and more intense V signals were detected from the slurry and solution, and the height, appearance times, and peak shapes of the emission signals from the slurry were very similar to those from the solution. In addition, there were no memory effects. Similar results were observed for Cu and Al, but the intense signals for the easily volatile elements (Zn, Cd, and Pb) could be recorded in both cases because they do not form the thermally stable oxides or carbides. From the comparison given above, it can be seen that PTFE is a very good chemical modifier in promoting the release of the analytes from the matrix and matches the vaporization behavior of the analytes from the matrix and the aqueous standard solution used for calibration. Therefore, it is feasible and effective to employ the aqueous standard solution for calibration of the slurry.

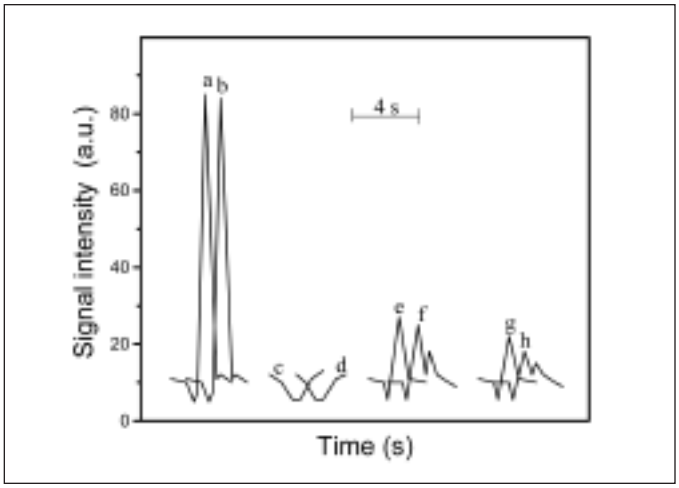

Fig. 3. Comparison of emission signal profiles for V. With PTFE: (a) in the solution; (b) in the slurry; (c) and (d) are their residual signals of the empty firing after vaporization of V, respectively. Without PTFE: (e) in the solution; (f) in the slurry; (g) and(h) are their residual signals of the empty firing after vaporization of V, respectively.

Study of Interferences

The effects of the main coexisting elements (K, Na, Ca, and Mg) in the determination of V, Cu, Al, Zn, Cd, and Pb from amber were investigated with PTFE. It is assumed that a species begins to interfere at a concentration where the signal of the analyte is increased or decreased by 10% in its absence. The results in Table II show that when the concentration of the matrix elements is within 2 mg L^{-1}–5 mg L^{-1}, no emission signal changes are observed.

Effect of PTFE Content

The extent of analyte release from the slurry depends directly on the amount of PTFE used as the chemical modifier. Thus, the effects of PTFE concentration on the signal intensities were studied. It was observed that the signal intensities for V, Cu, and Al increased with increasing amounts of PTFE, and then reached plateaus at a concentration up to 4%. However, PTFE could not affect the emission signals of the easily volatile elements Zn, Cd, and Pb. Taking into account that PTFE could be consumed by the matrix in real sample analysis, 6% of PTFE was selected for subsequent determinations.

Detection Limits and Precision

The detection limits (DL), calculated on the basis of three times the standard deviation of the blank, and the relative standard deviations (%RSD), obtained for nine replicate determinations at a concentration of 0.5 µg mL^{-1} V, Cu and Al, and 3.0 µg mL^{-1} Cd, Zn and Pb, are listed in Table III.

TABLE II
Effect of Matrix Concentration

Element	Wavelength (nm)	Tolerable Amount of Matrix Element (mg mL^{-1})			
		K	Na	Ca	Mg
V	290.882	5.0	5.0	5.0	5.0
Cu	324.754	5.0	5.0	5.0	5.0
Al	308.215	5.0	5.0	3.0	3.0
Zn	334.502	5.0	5.0	2.0	2.0
Cd	228.567	4.0	4.0	3.0	3.0
Pb	220.353	4.0	4.0	3.0	3.0

TABLE III
Detection Limit and Precision (n=9)

Element	Wavelength (nm)	Detection Limit (ng mL^{-1})	RSD (%)
V	290.882	2.0	3.5
Cu	324.754	1.3	2.3
Al	308.215	1.5	4.7
Zn	334.502	131	8.9
Cd	228.567	6.3	5.1
Pb	220.353	76	7.2

Sample Analysis

The proposed method, based on the aqueous standard addition method and the calibration curve method, was applied to directly determine the elements V, Cu, Al, Zn, Cd, and Pb in amber. The same sample was also analyzed by pneumatic nebulization (PN)-ICP-AES after decomposition of the sample using a dry ashing method. The results obtained by both techniques are in good agreement (Table IV). In addition, in order to confirm the accuracy of the method, the standard reference material GBW 07604 Poplar Leaves was analyzed. The obtained results are in good agreement with the certified values (Table V).

TABLE IV
Analytical Results of the Trace Elements in Amber (n=5)

Element	ETV-ICP-AES		PN-ICP-AES	
	Calibration Curve Method[a] ($\mu g\ g^{-1}$)	Standard Addition Method[a] ($\mu g\ g^{-1}$)	Calibration Curve Method[b] ($\mu g\ g^{-1}$)	Standard Addition Method[b] ($\mu g\ g^{-1}$)
V	5.41 ± 0.47	6.02 ± 0.74	5.24 ± 0.62	6.31± 0.53
Cu	13.2 ± 1.6	14.9 ± 1.3	15.8 ± 1.8	13.9 ± 1.2
Al	42.7 ± 2.4	40.3 ± 4.1	41.9 ± 3.5	39.4 ± 2.7
Zn	25.4 ± 3.1	26.7 ± 2.5	27.3 ± 3.0	24.9 ± 2.3
Cd	0.84 ± 0.13	0.73 ± 0.10	0.92 ± 0.15	0.85 ± 0.09
Pb	1.45 ± 0.2	1.51 ± 0.24	1.33 ± 0.18	1.39 ± 0.16

[a] Direct analysis with slurry sampling.
[b] Analysis after dry ashing decomposition of the sample.

TABLE V
Analytical Results of the Trace Elements in Standard Reference Material GBW 07604 Poplar Leaves (n=5)

Element	Determined Value[a] ($\mu g\ g^{-1}$)	Certified Value ($\mu g\ g^{-1}$)
V	0.73±0.10	0.64
Cu	10.2±0.87	9.3±0.5
Al	1105±62	1040±50
Zn	39.4±2.8	37±1.0
Cd	0.36±0.07	0.32±0.05
Pb	1.37±0.25	1.5±0.2

[a] Calibration curve method with slurry sample.

CONCLUSION

A slurry sampling technique coupled with ETV for the direct determination of trace elements in amber by ICP-AES has been developed. Compared to the traditional sample preparation methods, such as acid digestion or dry ashing, the slurry sampling technique offers benefits, such as small sample requirement, reduction of sample contamination, and no discharge of pollutants from sample decomposition. Furthermore, PTFE as the chemical modifier in ETV-ICP-AES greatly promotes the release of the analytes from the slurry, which leads to a similar vaporization behavior of the analytes in both the slurry and the solution. Thus, calibration of the slurry samples can be performed using aqueous standards. The proposed method could become a routine method for the direct determination of trace elements in biological and environmental samples.

ACKNOWLEDGMENTS

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A Combined Isopiestic and Sub-boiling Distillation Method for the Purification of Hydrofluoric Acid Used for ICP-MS Elemental Analysis

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ABSTRACT

Purification of hydrofluoric acid (HF) has been achieved by the combination of isopiestic and sub-boiling distillation. For better yield and purity, the collection vessel's position is optimized. The distillation assembly is made from polyethylene which is available in any chemical laboratory. Impure acid (100 mL) is placed in a 1-L HDPE container and the collection vessel (PTFE beaker) containing 25 mL pure water is kept inside the container on a perforated stand. The whole distillation set-up is heated in a water bath at 80ºC. After eight hours, 35 mL of pure HF of ~40% strength is obtained from 100 mL of impure 48% HF. The production of high purity HF can be increased by increasing the volume of the feed HF. The impurities in pure acid are preconcentrated in an *in situ* evaporating system and determined by ICP-MS after suitable dilution. The levels of impurity are in the sub-ng/g to ng/g range and the purity of the acid is close to a commercially available pure (Suprapur®) grade HF with respect to Cd, Co, Cr, Cu, Ga, In, Mg, Mn, Ni, Pb, Sr, and Zn.

INTRODUCTION

The analysis of high-purity materials demands high-purity reagents for sample preparation to ensure low experimental blank values (1). Hydrofluoric acid (HF) is one such reagent used extensively but it needs purification (2). High-purity HF is prepared either by isopiestic distillation in which the distill and the distillate are kept at the same temperature to attain equal vapor pressure at equilibrium, or sub-boiling distillation (3,4). Isopiestic distillation methods require around 100 hours to reach saturation of acidity (5). Moreover, for isopiestic distillation of HF, 35M (75%) HF is required as the feed solution (3). We reported on-line purification of HCl and HF for sample preparation and found that even though purification of HCl can be carried out through vapor generation at room temperature, heating is required for generating vapors of HF for purification if the feed solution is 48% HF (1,6). Hence sub-boiling distillation methods are preferred over isopiestic distillation methods. Sub-boiling distillation based on a Teflon® still requires a class 100 environment since the collection vessel is exposed to ambient environment (7). However, Mattinson's procedure, in which the collection vessel is also kept in an enclosed environment, solved the problem of environmental contamination and is used for the purification of HF (8,9). In this procedure, the rate of distillation depends on the position of the IR lamp and on the temperature of the collection vessel (10). However, it suffers from larger distillation times due to the condensation of HF vapors at cooler regions of the feed container. To our knowledge, further improvements on the procedure of HF purification have not been reported.

In this paper, we report a method for HF purification based on a combination of isopiestic and sub-boiling distillation resulting in an increase in production rate and providing a purity that is comparable to commercial systems based on sub-boiling distillation.

EXPERIMENTAL

Instrumentation

A VG Plasma Quad PQ 3, VG Elemental ICP-MS was used for the analysis. The instrumental parameters are given in Table I.

Reagents and Containers

Nitric acid and glycerol were of Suprapur® grade (E. Merck, Darmstadt, Germany) and AR grade (S.D. Fine Chemicals, Mumbai, India), respectively. 48% laboratory grade (LR) HF was used as the feed solution. Ultrapure water (18MΩ cm) was obtained by passing tap water through a reverse osmosis system (made in BARC, Mumbai, India) and then through a de-ionization system. This water was passed through a Milli-Q™ water purification system (Millipore Corporation, Bedford, MA, USA) and finally collected on a clean bench.

Standards

Multi-element standard solutions were obtained from E. Merck, Germany. Working standards at the ng/mL levels were prepared daily from µg/mL standards. The HDPE containers and the PTFE beakers used for the distillation process were procured from a local market and Nalgene, U.S.A., respectively. These containers were cleaned by

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soaking in 10% HNO_3 and then washed with de-ionized water. Acidities were estimated volumetrically by titration with standard sodium hydroxide solution and using phenolphthalein as an indicator.

Procedure

Impure HF (100 mL) was placed in a 1-L HDPE container, and a perforated stand was placed in the HF. A 100-mL PTFE beaker with 25 mL water was placed on the stand. The 1-L container was closed and the closed-stem funnel was centered over a 100-mL beaker (see Figure 1). This setup was placed in a water bath which was maintained at 80°C. After 8 hours, the contents of the beaker (i.e., 23M HF) were evaporated to dryness in a glycerol bath as reported earlier (11), diluted to 5 mL using 2% HNO_3, and analyzed for impurities using inductively coupled plasma mass spectrometry (ICP-MS). To study the acidity of HF that formed in the beaker with time, 1 mL solution from the beaker was removed with a pipette after appropriate times and titrated against standard NaOH.

Safety Note: Precautions during handling of HF are absolutely necessary. After purification, the assembly needs to be cooled to room temperature before opening in a well-ventilated fume hood to avoid inhalation. Gloves must be worn to avoid skin contact.

TABLE I
ICP-MS Instrumental Operating Conditions

RF Power	1350 W
Plasma Gas Flow Rate	13.4 L min^{-1}
Auxiliary Gas Flow Rate	0.66 L min^{-1}
Nebulizer Gas Flow Rate	0.85 L min^{-1}
Sampler Cone	Ni, 1-mm orifice
Skimmer Cone	Ni, 0.7-mm orifice
Torch Type	Fassel
Scanning Mode	Peak Jump
No. of Replicate	3
Dwell Time	300 µs $Channel^{-1}$
Isotopes monitored:	^{24}Mg, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{69}Ga, ^{88}Sr, ^{110}Cd, ^{115}In, ^{208}Pb

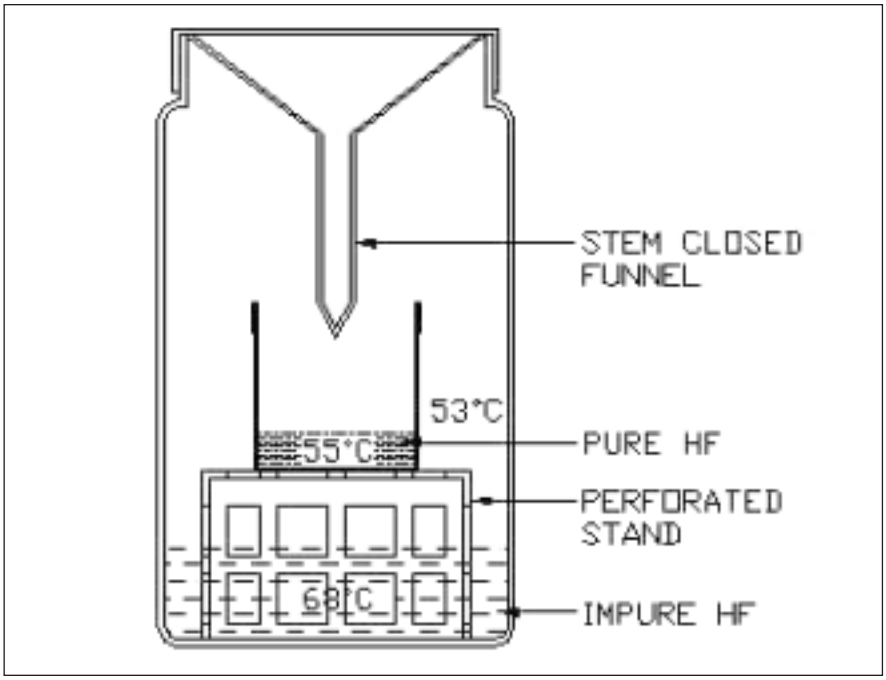

Fig. 1. HF purification system.

RESULTS AND DISCUSSION

Hydrofluoric acid can be purified using isopiestic and sub-boiling distillation methods. However, both procedures suffer from the problems mentioned above. A combination of these methods may result in a better and simpler way to produce high-purity HF. In the present study, use of a combination of these two distillation methods is described. The experimental setup is shown in Figure 1. The funnel is placed at the coolest part of the container such that the condensed HF can slide into the beaker. The yield of acid depends on the position of the collector which plays a crucial role. The collector is kept at the bottom and in the middle of the container for obvious reasons. However, the yield is low (~20 mL in 8 hours), primarily due to a higher rate of evaporation since the collector is immersed in the acid and directly heated in the water bath. To increase the yield, the collector is mounted on a perforated stand at a height at which the rate of evaporation is very low. The perforated stand serves to provide a larger area for evaporation in the outer container, increases yield, and reduces the chance of contamination due to any other transfer mechanism of the liquid. Hence, the setup shown in Figure 1 has

been chosen for the purification of HF. The advantages of the method are: (i) simple and fast, (ii) cost-effective, (iii) low risk of contamination, (iv) 48% or lower concentrations of HF can be used as the feed solution for the purification instead of 75% HF, (v) closed system enables purification even in a normal laboratory environment, and (vi) any volume of HF can be used for purification. In the present study, 100 mL of 48% impure HF was used as the feed solution, which resulted in the production of 35 mL of high-purity HF. However, to produce higher volumes of high-purity HF, the volume of the feed solution needs to be increased.

The acidity of the HF collected in the beaker is determined with time using alkali titration. The acidities obtained at different times with stand and funnel, with stand and without funnel, and without stand and funnel (shown in Figure 2) reveal the importance of the stand and the funnel. At optimum conditions, i.e., with funnel and stand, 23M HF was obtained at 8 hour (Figure 2). Under the same experimental conditions, the time required for room temperature isopiestic distillation is 12 days (Figure 2). The purified acid was evaporated to dryness in a clean environment with an acid evaporation system developed in our laboratory (11). The residue was diluted to the required volume in 2% HNO_3 and analyzed for Cd, Co, Cr, Cu, Ga, In, Mg, Mn, Ni, Pb, Sr, and Zn by ICP-MS. The concentrations of the impurities present in purified HF are listed in Table II along with the impurities present in impure HF. The levels of impurities in HF purified by the proposed procedure are comparable to commercially available high-purity HF, but requires much shorter production times (4). However, it should be noted that the purity of HF produced by sub-boiling distillation is marginally inferior to the isopiestic distillation methods. However, isopiestic distillations are not commonly used since concentrations of 75% HF are required in the feed solution, and distillation times are significantly lower.

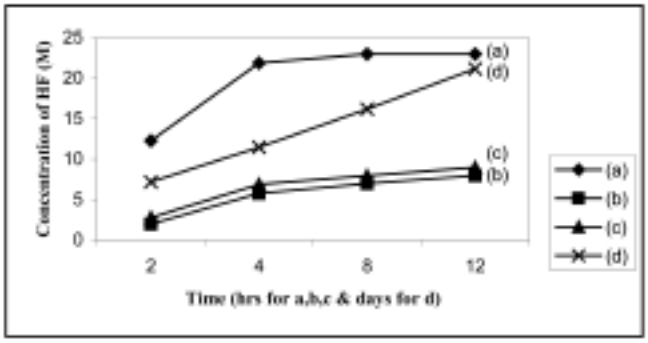

Fig. 2. Concentration of HF with time.
a: with stand and funnel; b: with stand and without funnel;
c: without stand and funnel; d: room temperature isopiestic distillation.

TABLE II
Comparison of Concentration of Impurities in Purified and Impure HF[a]

Element	Impure HF (ng/mL)	Purified HF (ng/mL)
Cd	0.04 ± 0.01	<0.03
Co	0.17 ± 0.06	0.04 ± 0.01
Cr	2.28 ± 0.02	1.02 ± 0.11
Cu	28.10 ± 0.01	0.56 ± 0.14
Ga	0.17 ± 0.02	0.06 ± 0.01
In	8.21 ± 0.10	<0.3
Mg	111.3 ± 3.4	2.82 ± 0.70
Mn	2.80 ± 0.02	0.30 ± 0.01
Ni	1.96 ± 0.02	0.63 ± 0.09
Pb	54.1 ± 10.6	0.50 ± 0.10
Sr	1.54 ± 0.01	0.20 ± 0.05
Zn	11.52 ± 0.11	2.85 ± 0.40

[a] Values are the mean of three different experiments.
Uncertainties are expressed as 1 σ variation in the respective measurements.

In the present procedure, the isopiestic distillation time has been decreased by increasing the temperature, and the loss of yield due to condensation of the HF vapors in sub-boiling distillation has also been alleviated by condensing the vapors on the funnel.

CONCLUSION

In this study, isopiestic and sub-boiling distillation working in tandem has demonstrated to be a better alternative for existing purification methods for HF. The method reported is simple and inexpensive. The yields are better and the time of operation is less than with either method alone. The final acid is of comparable purity to commercially available HF. The system can be assembled in any laboratory to produce high-purity HF

for day-to-day operation within reasonable time. This is beneficial in locations where importing of reagents takes a long time, such as in developing countries.

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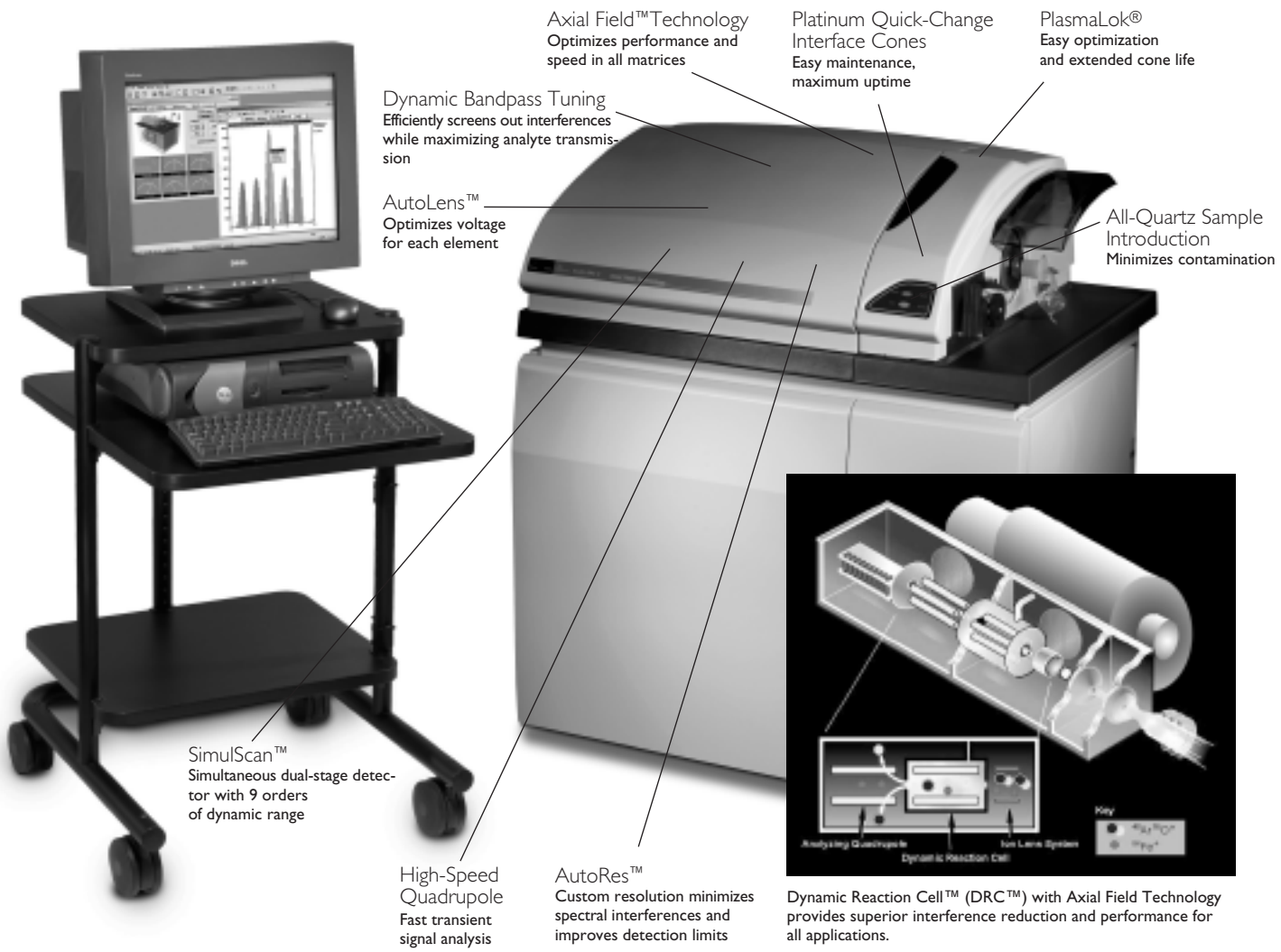

Dynamic Reaction Cell™ (DRC™) with Axial Field Technology provides superior interference reduction and performance for all applications.

Eliminates interferences **COMPLETELY**

When your applications extend beyond the capabilities of conventional ICP-MS, you need the power of the innovative ELAN® DRC II. The DRC II combines the power of patented Dynamic Reaction Cell (DRC) technology with performance-enhancing Axial Field Technology, providing uncompromised sensitivity and performance in all matrices for even the toughest applications. Unlike collision cell, high-resolution, or cold plasma systems, the DRC II completely eliminates polyatomic interferences providing ultratrace-level detection limits.

The DRC II uses chemical resolution to eliminate plasma-based polyatomic species before they reach the quadrupole mass spectrometer. This ion-molecule chemistry uses a gas to "chemically scrub" polyatomic or isobaric species from the ion beam before they enter the analyzer, resulting in improved detection limits for elements such as Fe, Ca, K, Mg, As, Se, Cr, and V.

Unlike more simplistic collision cells, patented DRC technology not only reduces the primary interference; it eliminates sequential side reactions that create new interferences. Unless kept in check by DRC technology, these uncontrolled reactions increase spectral complexity and create unexpected interferences.

PerkinElmer® precisely.