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Application of Solvent Extraction and Acid Hydrolysis of Nb/Ta Separation Methods for the Determination of Uranium in Geological Materials, Nb/Ta-type Samples, and Leach Liquors by ICP-OES

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ABSTRACT

Two methods are described for the separation and estimation of uranium using (a) solvent extraction for geological materials of silicate matrix, yellow cakes, and leach liquor-type samples and (b) acid hydrolysis for Nb/Ta- bearing samples by inductively coupled plasma optical emission spectrometry (ICP-OES). Solvent extraction separation of U from 1–4 M HNO_3 acid medium using tri-n-butyl phosphate (TBP) or tri-n-octyl phosphine oxide (TOPO) in carbon tetrachloride selectively separates U from the accompanying elements in different types of geological materials.

The extracted U content is back-stripped using sodium pyrophosphate/sodium tri-polyphosphate or ammonium carbonate in the presence of pentanol-1 for quantitative recoveries. This is performed before aspiration into the plasma for measurement at the U(II) 409.014-nm emission line. However, ammonium carbonate is recommended since it results in better signal-to-noise ratios. Acid hydrolysis separation of Nb/Ta-type samples quantitatively separates U from the major matrix elements and the remaining common elements do not influence the U signal in ICP-OES.

The silica-rich geological materials were dissolved by HF-HNO_3–H_2SO_4 treatment followed by dissolution in 4M HNO_3 acid before applying the solvent extraction procedure. In the case of Nb/Ta-bearing samples, U was separated from Nb and Ta by acid hydrolysis, involving fusion with Na_2O_2, dissolution in HCl, followed by NH_4OH precipitation and hydrolysis in HCl in the presence of sulfurous acid. The oxychloride precipitates of Nb and Ta are filtered off and the filtrates assayed for U.

The proposed methods were applied to some international geological reference standards (GXR-1, SY-2, SY-3, Mica-Fe, NBS-120b, and DH-1a), several yellow cake samples, leach liquors, and to some Nb/Ta-bearing samples including two British Geological Survey reference standards, IGS-33 and IGS-34. The results are compared with fluorimetric (in case of Nb/Ta samples) and gravimetric methods (in case of yellow cakes). Both methods described are simple, rapid, and accurate showing a relative standard deviation of less than 1% at the 2610-µg/g level and 4.8% at the 33-µg/g level, with the lowest determination limit obtained at 25 µg/g.

INTRODUCTION

Uranium (U) is a sparsely dispersed element in the earth's crust with an average crustal abundance of 1.8 µg/g (1). Even though the occurrence of independent uranium minerals like Uraninite (UO_2), Autunite [$Ca(UO_2)_2(PO_4)_2 . 10–12\ H_2O$], Torbernite [$Cu(UO_2)_2(PO_4)_2 . 12H_2O$], Carnotite [$K_2(UO_2)_2(VO_4)_2 . 1–3H_2O$], Uranophane [$CaO . 2UO_3 . 2SiO_2 . 6H_2O$], and Coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] is reported (2), their deposition and occurrence is very rare. Coupled substitutions and isovalent replacements of ions of Nb, Ta, Ti, rare earth elements (REEs), Th, etc. by uranium ion are observed in many minerals like Betafite [$(U,Ca)(Nb,Ta,Ti)_3 O_9 . H_2O$], Brannerite [$(U, Ca, Fe, Th, Y)_3 Ti_5O_{16}$], and Davidite [$(Fe, Ce, La, Y, U, Ca, Zr, Th)(Ti, Fe, V, Cr)_3 (O,OH)_7$]. Accordingly, high uranium values are reported (2) in Nb-Ta and other minerals such as Betafite (up to 27.15% UO_3), Brannerite (up to 51.76% U_3O_8), and Davidite (up to 9.8% U_3O_8), mainly of pegmatatic origin. However, the largest reserves of uranium are disseminated in sediments, usually sandstones and the majority of smaller deposits are pitchblende veins such as those of Great Bear Lake in Canada and Katanga in the Congo.

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There is an increasing demand worldwide for uranium and its nuclear products like radium due to their unique applications in new technologies such as pigment and chemical industries, medical and other industrial applications, uranium-fueled nuclear reactors for generation of electricity for civilian use, in addition to their uses for military/defense purposes.

The multifarious composition of geological samples and the refractory nature of many elements make multielement analysis of geological samples often difficult and time-consuming. The demand for fast, yet accurate multi-element analysis in geological prospecting has necessitated the development of new instrumental methods to replace some of the classical methods as described by Washington (3). Several methods have been reported (4–16) for the determination of uranium in various types of samples including geological materials. Cation-exchange column chromatography coupled to thermal ionization mass spectrometry (10), solvent extraction followed by fluorimetry/UV-VIS spetrophotometry (7,14), preconcentration on polyurethane foam coupled to X-ray fluorescence spectrometry (9), ashing of plant samples followed by instrumental neutron activation analysis (INNA) (12), inductively coupled plasma mass spectrometry (ICP-MS) (8,11,15,16), or inductively coupled plasma optical emission spectrometry (ICP-OES) (5,6,13) have been applied for the separation from major matrix elements and estimation of uranium. The most popular method routinely used in our laboratory is the extraction of uranium from the matrix elements with ethyl acetate in the presence of aluminum nitrate as a salting-out agent, followed by fusion of the dry aliquot using a mixture of (1:4) NaF/Na_2CO_3 and estimation by fluorimetry. The use of atomic absorption spectrometry (AAS) is limited to indirect methods where trace uranium is concerned (4) due to the refractory nature of the uranium oxides, resulting in low atomization efficiency and poor sensitivity. Almost all methods require preliminary separation of uranium from the other elements that may interfere with the determination of uranium, and also for better signal-to-noise background ratios at trace level determinations. However, an alternative method for the estimation of uranium in different types of geological materials including leach liquors and yellow cake samples using ICP-OES is proposed.

In the present study, two different separation procedures are described for the estimation of uranium in geological materials by solvent extraction and in Nb/Ta-bearing samples by acid hydrolysis (20,21). Detailed studies of different solvent extraction separation systems were conducted including tri-n-octyl phosphine oxide (TOPO)/CCl_4, and di-(2-ethylhexyl)phosphoric acid (D_2EHPA)/toluene systems from nitric acid solutions. The solvent extraction procedure using TBP/CCl_4 or TOPO/CCl_4 is quite effective for the quantitative and selective extraction of uranium into the organic phase. Different stripping systems such as sodium pyrophosphate, sodium tri-polyphosphate, or ammonium carbonate were attempted to backstrip the extracted uranium content from the organic phase. Comparing the results of all these systems, the ammonium carbonate system gave better signal-to-noise ratio for the trace level estimation of uranium. However, quantitative recoveries could not be obtained using ammonium carbonate/sodium tri-polyphosphate from D_2EHPA/toluene extracts and the results are presented.

The uranium content in Nb/Ta-bearing samples was quantitatively separated from Nb and Ta by acid hydrolysis using prior fusion of the sample with sodium peroxide, dissolution in HCl, followed by ammonia precipitation and dissolution of the precipitate in HCl (final concentration 10%, v/v) to carry out acid hydrolysis in the presence of added sulfurous acid. The precipitated oxychlorides of Nb and Ta are filtered off and the filtrate is monitored for uranium values by ICP-OES.

The proposed solvent extraction-stripping method was validated by applying it to various international reference standards such as GXR-1 [Jasperoid, United States Geological Survey (USGS)], SY-2, SY-3 [Syenites, Canadian Certified Reference Materials project (CCRMP)], Mica-Fe Biotite [Centre de Recherches Petrographiques et Geochimiques, France (CRPG)], NBS-120b Phosphate Rock [National Bureau of Standards, USA (NBS)], and DH-1a Uranium Thorium Ore [Canada Centre for Mineral and Energy Technology, Canada (CANMET)]. The method was also applied to some “yellow cakes” and leach liquor samples. The acid hydrolysis method was applied to several Nb/Ta-bearing samples, including two reference standards, IGS-33 and IGS-34 [Niobates-Tantalates, Institute of Geological Sciences, U.K (IGS)] and the results are compared with fluorimetric values. The procedures show excellent agreement with the certified values, whereas in case of IGS-33 and IGS-34, the obtained values are presented as the usable values.

EXPERIMENTAL

Instrumentation

Fluorimetric Measurements

All fluorimetric measurements were performed using a Jarrell Ash fluorimeter, Digital Model Jarrell Ash, 27-000.

ICP-OES Measurements

All ICP-OES measurements were made using a LABTAM (now GBC, Australia) Model 8410 Plasma scan ICP-OES instrument, equipped with a computer-controlled rapid scanning monochromator (focal length 0.75 m), employing a ruled grating of 1800 grooves/mm in a Czerny-Turner mounting. A more detailed description of the equipment is reported elsewhere (22,23). The optimum instrumental parameters and other operating conditions are given in Table I. All measurements were made under vacuum conditions. Calibration was done with a uranium standard (20 µg/mL), prepared by serial dilution of solutions made from 99.99 % specPure oxides (Johnson Matthey, Royston, U.K.). The instrumental detection limit of uranium at 409.014 nm was found to be 0.0686 µg/mL.

Reagents

All reagents and standards used were prepared from analytical grade and specPure chemicals (Johnson and Matthey). Double-distilled water was used for all subsequent dilutions wherever required. Uranium standard stock solution (1000 µg/mL) was prepared by dissolving 0.2948 g U_3O_8 in a minimum volume of nitric acid and made to 250-mL final volume, maintaining an overall acidity of 10% (v/v) HNO_3.

TABLE I
ICP-OES Instrumental Parameters and Operating Conditions

Instrument	LABTAM Model-8410 Plasmascan
Rf generator	27.12 MHz(crystal-controlled)
Plasma torch	Demountable type, DMT-2000 (GBC, Australia)
Pump	Peristaltic, ten-roller, Gilson® Minipuls-2
Nebulizer	G.M.K. (V-groove, modified Babington type)
Operating power	1.2 KW
Reflected power	<5 W
Viewing height	14-mm above load coil
Argon gas flow rates :	
Coolant	14 L/min
Auxiliary	1.0 L/min
Sample	0.8 L/min
PMT voltage	1000 V
Integration time	3 s (n=3)
Solution uptake rate	4.0 mL/min
Sample flush time	10 s
Entrance slit	20 µm and 3 mm height (fixed)
Exit slit	40 µm
Peak search window width	0.12 nm

PROCEDURE

Sample Decomposition

Geological Samples of Silicate Matrix

A 1.0-g sample (150–200 mesh) was digested in a platinum dish with a mixture of hydrofluoric acid (10 mL, 40 %) and nitric acid (10 mL, 8M) to dryness, followed by HNO_3 – H_2SO_4 treatment with a final dissolution in HNO_3. The residue, if any, was fused with a minimum of sodium carbonate in a platinum crucible, the cooled melt was dissolved in the original filtrate and made up to 50-mL volume in a final nitric acid concentration of 4M.

Leach Liquor Samples

A 2–10 mL aliquot of the liquor sample was evaporated to dryness in a 100-mL glass beaker, followed by HNO_3 treatment (twice, 10 mL of 8M each time) with a final dissolution in 50 mL of 4M HNO_3.

Solvent Extraction

The sample solution in 4M HNO_3 (50 mL) was extracted twice with 10 mL each time of 30% (v/v) TBP in CCl_4 (pre-equilibrated with 4M HNO_3) for a contact time of 5 min, using a separating funnel. Both organic extracts (20 mL) containing uranium were back-washed with 100 mL of 4M HNO_3 and the aqueous layer was discarded. The organic extract was back-stripped three times with 10 mL each of 0.5M ammonium carbonate + 3 mL pentanol–1 for a contact time of 5 min. The three aqueous layers were mixed, neutralized with HNO_3, boiled for 5–10 min, cooled and brought to 50-mL final volume (or above depending on the concentration of uranium), maintaining an overall acidity of 5% (v/v) HNO_3. This solution was aspirated into the plasma for estimating uranium concentration values at U(II) at 409.014 nm after prior calibration with the working standards.

TABLE II
Uranium Values Obtained by Proposed Solvent Extraction Method in Some Standard Reference Materials (SRM) Using ICP-OES (at 409.014 nm)

Sl No.	SRM	Uranium (µg/g) Proposed Method[a]	(%) RSD	Certifd Value[b] U (µg/g)
1.	GXR-1	33.0	4.79	34.9
2.	Mica-Fe	79.4	3.63	80.0
3.	NBS-120b	125.8	3.00	128.4
4.	DH- 1a	2610.0	0.55	2629.0 *
5.	SY-2	275.0	2.87	284.0
6.	SY-3	647.6	1.77	650.0

[a] Extraction with 30% TBP/CCl_4 (from 4M HNO_3 solution) and stripping with 0.5M Ammonium Carbonate + Pentanol-1 system.
[b] Certified values (24, 25*).

Table II lists the analytical values of uranium in reference materials GXR-1 (USGS), SY-2, SY-3, DH-1a (CCRMP/CANMET), Mica-Fe (CRPG), and NBS-120 b (NBS). The relative standard deviation (RSD) of the solvent extraction method is 0.55% (at the 2610-µg/g level) to 4.79% (at the 33.0-µg/g level).

The (%) analytical results for U_3O_8% in some yellow cake samples are presented in Table III and the values compare very well with the well-established homogeneous gravimetric procedure. Table IV shows the uranium values obtained by the proposed method for some of the leach liquor samples. The values obtained by direct estimation in all of the studied samples are on the higher side due to some spectral and background interferences.

Acid Hydrolysis (Nb/Ta-bearing Samples)

A 0.5-g sample (150-200 mesh) was fused with 10.0 g of Na_2O_2 in a nickle crucible and the cooled melt was put in dilute (5% , v/v) HCl and boiled for about 15 min. Ammonia precipitation was carried out in the presence of NH_4Cl and the hydroxide precipitate was filtered off through a Whatman 540 (15 cm) filter paper. The precipitate was thoroughly washed with a solution of 5% (v/v) NH_4OH in 1% (w/v) NH_4Cl, then transferred into the same beaker with a fine jet of 10% (v/v) HCl, and brought to a final volume of about 100 mL, maintaining an overall acidity of 10% (v/v) HCl. The solution was boiled gently to complete the hydrolysis of Nb and Ta (about 15 min). A few drops (5–6 drops) of sulfurous

TABLE III
Analytical Results for (%) U_3O_8 in Some Yellow Cake Samples at the 409.014-nm Emission Line Using ICP-OES

Sample	% U_3O_8 Dissolution[a] Procedure	Gravimetric[b] Procedure	(%) RSD[c]
AMD-15	62.64	62.45	0.66
AMD-16	67.22	67.45	0.88
AMD-17	64.72	64.80	0.34

[a] Average of five values, obtained by dissolution of the sample (0.2 g) after treatment with HNO_3 and residue if any (due to silica) was filtered off, ignited in a platinum crucible, treated with HF and final dissolution in 5% (v/v) HNO_3, both filtrate and residue solution were mixed and made to 100 ml volume. Suitable aliquot was subjected to the proposed solvent extraction – stripping method.
[b] Values obtained by the gravimetric procedure after homogeneous precipitation of uranium as uranyl ammonium phosphate and subsequent ignition to uranium pyrophosphate for measurement.
[c] Relative standard deviation of the above proposed method.

TABLE IV
Analytical Results for Uranium (mg/L) in Some Leach Liquor Samples Using ICP-OES at the 409.014-nm Emission Line

Sample	Proposed Method [a] (Average of five values) U (mg/L)	(%) RSD	Direct Estimation [b] (Average of five values) U (mg/L)	(%) RSD
AMD-18	144.4	0.63	147.2	1.06
AMD-19	403.0	0.46	425.4	0.76
AMD-20	247.8	0.38	276.0	0.48
AMD-21	193.0	0.41	216.6	0.68
AMD-22	279.4	0.73	301.2	1.00
AMD-23	165.1	0.53	183.5	0.73
AMD-24	225.1	0.37	242.4	0.58
AMD-25	215.0	0.47	243.4	0.63
AMD-26	375.8	0.59	412.2	0.77
AMD-27	254.4	0.91	274.8	1.06

[a] Estimated by the proposed method of solvent extraction separation of uranium using 30% TBP/CCl_4 followed by stripping using ammonium carbonate and final dissolution in 5% (v/v) HCl acid solution.
[b] Estimated direct, after evaporation of suitable aliquot followed by dissolution in 5% (v/v) HCl acid solution.

acid (5–6% SO_2 solution) and a quarter of a Whatman ashless filter tablet were added to the solution, which was then cooled and filtered through the same filter paper with thorough washing with 10% (v/v) HCl. The filtrate was made up to 100-mL volume, maintaining 10% (v/v) HCl before aspiration into the plasma for measurement of the uranium signal.

The analytical results of the determination of uranium in the Nb/Ta-bearing samples are presented in Table V. The results compared very well with the values obtained by the well-established fluorimetric method. The relative standard deviation of the method varies from about 1% (0.8% at the 0.210% U_3O_8 level) to 5.3% (at the 0.032% U_3O_8 level). During the acid hydrolysis stage, sulfurous acid was added to act as a coagulant for colloidal niobic and tantalic acids.

RESULTS AND DISCUSSION

Selection of Emission Line

Considering the expected elemental concentrations, spectral interferences, and detection limits, the 14 most sensitive emission lines of uranium, as listed in the Atlas of Spectral Lines (26), were scanned thoroughly and the ionic emission line at 409.014 nm was chosen for the matrix elements. The line gives a detection limit of 0.0686 µg/mL U with a net signal-to-background intensity of 21.9 for U, 50 µg/mL. The line is free from almost all major elements, except a minor correction from Nb, Ta, and Zr. The instrumental detection limits and background equivalent concentrations obtained for the 14 emission lines studied are presented in Table VI and the inter-elemental and spectral interferences studied are presented in Tables VII and VIII.

TABLE V
Analytical Results for (%) U_3O_8 in Some Nb-Ta Samples

Sample	(%) U_3O_8 Proposed Method[a]	Fluorimetr. Values[b]	(%) RSD[c]
IGS – 33 d	0.032	0.033	5.30
IGS – 34 d	0.433	0.432	0.97
AMD – 1	0.120	0.121	2.17
AMD – 2	0.115	0.116	1.99
AMD – 3	0.130	0.132	1.28
AMD – 4	0.139	0.142	1.64
AMD – 5	0.045	0.046	5.09
AMD – 6	0.126	0.127	1.18
AMD – 7	0.063	0.063	2.36
AMD – 8	0.167	0.168	1.37
AMD – 9	0.072	0.074	2.31
AMD – 10	0.151	0.153	1.11
AMD – 11	0.066	0.066	2.55
AMD – 12	0.210	0.213	0.80
AMD – 13	0.068	0.070	2.45
AMD – 14	0.150	0.151	1.12

[a] Average of five values, obtained using the proposed method by ICP-OES at the 409.014-nm line in acid hydrolysis solution.
[b] Values obtained by pellet fluorimetry (fusion of the sample with $KHSO_4$ and dissolution in citric acid followed by extraction of uranium using ethyl acetate in presence of $Al(NO_3)_3 . 9H_2O$ as salting out agent from 10% HNO_3 acid medium. The residue after evaporation of the ethyl acetate aliquot was fused with Na_2CO_3 + NaF (4:1) mixture in a platinum dish and fluorescence measurements were made on the cooled pellet.
[c] Relative standard deviation of the proposed method.
[d] International Reference Standards (Niobate-Tantalate) from British Geological Survey, U.K.

TABLE VI
Detection Limits (DLs) and Background Equivalent Concentrations (BECs) of U (50 µg/mL) in 10% (v/v) HCl With Peak Integration Time of 3 s (n=3). Ip = Peak intensity; I_b = Background Intensity

Wavelength (nm)	Ip	I_b	BEC (µg /mL)[a]	DL (µg /mL)[b]	$Ip-I_b/I_b$
385.958	3429	100	1.5020	0.0451	33.3
367.007	2092	123	3.1234	0.0937	16.0
263.553	2173	181	4.5432	0.1363	11.0
409.014	2676	117	2.2860	0.0686	21.9
393.203	2086	104	2.6236	0.0787	19.1
424.167	1590	128	4.3775	0.1313	11.4
294.192	348	36	5.7692	0.1731	8.7
385.466	1522	112	3.9716	0.1191	12.6
288.963	702	70	5.5380	0.1661	9.0
256.541	1251	75	3.1888	0.0957	15.7
279.394	1046	91	4.7644	0.1429	10.5
468.907	539	66	6.9767	0.2093	7.2
424.437	939	78	4.5296	0.1359	11.0
286.567	760	61	4.3634	0.1309	11.5

[a] BEC is calculated from: Concentration (µg /mL) x Ib / (Ip – Ib).
[b] DL is calculated based on three times the standard deviation of the blank at 1% RSD (DL = BEC x 0.03) (ref. No. 23).

TABLE VII
Inter-elemental and Spectral Interferent Studies on Different Uranium Emission Lines

Interferent/ Concn (100 µg/mL)	Equivalent Uranium Concentration (µg/mL) 385.958 nm	367.007 nm	263.553 nm	409.014 nm	393.203 nm	424.167 nm	294.192 nm
Nb	1.6737	2.0600	Nil	0.8220	0.4453	0.0815	1.0130
Ta	1.8560	0.0620	881.60	0.3189	0.3082	Nil	Nil
Fe	0.5613	0.4658	0.2175	Nil	Nil	Nil	Nil
Mn	0.1735	0.0593	4.8000	Nil	0.1346	Nil	Nil
Ti	0.2245	0.1355	2.1900	Nil	13.4600	Nil	54.68
Sn	0.2857	0.1694	0.5785	Nil	Nil	Nil	0.1089
W	Nil	0.1440	1.2600	Nil	Nil	Nil	Nil
Zr	0.0510	0.1186	1.5700	0.3069	0.1767	23.1600	0.1634
V	0.3929	0.0762	4.6600	Nil	0.6648	0.1255	0.9259
Mo	0.0867	0.0593	2.3700	Nil	Nil	Nil	0.0545
Th	1.9900	14.6900	0.1531	Nil	18.6200	Nil	5.500
Ca	Nil	0.3049	0.3179	Nil	18.6800	Nil	0.1634
Mg	0.3113	0.0932	0.2845	Nil	Nil	Nil	2.6700
Al	Nil	0.1355	Nil	Nil	Nil	0.0456	0.2179
Y	0.1750	0.1184	0.5294	Nil	Nil	Nil	0.2075

Nil = indicates no interference.

TABLE VIII
Inter-elemental and Spectral Interferent Studies on Different Uranium Emission Lines

Interferent Concn (100 µg/mL)	Equivalent Uranium Concentration (µg/mL) 385.466 nm	288.963 nm	256.541 nm	279.394 nm	468.907 nm	424.437 nm	286.567 nm
Nb	19.5365	0.7699	4.5205	Nil	Nil	Nil	84.9108
Ta	17.7700	Nil	1.2455	20.6480	Nil	Nil	Nil
Fe	Nil	Nil	0.1985	1.3600	Nil	0.0783	Nil
Mn	Nil	58.1490	16.9500	Nil	0.1762	Nil	0.1700
Ti	Nil	0.2109	2.4400	Nil	Nil	Nil	1.8100
Sn	0.2500	Nil	0.8225	Nil	Nil	Nil	Nil
W	Nil	Nil	0.6098	Nil	Nil	8.9116	Nil
Zr	0.2500	Nil	0.9359	Nil	Nil	Nil	25.5300
V	Nil	396.9190	4.4400	Nil	0.1409	Nil	Nil
Mo	0.4900	Nil	1.1500	0.2798	Nil	Nil	9.8300
Th	84.92	Nil	298.4800	Nil	79.5300	Nil	Nil
Ca	0.1400	Nil	0.8366	Nil	Nil	Nil	Nil
Mg	Nil	Nil	0.9217	Nil	Nil	0.1175	0.8800
Al	Nil	Nil	0.8508	Nil	Nil	0.1175	Nil
Y	Nil	Nil	1.1346	Nil	Nil	Nil	Nil

Nil = indicates no interference.

Effect of Different Acids and Their Concentrations on the Uranium Emission Signal

The effect of different acids such as HCl, HNO_3, $HClO_4$, H_2SO_4, and H_3PO_4 and their concentrations in the range from 0.5 N to 8.0 N on the uranium emission signal (20 µg/mL) at the six most sensitive emission lines (385.958, 367.007, 263.553, 409.014, 393.203, and 424.167 nm) were studied and the results presented pictorially in Figure 1. The depression in the uranium signal varied up to 37.5% and was severe at the 263.553-nm line in the presence of 8.0 N H_2SO_4. The depression effect is minimum on the uranium signal at the 409.014-nm line in the presenceof HNO_3 acid. The ICP-OES, equipped with a G.M.K. nebulizer (modified Babington type), provided drift-free analytical signals in an aqueous solution of 0.5–8.0 N HNO_3 even after a continuous run of 3–4 hours.

Solvent Extraction Studies for the Recovery of Uranium From Matrix Elements

In order to avoid the spectral and matrix interferences from major elements, three different solvent extraction systems [30% (v/v) TBP/CCl_4, 0.5% (w/v) TOPO/CCl_4, and 30% (v/v) D_2EHPA/toluene] were studied and the results are presented in Table IX. Quantitative extraction of uranium was found in all systems in the presence of some synthetic major matrix elements, but the recovery was not quantitative in the D_2EHPA/toluene system using the stripping agents 0.2M sodium tripolyphosphate (plus pentanol-1) or 0.5M ammonium carbonate (plus pentanol-1), while quantitative recoveries were observed using 0.2M sodium pyrophosphate (plus pentanol-1) in all the extraction systems studied. Even though quantitative recoveries were obtained using the ammonium

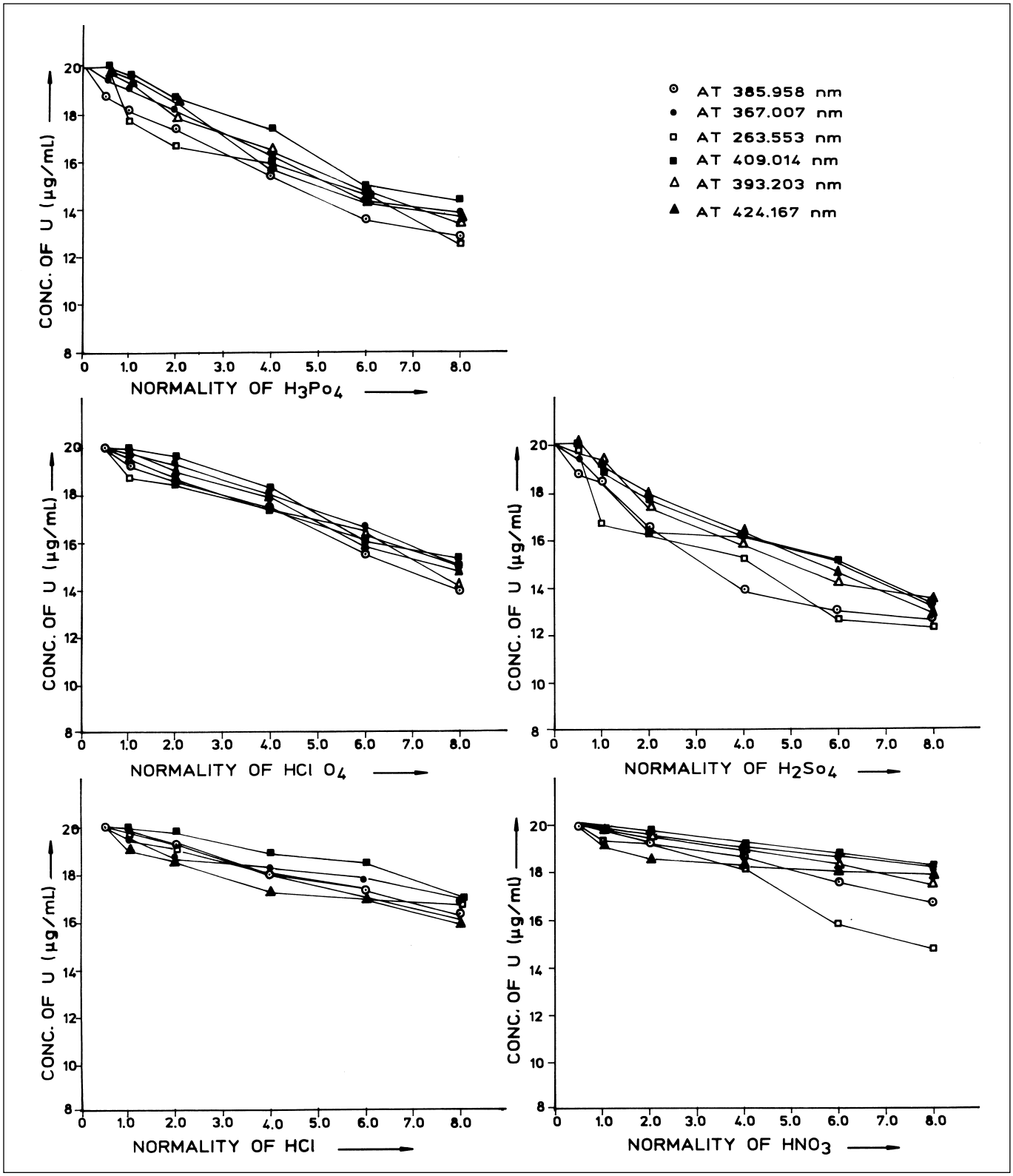

Fig. 1. Effect of different acids on uranium (20 µg/mL).

carbonate-pentanol-1 stripping system in both TBP or TOPO/CCl_4 extraction systems, TBP/CCl_4 is recommended from an economical point of view and also because TBP in comparison to TOPO is a reagent commonly used in most laboratories. However, the addition of pentanol-1 during the stripping stage is essential as its presence facilitates the quantitative recoveries for uranium values, otherwise the recoveries are not found beyond 60% of the added or present value.

Acid Hydrolysis Separation Studies for the Recovery of Uranium From Nb/Ta-bearing Samples

Three synthetic niobate-tantalate samples, prepared by doping known amounts of uranium (500 µg) were also studied by adopting the proposed method; the results are presented in Table X. Quantitative recoveries (97–99%) were obtained in the three cases, using the experimental conditions of the proposed method with the addition of sulfurous acid, as recommended in the above procedure. Further, the addition of sulfurous acid helps in producing a dense and easily filterable precipitate, thus facilitating the quantitative separation of Nb and Ta.

TABLE IX
Comparison of Different Solvent Extraction/Stripping Systems for Separation and Estimation of Uranium in Synthetic Mixtures by ICP-OES (at 409.014 nm)

	Uranium Concentration (µg)					
	30% TBP/CCl_4		0.5%TOPO/CCl_4		30% D_2EHPA/Toluene	
Extraction/Stripping System* Sample No.	Added	Found	Added	Found	Added	Found
1. 0.2M Sodium pyrophosphate (10 mL) + Pentanol-1 (3 mL)	200	202	200	203	200	190
2. 0.2M Sodium tri-polyphosphate (10 mL) + Pentanol-1 (3 mL)	200	203	200	203	200	30
3. 0.5M Ammonium carbonate (10 mL) + Pentanol-1 (3 mL)	200	198	200	204	200	48

Composition of synthetic mixture:
Fe, Al, Ca, Mg - 100 mg each;
Na, K, P, Mn, Ti - 50 mg each.

* Aqueous solution for extraction: 50 mL (1–4M HNO_3);
No. of extractions: 2 (5 min each extraction).
Organic solution: 10 mL (extraction);
No. of strippings: 3 x 10 mL (5 min each stripping).

TABLE X
Analytical Results for Uranium in Some Synthetic Nb-Ta Samples Obtained at the 409.014-nm Emission Line Using ICP-OES After Acid Hydrolysis Separation

Sample/ matrix	Uranium (µg) Added	Found	(%) Recovery
SYN-1	500	490	98
SYN-2	500	485	97
SYN-3	500	495	99

SYN-1: Nb_2O_5 - 350 mg; Ta_2O_5 - 100 mg; TiO_2 - 25 mg; Mn - 25 mg; Fe - 25 mg.
SYN-2: Nb_2O_5 - 100 mg; Ta_2O_5 - 350 mg; TiO_2 – 25 mg; Mn - 25 mg; Fe - 25 mg.
SYN-3: Nb_2O_5 - 250 mg; Ta_2O_5 - 250 mg; TiO_2 - 25 mg; Mn - 25 mg; Fe - 25 mg.

CONCLUSION

The solvent extraction-stripping method described is rapid, precise, accurate, and highly selective for the extraction of uranium in different types of geological materials including leach liquors and yellow cake samples. The method offers a detection limit of 25 µg/g and above in a variety of samples. The proposed acid hydrolysis method for the separation and determination of uranium in Nb/Ta-bearing samples is a simple method and offers the best results over other methods, because of the hydrolyzable nature of Nb and Ta. The sample preparation and matrix separation procedures are recommended for routine ICP-OES analysis of samples such as Niobate-Tantalate, Pyrochlore, Samarskite, Aeschynite, Betafite, and Brannerite type of samples. The acid hydrolysis procedure also enables the determination of the trace rare earth elements Y, Sc, and Th, in addition to uranium, in the same sample solution, which is not possible in other separation techniques.

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Direct Determination of Trace Elements in Micro Amounts of Biological Samples Using Electrothermal Vaporization Coupled to ICP-AES

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ABSTRACT

A method is described for the direct analysis of micro amounts of biological samples by electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-AES) with slurry sampling. The main factors affecting signal intensities of analytes were investigated. The experimental results show that the matrix effects in fluorination-assisted electrothermal vaporization (FETV)-ICP-AES were reduced significantly. The detection limits for Ti, Cu, Cr, Fe, Ca, Y, and Zn were 1.0, 1.2, 2.0, 2.5, 11, 5.8, and 242 ng mL^{-1}, respectively, and the relative standard deviations (RSDs) in the range of 2.1% (Ti) - 4.4% (Cr). The recommended approach was applied to the direct determination of trace elements in biological samples (solid or fluid) with satisfactory results. Compared with conventional pneumatic nebulization (PN) ICP-AES, the proposed method offers the advantages of no sample pretreatment, small sample requirements, and reduction of matrix effects.

INTRODUCTION

Trace elements play an important biochemical and physiological role in the regulation of the metabolism and influence human growth, development, health, and disease (1–4). Several investigations show that the content, speciation, and distribution of trace elements in the living body are directly involved with its fluids and tissues. Since in most cases only very small amounts of the biological samples are available for this type of analysis (usually at the mg or mL levels), the development of a rapid, simple, sensitive method without chemical pretreatment is essential in the clinical, biomedical, nutritional, environmental, and life sciences.

It is well known that inductively coupled plasma atomic emission spectrometry (ICP-AES) has become a widely used technique for the simultaneous multielement determination of trace and ultra-trace elements in biological samples (5–8). However, conventional ICP-AES generally requires chemical pretreatment of the sample prior to analysis, which can lead to a long analysis time, large sample requirements, high contamination risk, and loss of analyte. Electrothermal vaporization, as an effective sample introduction approach for ICP-AES, has excellent features such as high transport efficiency, small sample requirements, low absolute detection limits, and elimination of the organic or inorganic matrix. Furthermore, various chemical modifiers are required with ETV-ICP-AES analysis to improve the detection power of refractory and carbide-forming elements (9–11). In our previous works, a fluorination-assisted electrothermal vaporization (FETV)-ICP-AES method using a polytetrofluoroethylene (PTFE) slurry as the fluorinating reagent has been described and successfully applied to the direct analysis of trace elements in real samples (12–14).

The objective of this study was to develop a method for the direct analysis of micro-amounts of biological samples (solid or fluid) by ETV-ICP-AES with PTFE slurry as the chemical modifier. The proposed method offers high sensitivity, is rapid and simple, and requires very small sample amounts and no chemical pretreatment of the sample.

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EXPERIMENTAL

Instrumentation

A 2 kW power, 27±3 MHz ICP spectrometry source (Beijing Second Broadcast Equipment Factory, China) and a conventional plasma torch were used in this study. 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, China) with a reciprocal linear dispersion of 1.6 nm/mm. The evolved components were swept into the plasma excitation source through a 0.5-m long Teflon® tube (4 mm i.d.) by a stream of carrier gas. The transient signals were detected with a R456 type photo-multiplier tube (Hamamatsu, Japan) and a home-built direct current amplifier, and the results recorded using a U-135 recorder (Shimadzu, Japan). The instrumental and operating conditions are listed in Table I.

Reagents

The stock standard solutions (1 mg mL^{-1}) for Ti, Cu, Cr, Fe, Zn, Ca, and Y were prepared from their specPure oxides using the conventional method. A 60% (m/v) PTFE emulsion (d<1mm; viscosity, $7x10^{-3}$ –$15x10^{-3}$ Pa s) was purchased

TABLE I
ETV-ICP-AES Operating Conditions

Incident power	1.1 kW
Carrier gas (Ar) flow rate	0.5 L min^{-1}
Coolant gas (Ar) flow rate	18 L min^{-1}
Observation height	12 mm
Entrance slit width	25 µm
Exit slit width	25 µm
Drying temperature	100°C, ramp 10 s, hold 20 s
Ashing temperature	500°C, ramp 10 s, hold 50 s
Vaporization temperature	2400°C
Clear-out temperature	2700°C
Vaporization time	4 s
Sample volume	10 µL

from the Shanghai Institute of Organic Chemistry, China. All other chemicals used in this work were of specPure grade or analytical grade. Double-distilled water was used throughout.

Sample Preparation

Human Hair

Human hair was washed, dried, and chopped into smaller pieces (2 mm). Portions of 5.0 mg were accurately weighed into a micro-test tube with graduation and immersed with 20 µL of concentrated HNO_3 for 3 hours. Then, 5.0 µL of 60% (m/v) PTFE emulsion and 2.0 µL of 0.1% Triton® X-100 were added, and diluted to 50 µL with double-distilled water for analytical use.

Human Serum

A 20-µL serum sample was accurately taken into a micro test tube with graduation, 5.0 µL of 60% (m/v) PTFE emulsion and 2.0 µL of 0.1% Triton X-100 were added, then diluted to 50 µL with double-distilled water for measurement.

Chinese Medicine Loulu

A 5.0-mg powder sample was accurately weighed into a micro test tube; 5.0 µL of 60% (m/v) PTFE emulsion and 2.0 µL of 0.1% Triton X-100 were then added, finally diluted to 50 µL with double-distilled water for analytical use.

The aqueous standard solutions containing 6% (w/v) PTFE were used for calibration. The slurry samples above-mentioned were dispersed with an ultrasonic vibrator for 20 min; then the micro test tube was shaken prior to sampling.

Procedure

After the ICP was stabilized, a 10-µL sample was pipetted into the furnace. After being dried and ashed, the analyte was vaporized and carried into the plasma by the argon gas under the selected operating conditions. Peak height measurement was used for calibration.

RESULTS AND DISCUSSION

Vaporization Behavior of the Analyte

The signal profiles of the analyte with or without PTFE slurry as the fluorinating reagent are shown in Figure 1, where Ti, Cu, and Zn were chosen as the representatives for refractory, mild volatile, and easy volatile elements, respectively. As can be seen, the addition of PTFE greatly changes the vaporization behavior of the refractory element (Ti). Compared with no PTFE, an intense analytical signal was obtained, and there was no memory effect in the vaporization process. For the medium volatile element Cu, the analytical signal without PTFE is slightly weaker than with PTFE. However, for the easy volatile element Zn, an intense analytical signal was observed, no matter whether PTFE was used or not. Thus it can be concluded that PTFE slurry as an effective fluorinating reagent can convert the refractory compound into volatile fluoride.

Ashing Temperature

The selection of an appropriate ashing temperature is very important for removing the organic matrix in biological samples. Figure 2 shows the influence of ashing temperature on signal intensity of the analyte with PTFE. Based on the experimental results, an ashing temperature of 500°C was chosen for the simultaneous multielement determination. Using the selected conditions, a complete removal of the organic matrix and no analytical signal loss of the elements of interest was observed.

Vaporization Temperature

Using an ashing temperature of 500°C, the influence of the vaporization temperature on signal intensity of the elements of interest was investigated. The results (shown in Figure 3) indicate that

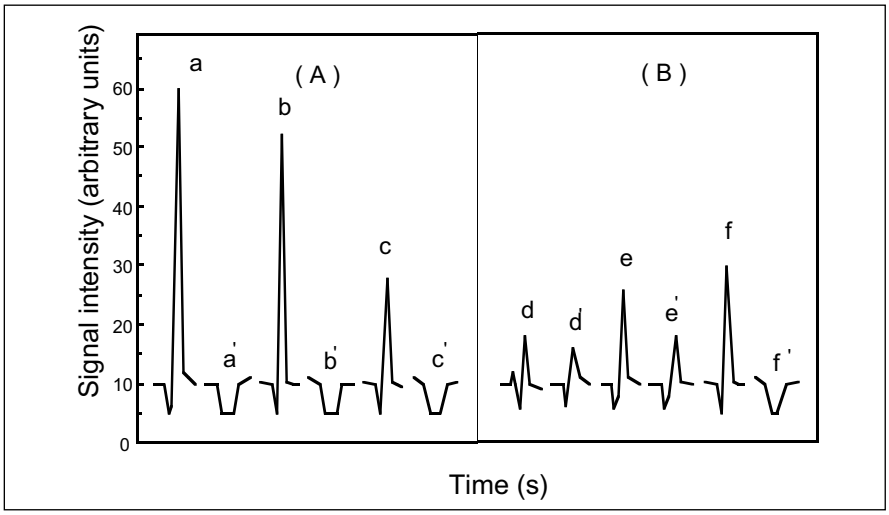

Fig. 1. Comparison of analytical signals for Ti, Cu, and Zn. (A) with PTFE: a = 0.2 μg mL^{-1} Ti; b = 0.6 μg mL^{-1} Cu; c = 20 μg mL^{-1} Zn. (B) without PTFE: d = 10 μg mL^{-1} Ti; e = 3.0 μg mL^{-1} Cu; f = 20 μg mL^{-1} Zn; a', b', c', d', e', and f ' are their residual signals of the empty firing, respectively.

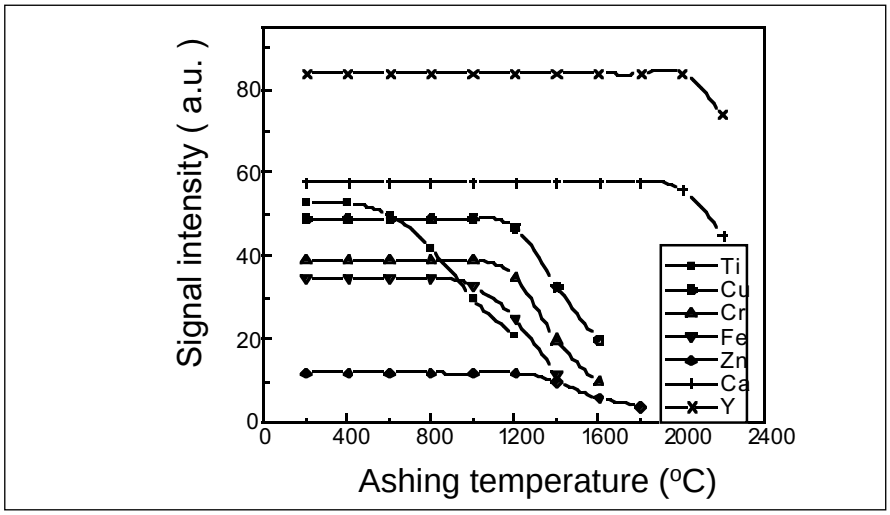

Fig. 2. Influences of ashing temperature on signal intensity with PTFE: Ti, 0.2 μg mL^{-1}; Cu and Fe, 0.6 μg mL^{-1}; Cr, 0.4 μg mL^{-1}; Zn, 10 μg mL^{-1}; Ca, 0.1 μg mL^{-1}; Y, 1.5 μg mL^{-1}.

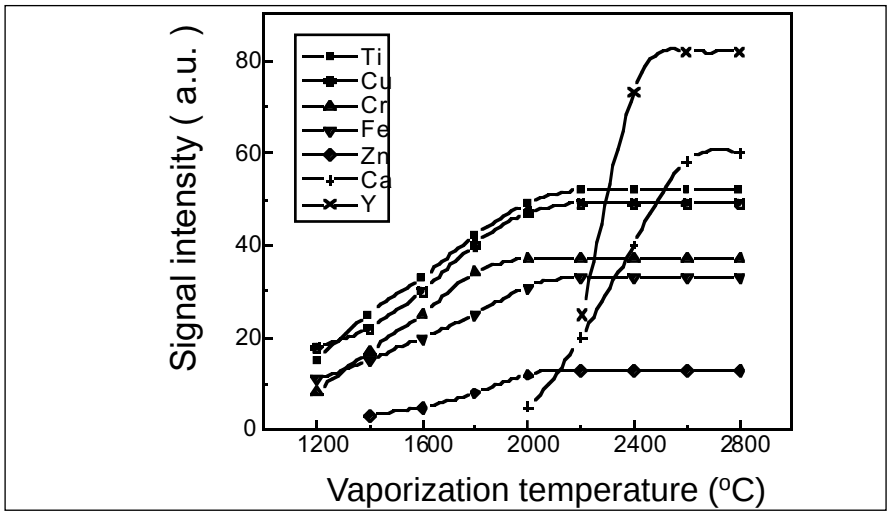

Fig. 3. Analytical signal versus vaporization temperature with PTFE: Ti, 0.2 μg mL^{-1}; Cu and Fe, 0.6 μg mL^{-1}; Cr, 0.4 μg mL^{-1}; Zn, 10 μg mL^{-1}; Ca, 0.1 μg mL^{-1}; Y, 1.5 μg mL^{-1}.

the analytical signal intensity for most elements (Ti, Cu, Cr, Fe and Zn) enhanced with an increase in temperature and reached a plateau at about 2000°C. However, for Y and Ca, a higher vaporization temperature (at about 2400°C) is required in order to achieve maximum signal intensity. In this work, a compromise vaporization temperature of 2400°C and a vaporization time of 4 s was used for the simultaneous multielement determinations.

Investigation of Matrix Effect

Under the optimized experimental conditions, the influence of the main matrix elements (Na, K, Ca, and Mg) on the signal intensities of the elements of interest in FETV-ICP-AES analysis were examined. The tolerable amounts of the matrix elements are given in Table II. It can be seen, when the matrix concentrations ranged within 2-5 mg mL^{-1}, no significant influences were observed. Compared with conventional ICP-AES, the proposed FETV-ICP-AES method remarkably decreases matrix effects.

In order to explore the reasons for reduced matrix effects with FETV-ICP-AES, the vaporization behavior of the analyte Y and the matrix elements Na, Ca, and Zn was carried out. The results given in Figure 4 show that the analytical signals successively appeared in the sequence of Zn, Na, Y, and Ca. In other words, the selective volatilization among the elements examined took place in the vaporization process. This selective volatilization behavior is beneficial to a decrease in the matrix effects.

The experimental results also show that the excitation temperature in FETV-ICP-AES is higher than that in PN-ICP-AES. It is obvious that a higher excitation temperature is also beneficial for the excitation / ionization of the analytes. Thus, it can be concluded that the addition of PTFE slurry as the chemical modifier can greatly reduce the matrix effects. This can be explained as follows: (a) Selective volatilization occurs between the analyte and the matrix; (b) compared with the pneumatic nebulization ICP system, the ETV-ICP system has a higher atomization/excitation temperature; (c) the influence of the solvent can be eliminated with the ETV-ICP system. Further studies on the interference mechanism are currently underway.

TABLE II
Effect of Matrix Concentration

Element	Wavelength (nm)	Tolerable amount of matrix element (mg mL^{-1}) K	Na	Ca	Mg
Ti	334.941	5.0	5.0	5.0	5.0
Cu	324.754	5.0	5.0	5.0	5.0
Cr	267.716	5.0	5.0	5.0	5.0
Fe	259.940	5.0	5.0	2.0	2.0
Zn	334.502	5.0	5.0	2.0	2.0
Ca	317.933	5.0	5.0	-	2.0
Y	371.030	5.0	5.0	5.0	5.0

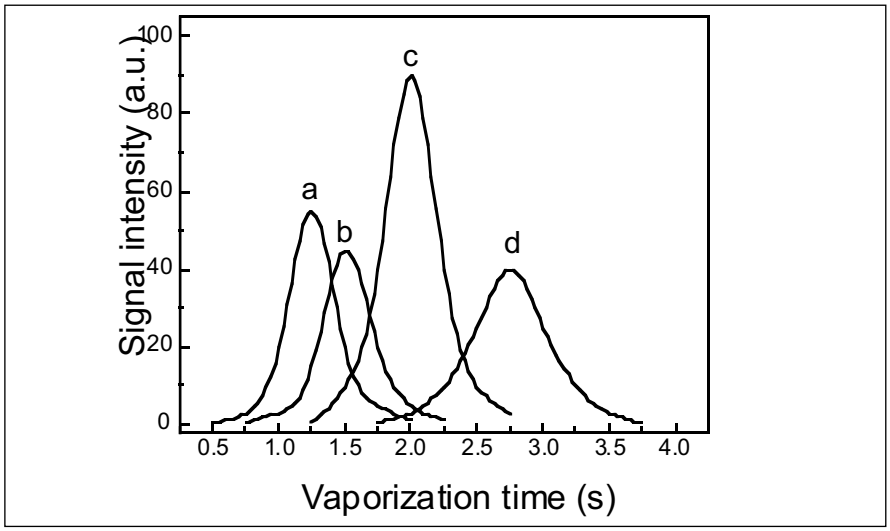

Fig. 4. Analytical signals vs. vaporization time in the presence of PTFE. A = Zn, 5.0 mg mL^{-1}; b = Na, 5.0 mg mL^{-1}; c = Y, 1.0 µg mL^{-1}; d = Ca, 5.0 mg mL^{-1} using 2400°C.

Detection Limit and Precision

The detection limit is defined as the analyte concentration yielding an analytical signal equal to 3 times the standard deviation of the background noise. The detection limits and relative standard deviations of the proposed method were summarized in Table III. It should be noted that a less sensitive Zn wavelength was used for this study, while a lower Zn detection limited could be achieved with a more sensitive line.

TABLE III
Detection Limit and Precision (n=9)

Element	Wavelength (nm)	Detection limit ($ng\ mL^{-1}$)	(pg)	($\mu g\ g^{-1}$)	RSD (%)
Ti	334.941	1.0	5.0	0.012	2.1
Cu	324.754	1.2	6.0	0.014	3.5
Cr	267.716	2.0	10	0.024	4.4
Fe	259.940	2.5	13	0.030	3.6
Zn	334.502	242	1210	2.91	4.1
Ca	317.933	11	55	0.13	3.3
Y	371.030	5.8	29	0.058	2.9

TABLE IV
Analytical Results of the Elements of Interest in Biological Samples (n=5)

	FETV-ICP-AES			PN-ICP-AES
Sample/ Element	Calibration curve[a]	Standard addition[b]	Calibration curve[b]	Calibration curve[b]
Hair ($\mu g\ g^{-1}$)				
Ti	2.32 ± 0.31	2.55 ± 0.40	2.97 ± 0.53	2.64 ± 0.33
Cu	14.5 ± 2.8	15.2 ± 3.1	16.4 ± 3.6	15.0 ± 2.4
Cr	1.12 ± 0.16	1.20 ± 0.20	1.04 ± 0.11	0.98 ± 0.14
Fe	35.7 ± 2.7	34.8 ± 3.1	30.9 ± 2.4	31.7 ± 2.0
Zn	172 ± 10	168 ± 8.5	159 ± 12	176 ± 9.8
Ca	1180 ± 110	1245 ± 108	1064 ± 115	1291 ± 121
Serum ($\mu g\ mL^{-1}$)				
Ti	0.14 ± 0.03	0.16 ± 0.02	0.15 ± 0.03	0.13 ± 0.02
Cu	1.85 ± 0.31	1.93 ± 0.41	1.78 ± 0.25	1.90 ± 0.33
Cr	0.20 ± 0.03	0.18 ± 0.02	0.19 ± 0.04	0.21 ± 0.02
Fe	2.31 ± 0.30	2.48 ± 0.44	2.25 ± 0.20	2.51 ± 0.22
Zn	3.61 ± 0.42	3.25 ± 0.36	4.03 ± 0.45	4.26 ± 0.50
Ca	87.3 ± 9.1	84.9 ± 7.4	91.4 ± 10	95.6 ± 8.7
Loulu ($\mu g\ g^{-1}$)				
Ti	31.6 ± 2.4	30.2 ± 1.8	33.5 ± 2.1	35.3 ± 1.9
Y	1.31 ± 0.14	1.37 ± 0.18	1.31 ± 0.14	1.35 ± 0.11
Cu	18.8 ± 1.6	16.5 ± 3.1	18.8 ± 1.6	20.5 ± 2.0
Cr	6.59 ± 0.63	6.09 ± 0.71	6.59 ± 0.63	5.50 ± 0.98

[a] Direct analysis with slurry sampling.
[b] Analysis after digestion with HNO_3 + $HClO_4$.

TABLE V
Analytical Results of Standard Reference Material of Human Hair (GBW 07601) (n=5)

Element	Determined value[a] ($\mu g\ g^{-1}$)	Certified value[a] ($\mu g\ g^{-1}$)
Ti	2.4 ± 0.3	2.7 ± 0.4
Cu	9.5 ± 1.2	10.6 ± 0.7
Cr	0.41 ± 0.07	0.37 ± 0.05
Fe	61 ± 8	54 ± 6
Zn	205 ± 11	190 ± 5
Ca	2780 ± 224	2900 ± 200

[a] Calibration curve method with slurry sample.

Sample Analysis

Under the selected conditions, the concentration of Ti, Cu, Cr, Fe, Zn, Ca, and Y in Chinese medicine Loulu, human hair, and serum was determined directly by using the standard addition method and working curve. The analytical results are listed in Table IV. The results obtained by the proposed methods were also compared with the results obtained by pneumatic nebulization (PN)-ICP-AES.

In addition, the standard reference material of human hair (GBW 07601) was analyzed (see Table V) and the determined values are in good agreement with the certified values.

CONCLUSION

A fluorination-assisted ETV-ICP-AES method with slurry sampling has been developed for the direct determination of the trace elements Ti, Cu, Cr, Fe, Ca, Y, and Zn in various biological samples. In comparison to conventional pneumatic nebulization ICP-AES, the proposed method requires no chemical sample pretreatment, uses micro-amounts of sample, and results in reduced matrix effects.

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Simple Method for the Selective Determination of As(III) and As(V) by ETAAS After Separation With Anion Exchange Mini-column**

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ABSTRACT

A simple approach is described for the separation and determination of inorganic arsenic species using solid phase extraction and electrothermal atomic absorption spectrometry (ETAAS). A Dowex 1-X8 anion exchange mini-column was used to separate As(III) and As(V). The chemical (pH, type and concentration of eluent) and physical (flow rate of sample and eluent) parameters affecting the separation were studied. Under optimized conditions, As(V) showed a strong affinity for the mini-column, while As(III) was collected in the effluent. As(V) was recovered by elution with 0.8 mol L^{-1} hydrochloric acid. The influence of other competing ions on the separation of As(III) and As(V) was also evaluated. The detection limit achieved for As(III) was 4 ng mL^{-1} and for As(V) 4 ng L^{-1}.

The relative standard deviation (%RSD) ranged from 0.7 – 1.3% for replicated tap, lake, and well water samples at the 20 ng mL^{-1} level. A preconcentration factor of 100 was achieved for As(V) when 300 mL of water was processed. Arsenic recoveries (full procedure) ranged from 92 – 106%.

INTRODUCTION

The toxicological properties of the different arsenic species vary widely and inorganic As(III) and As(V) are the most toxic. Organic species, like monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), have a moderate toxic effect on humans and biota. Arsenobetaine (AsBet) and arsenocholine (AsChol) are non-toxic. From the toxicological and regulatory point of view, it is mandatory to develop analytical techniques aimed at differentiating between these species.

A variety of separation and detection techniques have been reported for As speciation analysis (1–4). Inorganic species of As are most often determined in waters, soils, and sediments, while the organic species are common constituents of biological tissues.

Relatively simple methods based on the selective reduction of arsenic species by continuous hydride generation have been proposed (5–7). Although these methods offer excellent sensitivity, some analytical limitations such as molecular rearrangements (8) and incomplete recoveries (9) have been reported. Hyphenated techniques based on the combination of a powerful separation technique with a sensitive element-specific detector are among the most promising approaches to determine selectively As compounds in a variety of matrices. Analytical methods reported in the literature normally require separation schemes, such as cold trapping (CT), high-performance liquid chromatography (HPLC), gas chromatography (GC), or capillary electrophoresis (CE) that are relatively complex for routine analysis (10-12). It is therefore necessary to develop other alternatives for the reliable, sensitive, and low-cost determination of species at trace levels in a particular sample or matrix.

Solid-phase extraction (SPE) using mini- or micro-columns offers advantages such as simplicity of operation, low cost, the possibility to achieve high preconcentration factors, the ability to combine with different detection techniques, and relative freedom from matrix interferences. The possibility of field sampling is another important advantage, which combines preconcentration of water samples in the field and subsequent transport of the columns for elution and analysis in the laboratory.

Numerous SPE methods for separation and experimental approaches have been proposed in recent years which separate and measure inorganic and organic species of As. Yalcin and Le (13) employed solid-phase extraction cartridges as low-pressure chromatographic columns for the separation and subsequent determination of inorganic arsenic species. Detection limits of 0.2 and 0.4 ng mL^{-1} were achieved for As(III) and As(V), respectively. Grabinski (14) used a single column containing both cation and anion-exchange resins to separate four arsenic species. The overall analytical detection limit was 10 ng mL^{-1} for each individual

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arsenic species. According to another study, As(III), As(V), MMA, and DMA were determined by graphite furnace atomic absorption spectrometry (GFAAS) after separation of the species by ion-exchange chromatography (15). In the separation scheme proposed, As(III) was calculated by establishing the difference.

The aim of this study was to develop a simple off-line method based on the use of a mini-column filled with an anion-exchange resin to separate As(III) and As(V) at trace levels. After separation, the As species were quantified by GFAAS. The method's simplicity and low cost make it suitable for routine inorganic arsenic speciation analysis.

EXPERIMENTAL

Instrumentation

A PerkinElmer Model 5100 ZL atomic absorption spectrometer (PerkinElmer, Shelton, CT, USA), equipped with a PerkinElmer Model THGA graphite furnace, PerkinElmer Model AS-71 autosampler, and longitudinal Zeeman-effect background corrector, was used for the atomic absorption measurements. Electrodeless discharge lamps (EDL, PerkinElmer) were used as the sources of radiation for As determination. Arsenic was measured at its most sensitive line at 193.759 nm. Pyrolytically coated graphite tubes with pyrolytic graphite L'vov platforms were employed. High-purity Ar (flow rate 300 mL min^{-1}) was used to purge air from the graphite tubes, except during the atomization step where stopped flow conditions were used. The analytical measurements were based on peak area. Autosampler volumes of 20 µL of sample followed by 5 µL of chemical modifier were employed for all studies. Each analysis was repeated at least three times to obtain the average value and its relative standard deviation (%RSD). The program was optimized using water samples spiked with As. The main ETAAS operating conditions and matrix modifier used are summarized in Table I.

Reagents

All chemicals were of analytical reagent grade unless otherwise stated. Deionized water (Barnstead, Dubuque, IA, USA) was used throughout. All solutions were stored in high-density polypropylene bottles. Plastic bottles, autosampler cups, and glassware were cleaned by soaking in 20% (v/v) HNO_3 for 24 h. The material was then rinsed three times with deionized water. Commercially available 1000 mg L^{-1} As(III) and As(V) standard solutions (Titrisol, Merck, Darmstadt, Germany) were prepared daily by serial dilutions of the stock solutions.

A 0.3% (m/v) magnesium nitrate solution was prepared by dissolving an appropriate amount of $Mg(NO_3)_2 \cdot 6H_2O$ (Merck, Suprapure) in deionized water. The mixed Pd and $Mg(NO_3)_2$ matrix modifier solution was prepared by adding 5 mL of 0.3% $Mg(NO_3)_2$ solution and 2.5 mL of 10 g L^{-1} Pd solution (Merck) into a volumetric flask of 25 mL and brought to volume with deionized water. The final concentration of the matrix modifier solution was: 0.06% $Mg(NO_3)_2$ and 0.1% Pd.

High-purity Ar was used to purge air from the graphite tubes.

Column Packing and Conditioning

The resin Dowex 1-X8 (100-200 mesh; Cl^-; form; analytical grade; Bio-Rad Labs, Richmond, CA, USA) was loosely packed into a glass column (7 cm x 3 mm i.d.). Glass wool plugs were placed at both ends of the column so that the net length of the resin zone was about 5 cm. The method consists of the separation of As(III) from As(V) on the acetate form of the Dowex 1-X8 ion exchange resin. Before running the sample, the resin was converted into the acetate form by passing 3 mL of 1.0 mol L^{-1} sodium hydroxide, followed by 5 mL of 4.0 mol L^{-1} acetic acid at a flow rate of 1.0 mL min^{-1}. Then, the mini-column was washed with 10 mL of deionized water. Column degradation was not observed after several weeks of usage.

Analytical Procedure

An aqueous solution containing As(III) and As(V) was passed through the column at a flow rate of 1.0 mL min^{-1} using a peristaltic pump. As(V) was retained in the column while As(III) was collected (in a polyethylene flasks) in the effluent. A solution of 0.8 mol L^{-1} was used to elute As(V) from the column. The eluate was collected in other polyethylene flasks. After each run, the column was washed with a few mL of 1.0 mol L^{-1} HCl and then with 5 mL of water. The arsenic concentration was determined in the two fractions by ETAAS by injecting 20-µL aliquots

TABLE I
Graphite Furnace Temperature Program for As Determination

Parameter	Drying	Pyrolysis	Atomization	Conditioning
Temperature (°C)	120	800	2400	2700
Ramp time (s)	1	10	0	1
Hold time (s)	30	20	5	2
Ar flow rate (mL min^{-1})	300	300	(0) read	300

into a pyrolytic tube applying the optimized program given in Table I. All experiments were performed in duplicate.

RESULTS AND DISCUSSION

The difference in dissociation constants between arsenious acid (pKa_1 = 9.2; pKa_2 = 12.1; pKa_3 = 13.4) and arsenic acid (pKa_1 = 2.2; pKa_2 = 6.9; pKa_3 = 11.5) allows to separate As(III) and As(V) on the basis of ion exchange. At neutral pH, arsenious acid is present as $As(OH)_3$ and is not dissociated. For this reason, when using an anion-exchange resin it will not be retained on the column. On the other hand, As(V) will be present as $H_2AsO_4^-$ and will be retained on an anion-exchange resin and the separation of both species is possible. This separation is pH dependent.

To establish the optimum separation conditions, chemical and physical parameters affecting the retention/elution of arsenic species were studied. The pH of the medium, flow rate of sample and eluent, maximum sample volume, and minimum elution volume were the variables considered. To evaluate the effect of different variables affecting the selective retention, the separation process was carried out on each oxidation state separately. After optimization, mixtures of As(III) and As(V) were prepared in water to check the capacity of the resin to retain selectively As(V) in the presence of As(III).

Effect of pH on As Retention

Five mL of water samples containing 100 ng of As(III) were passed through the column at a flow rate of 0.8 mL min^{-1}. The pH of the samples was varied between 3 and 8 (below the pKa_1 of arsenious acid and above pKa_1 of arsenic acid) because in this range the difference in their ionic property is maximized. No retention of the uncharged As(III) was observed and it was collected quantitatively in the effluent. When a 5-mL water sample, spiked with 100 ng of As(V), was passed through the column, the negatively charged As(V) was quantitatively bound to the anion-exchange resin. Pentavalent arsenic was stripped with hydrochloric acid. In this screening experiment, 5 mL of 0.5 mol L^{-1} HCl was used for elution. This study demonstrates that the separation is possible in a wide pH range. A working pH of 7 for As(V) retention was selected to perform further experiments.

Influence of HCl Concentration on As(V) Elution

Experimental data obtained using HCl concentrations ranging from 0.05 to 1.0 mol L^{-1} show that the separation of the arsenic species improves with increasing acid concentration up to 0.8 mol L^{-1}. No significant changes in As(V) recovery were observed at higher concentrations. A 0.8 mol L^{-1} HCl solution was used as the eluent in subsequent studies. Figure 1 shows the influence of acid concentration on As(V) recovery.

Influence of Sample and Eluent Flow Rates

Different sample flow rates (0.4–1.0 mL min^{-1}) were tested to determine the efficiency of As(V) retention using in all cases a 20-ng mL^{-1} standard arsenic solution and a constant elution flow rate of 0.8 mL min^{-1}. A sample flow rate of 1.0 mL min^{-1} was chosen for further work (Figure 2). Overpressure was observed when higher flow rates were tested. A parallel study showed that the recovery of As(V) did not change significantly when the elution flow rate (0.8 mol L^{-1} HCl eluent) was varied from 0.4–1.0 mL min^{-1}. In view of these results, the samples were passed through the column and eluted at a constant flow rate of 1.0 mL min^{-1}.

Elution Volume

The next step in assessing the efficiency of As(V) preconcentration was to determine the minimum volume required to completely elute the analyte from the mini-column. After running 5 mL of 20-ng mL^{-1} As(V) solutions, increasing volumes (0.1-5.0 mL) of 0.8 mol L^{-1} HCl were successively used to elute the analyte retained.

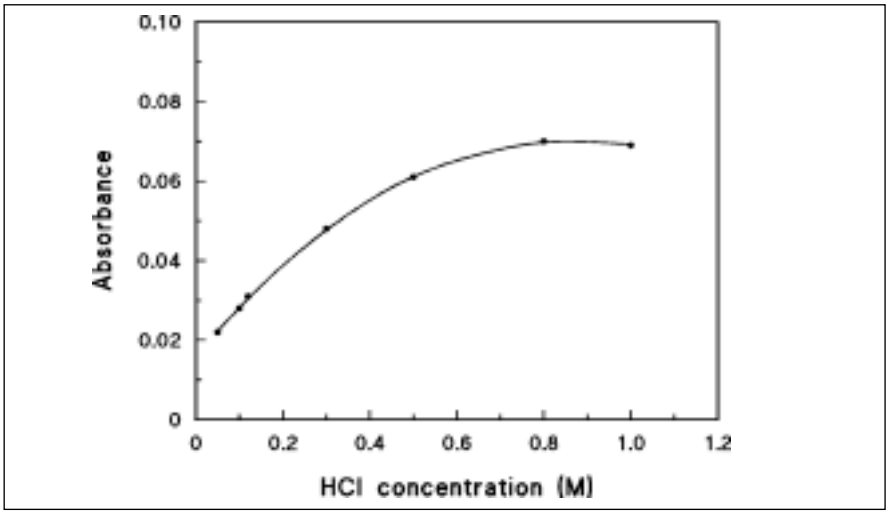

Fig. 1. Influence of HCl concentration on As(V) recovery.

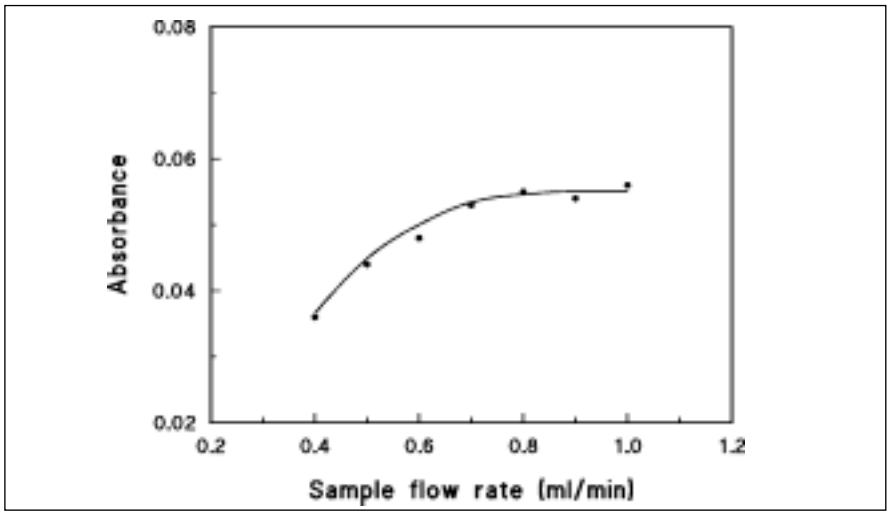

Fig. 2. Influence of sample flow rate on As(V) retention/elution.

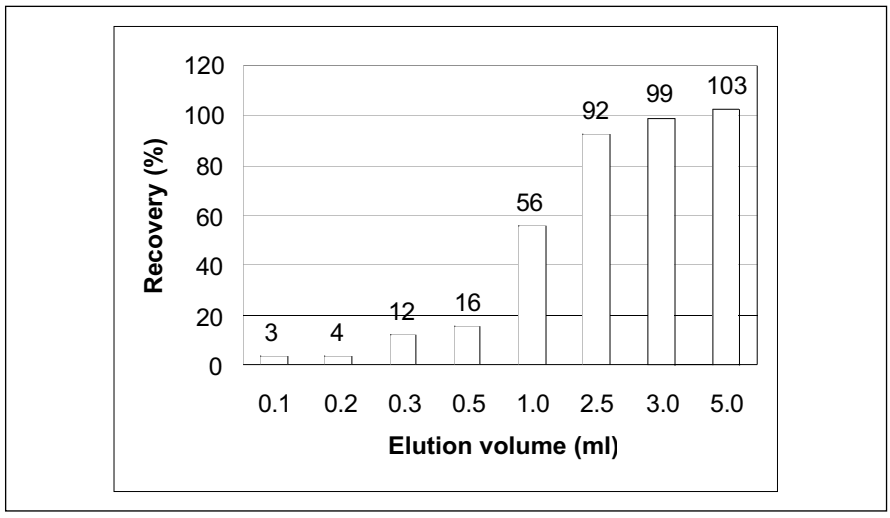

Fig. 3. Minimum elution volume of HCl necessary to strip As(V) quantitatively from the column. Figures in the top of the bars indicate the percentage of As(V) recovery.

The eluates were collected and measured by ETAAS. Figure 3 shows that 3 mL is the minimum volume of acid required to quantitatively strip the analyte from the column.

Influence of Sample Volume on As(V) Retention

A total constant amount of arsenic (20 ng) in different volumes (5–300 mL) was passed through the column. Figure 4 shows that in deionized water, the amount of As(V) retained in the column remains constant up to a volume of 300 mL. For higher volumes, a significant reduction in the absorbance signal was observed.

The maximum volume that can be run through the column without any decrease in recovery of As(V) depends on the complexity of the matrix. The recovery achieved was lower when tap, lake, and well water spiked with 20 ng of As(V) were passed through the column.

Evaluation of As(V) Retention Capacity of the Mini-column

The enrichment factor was calculated as the ratio between the maximum volume of deionized water spiked with As(V) that was possible to pass through the column with respect to the minimum volume of 0.8 M HCl required to elute the analyte. According to the results obtained, As(V) can be preconcentrated by a factor of 100. The column properties remained constant during about 100 cycles of retention/elution of As(V). Slight column degradation was observed after 100 cycles and the column was repacked with new resin.

Interference Study

The possible interferences produced by different cations, namely, Ca(II), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), Mn(II), Na(I), Ni(II), Pb(II), Sb(III), Se(IV), and Zn(II) were studied. To perform this study, 10 mL of sample containing 20 ng mL^{-1} of a mixture of As(III) and As(V) and the interfering ion tested was passed through the column. As(III) was collected in the effluent and As(V) was stripped from the column with 3 mL of 0.8 mol L^{-1} HCl. Variations over (±5% in the analytical signal of As were taken as an interference. Under optimized conditions, no variation in As(III) or As(V) recovery was observed in the presence of up to 1000 ng mL^{-1} of the ions evaluated except for Cu(II), Hg(II) and Pb(II) and Sb(III). A slight depression in As(III) was observed in the presence of more than 750 ng mL^{-1} of these ions. The possible interference from typical anions (Cl^-, NO_2, SO_4^{2-}) found in waters was also investigated. Concentrations higher than 100 ng mL^{-1} did not allow quantitative retention of arsenic on the column, which is the major drawback of the method when seawater samples are analyzed. The results are set forth in Figure 5.

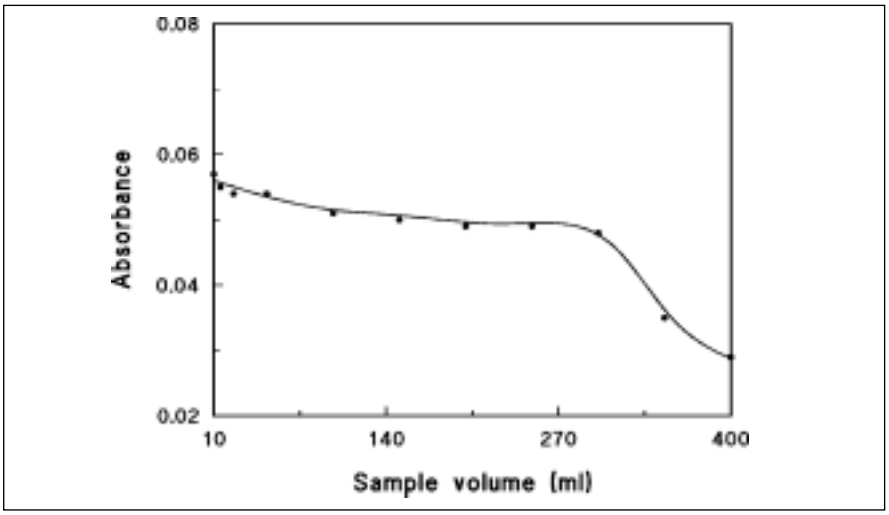

Fig. 4. Influence of sample volume on As(V) retention.

Analytical Performance

The detection limits calculated on the basis of the 3 σ criterion for 10 replicated measurements of the blank signal were 4 ng mL^{-1} for As(III) and 4 ng L^{-1} for As(V) (preconcentration factor: 100). The relative standard deviation (RSD) ranged from 0.7 to 1.3% for tap, lake, and well water for 10 successive measurements of samples containing a final concentration of 20 ng mL^{-1}.

Unfortunately, certified reference materials (CRM) of arsenic species are not available and for this reason a recovery test was performed (Table II). Although it cannot replace accuracy tests, some information is gained about the good performance of the overall procedure. Different combinations of spiked water samples and elution volumes were tested. The recovery data ranged between 92 and 106 %.

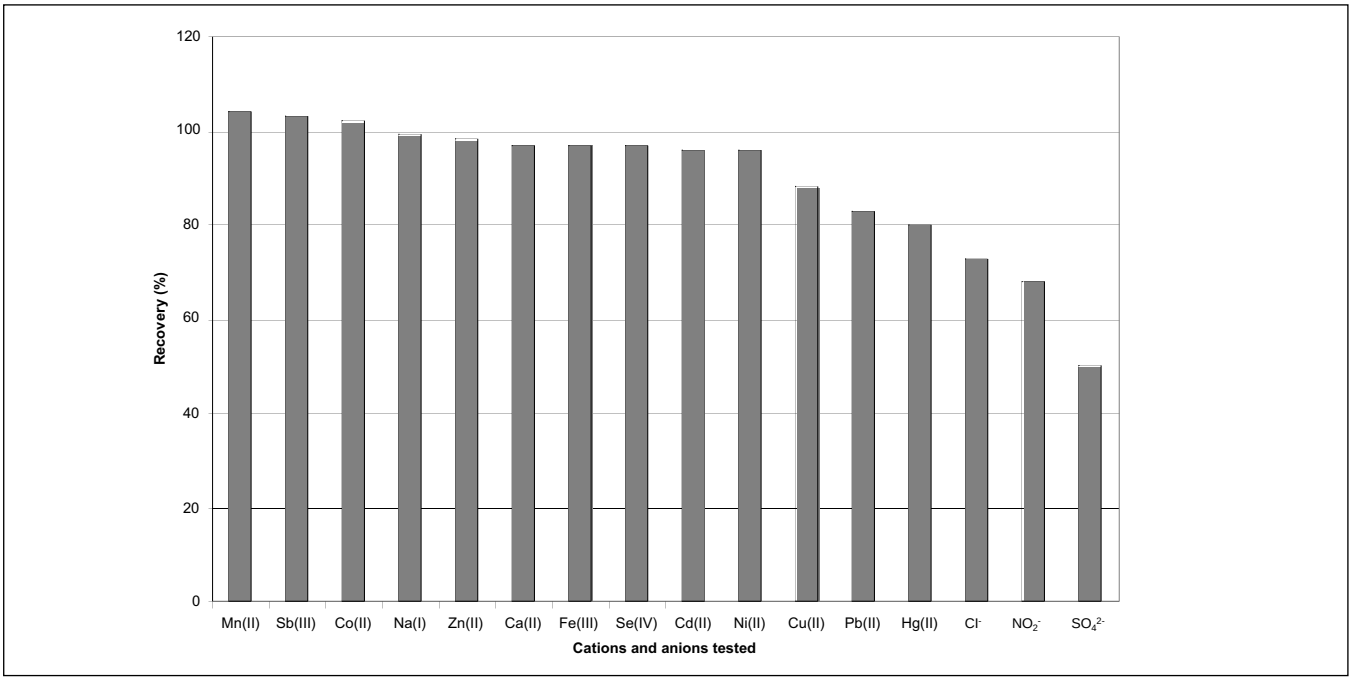

Fig. 5. Interference study. As(III) and As(V) concentrations: 20 ng mL^{-1}. Cations concentration: 1000 ng mL^{-1}; anions concentration: 200 ng mL^{-1}.

TABLE II
Recovery of Mixtures With Different Concentration Ratios of As(III) and As(V)
Mean value ± standard deviation (n=3).
Concentrations are expressed in ng mL^{-1}.

	Arsenic added		Arsenic found		Recovery (%)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Tap	5	5	49 ± 0.2	4.7 ± 0.2	98	94
Well 1	10	50	9.2 ± 0.4	46 ± 1.9	92	92
Lake 1	0	0.5	–	0.53 ± 0.03	–	106
Lake 2	50	100	47 ± 1.7	105 ± 5	94	105

TABLE III
Determination of Total As, As(III), and As(V) in Real Water Samples
Mean value ± standard deviation (n+3).
Concentrations are expressed in ng mL^{-1}.

Sample	Total As	As(III)	As(V)
A	111 ± 4	14.2 ± 0.7	92.8 ± 3.9
B	194 ± 8	16.9 ± 1.0	172 ± 8
C	64.4 ± 2.9	<LOD	59.0 ± 3.3

Application to Natural Water Samples

To investigate the applicability of this method, the content of total As, As(III), and As(V) in different categories of waters was determined. The calibration graph method was employed for the determination of total As and inorganic arsenic species. Total As was determined by hydride generation (HG)-AAS. Groundwater samples were collected in Venado Tuerto (Santa Fe province, Argentina) from wells where a contamination phenomenon with arsenic had been detected in some areas. Geological studies (16) demonstrated that this contamination was from natural causes. Water samples were collected in Teflon® containers that were previously rinsed with the sample. Samples were stored at about -4ºC until their analysis in the laboratory. The analysis was carried out as soon as possible after sampling in order to prevent the oxidation of As(III) during storage. The results are set forth in Table III.

CONCLUSION

The use of an anion-exchange mini-column for the separation of As(III) and As(V) and the subsequent determination of the species by ETAAS provides a simple, effective, selective, and low-cost method for speciation studies. The methodology is easy to implement in laboratories dedicated to routine analysis. In addition, the detection limits are more than adequate in view of the maximum concentration fixed for arsenic in drinking waters by different international regulations.

At no time was there any evidence that the system allowed any interconversion of species.

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Preconcentration and Speciation of Chromium in Natural Waters Using Ion-Pair Extraction and Graphite Furnace AAS

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ABSTRACT

The speciation analysis of chromium was studied using sequential ion-pair extraction of Cr(VI) and Cr(III) [previously oxidized to $C1^{-}$(VI)] with Tetrabutylammoniumbromide (TBAB) as the counter ion], in combination with graphite furnace atomic absorption spectrometry (GFAAS). The Cr(VI) in 100-mL acidic samples is extracted into methyl isobutylketone (MIBK) as TBAB-Cr(VI) ion-pair; then back-extracted and preconcentrated into 5 mL of acetate buffer (pH=5), and finally determined by GFAAS.

The calibration curve was linear up to 5 µg/L of Cr(VI) with a sample injection volume of 10 µL. The detection limit (three times the standard deviation of the blank) was 3 ng/L. The RSD was 2.32% (n=4) for Cr(VI) and 2.39% (n=4) for Cr(III). The influence of probable concomitant species in natural water on the determination of chromium was studied. The recovery was 97.5–101.5% for Cr(VI) and 99.5–104.5% for Cr(III). For verification of the accuracy, some natural water reference samples were utilized.

INTRODUCTION

The two primary oxidation states of chromium in natural waters, Cr(VI) and Cr(III), differ significantly in their biological, geochemical, and toxicological properties (1,2). The total chromium concentration in unpolluted rivers is in the 0-50 µg/L range, while seawater contains around 0.04 µg/L (3). Chromium (VI) probably exists in natural waters at the mg/L or lower levels and must therefore be preconcentrated prior to analysis with methods that are usually not sensitive enough to directly detect trace Cr(VI). The most common techniques for the determination of chromium are atomic absorption spectrometry (AAS) employing flame (FAAS) or graphite furnace atomization (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), although by themselves these techniques only yield information on total concentrations. This is the reason why sample pretreatment methods such as ion exchange (3) solvent extraction (4), microwave field (5), fast protein anion-exchange liquid chromatography (6), and solid-phase extraction (7,8), which includes analyte element separation and preconcentration, are required in order to determine the low levels of individual Cr species even with the most sensitive techniques such as GFAAS.

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The present paper describes the development of a speciative GFAAS procedure for the determination of Cr(VI) and Cr(III) in seawater, using tetrabutylammoniumbromide (TBAB) as the counter ion for the selective ion-pair extraction of Cr(VI) from acidic solutions into MIBK and preconcentration of this ion-pair by back-extraction into acetate buffer. By oxidation of Cr(III) to Cr(VI) with sodium metaperiodate, the Cr(III) concentration can then be measured by GFAAS.

EXPERIMENTAL

Instrumentation

For this study, a PerkinElmer Model 1100 B atomic absorption spectrometer was used, equipped with an HGA®-700 graphite furnace (PerkinElmer Instruments, Shelton, CT USA). The instrumental parameters (Table I) were optimized for maximum absorbance. The samples were directly injected onto the tube wall of the pyrolytically coated graphite tubes using a PerkinElmer Model AS-70 Furnace autosampler. A rotator Model AR.14 (E.L.M.) was used for shaking the solution.

Reagents

All reagents were of analytical reagent grade. Doubly distilled and demineralized water was used to prepare all solutions.

Stock solutions of 100 mg/L of Cr(III) and Cr(VI) were prepared by dilution of a Titrisol® stock solution (Merck) and from K_2CrO_4 (Merck), respectively. The HAC/AC- buffer, pH 5, was prepared by mixing 5.8 mL of CH_3COOH (Merck, 99%) and 158 mL of 0.4 mol/L alkaline solution and diluting to 500 mL. The alkaline solution was prepared by dissolving sodium hydroxide (Merck, 98.5%) in water and stored in a polyethylene bottle. The stock solution of TBAB 0.02 mol/L was prepared from this reagent in methyl isobutylketone (MIBK)

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TABLE I
Operating Parameters of GFAAS

Step	Atomization Program for the Estimation of Cr Temp. (°C)	Hold Time
Dry	90–120	15.0 sec
Ash	1100–1200	10.0 sec
Atomization	2400	5.0 sec
Background correction	D_2 lamp	
Measurement	Peak height	
Argon flow	10 L/min	
Sample volume	10 µL	
Wavelength	357.9 nm	
Slit width	0.7 nm	
Lamp current	7.0 mA	

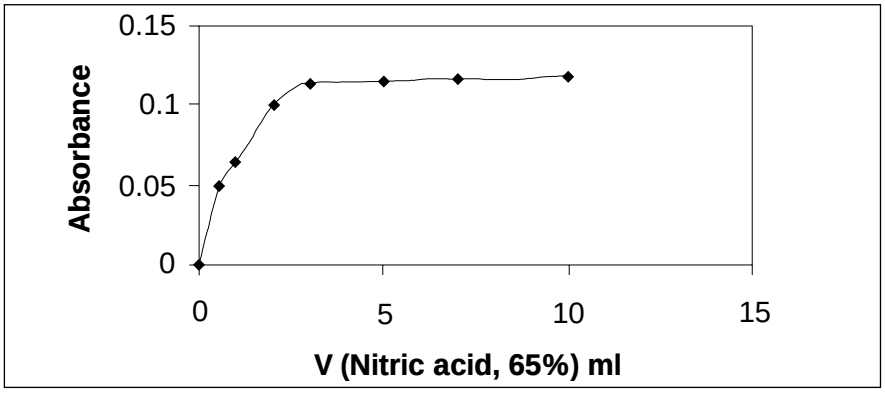

Fig. 1. Acidity dependence of the Cr(VI)–TBAB ion-pair stability: [TBAB]=0.02 M, shaking time=5 min and [Cr(VI)] = 1 µg/L.

(Mak & Baker). Metaperiodate 0.1 mol/L solution was prepared from its sodium salt and was stored in a dark bottle.

Procedure

For the Cr(VI) determination, 100 mL of the samples or standard solutions [containing both Cr(III) and Cr(VI)] was pipetted into a 250-mL separatory funnel, and 4 mL HNO_3 65% and 10 mL of TBAB solution were added. The ion-pair compound was extracted by shaking the mixture for 5 min. The two phases were allowed to separate and then the organic phase was transferred into a new separatory funnel, 5 mL of acetate buffer solution added, thoroughly mixed and the ion-pair compound back-extracted from MIBK into the acetate solution. Ten µL of the acetate-separated phase were used for GFAAS measurement of Cr(VI). For the determination of total chromium in these binary solutions, apply the same procedure but before adding HNO_3 to the separatory funnel, add periodate and alkaline solution (5 mL of each) and shake for 5 min. Sodium metaperiodate in alkaline solution oxidizes the Cr(III) into Cr(VI).

RESULTS AND DISCUSSION

Ion-Pair Extraction Conditions

Tetrabutylammoniumbromide [$R_4N^+Br^-$] as a counter ion reacts with oxyanions of chromium in acidic aqueous solution and results in Cr(VI)–TBAB ion-pair (9). This ion-pair can be separated from other species (cations, anions) present in sample solution by selective extraction into an organic solvent.

In the present work, the Cr(VI) content of a 100-mL water sample was reacted with TBAB and the formed Cr(VI)–TBAB ion-pair was first extracted into MIBK and then back-extracted into 5 mL HAC/AC^- buffer solution. Finally, the Cr(VI) content of the buffer solution was determined by GFAAS.

The Cr(VI)-TBAB ion-pair extraction conditions were optimized. For this purpose, solutions containing 1 µg/L of Cr(VI) and Cr(III) were prepared and tested using the proposed method.

Several water-immisible organic solvents such as chloroform, MIBK, and carbontetrachloride were tested as the extracting solvent. MIBK is recommended as a convenient solvent for this work. Chloroform did not extract the ion-pair at all and the extraction of this ion-pair with carbontetrachloride was not quantitative.

The Cr(VI)–TBAB ion-pair is stable only in acidic solutions. The effect of acidity on this stability, the efficiency of the ion-pair formation, and hence the extraction of this ion-pair into the organic solvent were investigated by adding various volumes of nitric acid (65%) to 100-mL volume of 1-µg/L Cr(VI) samples and measuring the absorbances of the extracted Cr(VI). The results are shown in Figure 1. By increasing the volume

of acid added, the efficiency of extraction (absorbance) increases. Although the absorbance reached a fixed value by adding 4 mL of the acid, we chose 5 mL as the optimum acid volume to ensure that sufficient acid is available for total chromium determination. In addition, we studied the effect of pH on the back extraction of the ion-pair into the HAC/AC$^-$ buffer. Working at a pH<4 or pH>6, the signal decreased. It was found that the HAC/AC$^-$ buffer at pH=4.5 provides the best conditions for back extraction and stability of the ion-pair.

The influence of shaking time on the efficiency of the ion-pair formation and extraction was studied using a rotator. The Cr(VI)–TBAB ion-pair is formed and extracted into MIBK by mixing 100 mL of chromium solution with MIBK containing TBAB. The mixture was thoroughly shaken using the rotator. The ion-pair of this separated MIBK was then back-extracted into the HAC/AC$^-$ buffer solution. The influence of shaking time on the efficiency of these two extraction processes was tested by evaluating shaking times of 1 to 7 min. It was found that a 5-min shaking time is required for each of the above extractions. When shorter shaking times were used, the Cr(III) was not quantitatively extracted.

By adding different volumes of MIBK to 100-mL chromium solutions and measuring the amount of the extracted Cr(VI), it was found that the 10-mL volumes of MIBK gave the best results. By back-extracting the ion-pair from MIBK into different volumes of HAC/AC$^-$ buffer solution, 5 mL of this buffer was found to be optimum.

Finally, the effect of TBAB concentration on the extraction efficiency was studied by using

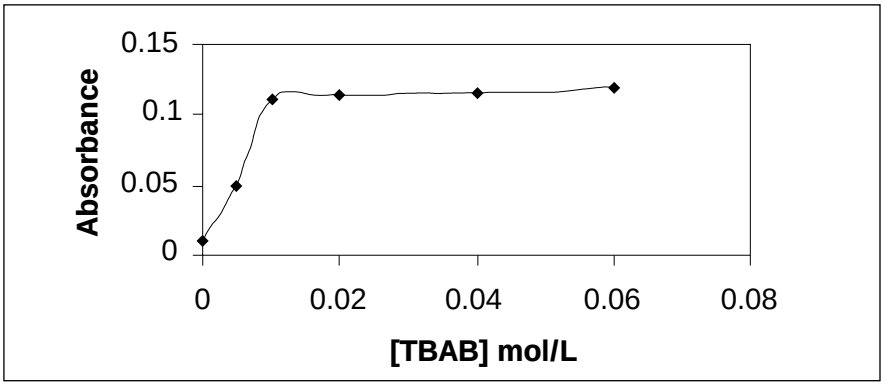

Fig. 2. TBAB concentration effect on the ion-pair extraction: Volume of nitric acid (65%) = 5 mL, shaking time = 5 min and [Cr(VI)] = 1 µg/L.

10-mL volumes of MIBK with different concentrations of TBAB (see Fiqure 2). The results in Fiqure 2 show that TBAB 0.02 mol/L provides the best results.

The applicability of this procedure for speciation and quantitative analysis of chromium was tested by analyzing three different standard solutions of chromium: Cr(III) standard solution (1 µg/L), Cr(VI) standard solution (1 µg/L), and binary standard solution of Cr(III) and Cr(VI) (1 µg/L each). Table II lists the absorbances of these solutions for extracted chromium under optimized conditions of extraction. In analyzing the single-component Cr(III) solution and also the total chromium determination of binary solution, Cr(III) was oxidized to Cr(VI) by sodium metaperiodate prior to ion-pair formation and extraction.

As can be seen in Table II, the extraction and determination of Cr(VI) using the proposed method is quantitative and the presence of Cr(III) does not cause interferences (samples S_1, S_2, and B_1). These results also show that total chromium [and Cr(III)] determination is possible by applying the method described (samples S_4 and B_2).

Interferences

The influence of probable concomitant species in natural water on the extraction and determination of Cr(VI) and Cr(III) (total chromium) was studied. The tolerance limit was set as the concentration of foreign ions that produced an error of <5% in the determination of Cr(VI). Close results were obtained working with either Cr(III) or Cr(VI) solutions. The results in Table III show that these cations and anions cause no severe interference effects.

Calibration Curve, Detection Limit, and Reproducibility

The calibration curve was linear up to 5 µg/L of Cr(VI) with a correlation coefficient of r=0.9993. The intercept and slope of the calibration curves obtained from single and binary solutions of Cr(III) and Cr(VI) were statistically comparable.

The detection limit (evaluated as the concentration corresponding to three times the standard deviation of the blank signal) was 0.003 µg/L for Cr(VI).

The RSDs, evaluated by repeated analysis of the standard solutions of Cr(VI) and Cr(III) with a concentration of 1 µg/L (n=4), were 2.32% and 2.39%, respectively.

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TABLE II
Analysis of Single and Binary Standard Solutions of Cr(III) and Cr(VI) Extracted Under Various Conditions

Samples[a,b]	Abs[c]	RSD (%)
S_1	0.117	2.32
S_2	0.001	2.34
S_3	<0.001	2.40
S_4	0.115	2.39
B_1	0.118	2.33
B_2	0.231	2.31

[a] Solutions and conditions of extractions:
S_1 = Cr(VI) solution without oxidation;
S_2 = Cr(III) solution without oxidation;
S_3 = acetate buffer solution with oxidation;
S_4 = Cr(III) solution with oxidation;
B_1 = solution of Cr(III) and Cr(VI) without oxidation; and
B_2 = solution of Cr (III) and Cr(VI) with oxidation.
[b] [Cr(III)] = [Cr(VI)] = 1 µg/L.
[c] Based on four measurements.

TABLE III
Effect of Foreign Ions on the Determination of Cr (VI), 1.5 µg/L

Interferent	Tolerance[a]
F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-	
$S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_2O_8^{2-}$	>700[b]
Ca^{2+}, Mg^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}	>550[b]
Fe^{3+}, Ni^{2+}, Pb^{2+}, Cd^{2+}	>300[b]
Cu^{2+}, Mn^{2+}, Sn^{2+}	>200[b]
VO_3^-, MnO_4^-	100

[a] Maximum weight ratio of interfering species to Cr(VI) giving an error of <5%.
[b] Maximum amount tested.

TABLE IV
Natural Water Sample Analysis and Recovery Studies

Sample	Cr added (µg/L)		Cr found[a] (µg/L)		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)[b]	Cr(VI)	Cr(III)	Cr(VI)
Underground water	0.00	0.00	0.80±0.018	2.23±0.052	–	–
	2.00	2.00	2.84±0.068	4.32±0.098	101.5	104.5
Oman Seawater	0.00	0.00	1.60±0.038	2.30±0.055	–	–
	2.00	2.00	3.56±0.082	4.38±0.105	98.0	104.0
Untreated water from Zahedan City	0.00	0.00	0.00	3.83±0.078	–	–
	2.00	2.00	1.95±0.048	5.89±0.190	97.5	103.0
Hamoon Lake water	0.00	0.00	0.00	1.81±0.048	–	–
	2.00	2.00	2.00±0.066	3.80±0.081	100.00	99.5

[a] Based on four measurements.
[b] Obtained from the difference between total chromium and Cr(VI).

TABLE V
Chromium Concentration in Reference Water Samples Using Proposed Method and Comparison to Certified Values

Sample	Chromium (µg/L)	
	Proposed method[a]	Certified value[b]
LGC 6010 (Hard drinking water)	48.5±1.19	49.0
LGC 6011 (Soft drinking water)	48.2±1.16	48.0
CASS-3 (Near shore seawater)	0.089±0.002	0.092
SLRS-4 (River water)	0.32±0.008	0.33

[a] Average of three determinations.
[b] Provided by LGC (UK) and MRC (Canada).

Recovery Study and Reference Sample Analysis

A recovery study was carried out by measuring the Cr(VI) and Cr(III) concentration in four different natural water samples spiked with Cr(III) and Cr(VI). The original chromium concentration of these samples was also determined before spiking. The recovery, established by the above experiment, was 97.5–101.5% (n=4) for Cr(VI) and 99.5–104.5% (n=4) for Cr(III) (see Table IV).

Finally four reference water samples [two LGC drinking water (UK) and two NRC natural water samples (Canada)] were subjected to the proposed method and their total chromium concentration was determined. The results in Table V show good agreement between the certified values and those obtained by the method proposed.

CONCLUSION

The results of this study show that ion-pair extraction results in good separation of Cr(III) and Cr(VI) and simultaneous preconcentration. Back-extraction was applied to achieve further preconcentration by a factor of 20. Chromium concentration in real samples down to the 6-ng/L level is measurable by using this extraction method in combination with GFAAS analysis. The method is simple and sensitive and using the optimized conditions described has been successfully applied to the analysis of two kinds of natural water reference samples.

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