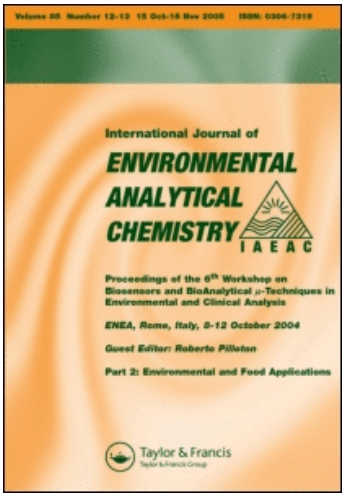

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Niobium in the Environment and a New Method for its Trace Analysis Using Molecular or Atomic Absorption Spectrometry

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The status of niobium in the environment is briefly reviewed and a new method suitable for the trace analysis of the metal in ores, alloys, plant tissues, animal tissues, and natural waters is presented. The method is based on the selective extraction of niobium as its complex with N-*p*-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA) in organic solvents. For molecular absorption spectrophotometric analysis chloroform is used in extraction and a ternary complex is formed in the extract by adding 4-(2-pyridylazo) resorcinol (PAR). The ternary complex has an absorbance maximum at 550 nm ($\varepsilon = 3.6 \times 10^4$ 1 mole^{-1} cm^{-1}). Solvent extraction from the aqueous phase to lower volumes of organic phase enables up to 20-fold enrichment of niobium(V) and the method is capable of determining niobium levels down to 10^{-4} ppm (0.1 ppb). For the atomic absorption spectrometric determination, methyl isobutyl ketone is used as extracting solvent and a sensitivity of 0.3 ppm, which is over 3 times higher than attained so far with flame AAS, is achieved. Both the instrumental methods were applied to the environmental analysis of niobium and excellent agreement was observed.

KEY WORDS: AAS, environment, extraction, niobium(V), spectrophotometry, ores, alloys, biological materials, natural waters.

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INTRODUCTION

Niobium in the environment

Niobium is widely distributed in nature and has been detected in clays, soils, rocks, seawater, freshwaters, animals and plants.[1] It has been reported to be present in concentrations ranging from 2–150 ppm in igneous rocks, 0.02–6.3 ppm in meteorites and 2–80 ppm in Lunar materials.[2] Tyutina *et al.*[3] found niobium levels of less than 0.4 ppm in dry tissues of terrestrial plants *Sphyagnum salix*, *Picea obovata*, *Carex vesicaria* and *Ribes nigrum* but several other plants *Rubus arcticus*, *Chamaenerium angustofolium*, *Vaccinium myrtillus* and *Rubus chamaemorus* which were sampled near and over a niobium deposit in the Srednil Timan region, USSR, showed a great capacity of enriching themselves with niobium by extracting niobium from the soil. Niobium concentration in these plants reached levels of 8.4 ppm (dry weight basis) and the metal appeared to be concentrated preferentially in roots and leaves rather than in branches and twigs. Amongst animals, the marine mollusc *Mytilus edulis* was found to contain less than 1 ppb niobium in dry weight[4] but ascidians *Molgula manhattensis* and *Styela plicata* showed such a strong tendency to bioaccumulate niobium that their tissues contained, on a dry weight basis, an average of 250 ppm niobium.[5]

An analysis of twenty lateritic soils from West Africa by Grimaldi and Berger[6] showed an average niobium content of 24 ppm. Of these, four from within a few miles of the niobium deposit contained 79–87 ppm of niobium. In bauxites, analysed by Pachadzhanow,[7] the niobium content varied from 4.5 to 91.8 ppm in the samples from USSR while four samples from Hungary and two from France indicated average concentrations of 35.6 ppm and 61 ppm niobium respectively. Another survey, based on 803 soil or other rigolith samples taken from about 50 miles apart throughout conterminous United States revealed mean niobium levels of 12 ppm.[8]

The prevalence of niobium in seawater, rocks and soils, and the available reports on the presence of niobium in biological systems, especially the reports on bioaccumulation of niobium by animals and plants, open up the possibility that niobium may be physiologically significant, at least to some of the species. Such possibility has not so far been discussed.[1,2,9] In order to be of assistance in these

and other environmental studies concerning niobium, a highly selective and sensitive method has been developed for the analysis of niobium in environmental samples, the details of which are presented.

The present method

The present method is based on selective extraction of niobium(V) from acidic (~ 5 M HCl) media with N-*p*-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA) in chloroform and subsequent spectrophotometric determination as its mixed ligand complex with MFHA and 4-(2-pyridylazo) resorcinol (PAR). The colour of the ternary complex is very intense (molar absorptivity 3.8×10^4 l mol^{-1} cm^{-1} at 550 nm). The sensitivity can be further enhanced by enriching niobium through solvent extraction from the aqueous phase to a 20 times lower volume of organic phase enabling determination of niobium at levels as low as 10^{-4} ppm (0.1 ppb). The method is significantly more sensitive than the prevailing analytical methods[10–13] (Table 1). It is also highly selective and tolerates the presence of a large number of anions and cations commonly found with niobium in environmental matrices. The method was applied to the determination of niobium in ores, alloys, plant tissues, animal tissues and natural waters.

Table 1 Sensitivities of the prevailing analytical methods for the analysis of niobium(V)

Analytical technique	*Limit of determination of niobium*	*Reference*
Flame AAS	1 ppm	10, 11
Flame AAS (Present method)	0.3 ppm	Present work
Atomic fluorescence spectroscopy	1 ppm	10, 11
Flame atomic emission spectroscopy	0.06 ppm	10, 11
Direct current plasma spectroscopy	0.038 ppm	10, 11
Spectrophotometry (with 8-quinolinol)	9 ppb	12
Spectrophotometry (with N-*m*-tolyl-*p*-methyl benzohydroxamic acid)	4 ppb	13
Spectrophotometry (Present method)	0.1 ppb	Present work

Choice of MFHA and PAR

We have recently reported[14] the determination of titanium(IV) in environmental samples employing N-*p*-methoxyphenyl-2-furohydroxamic acid (MPFA). MPFA is an analogue of N-phenylbenzohydroxamic acid (PBHA) which has been a versatile analytical reagent for the qualitative and quantitative estimation of metal ions.[15] We had prepared MPFA following reports[16] that substitution of the benzene ring by heteroaromatic rings enhances the selectivity and sensitivity of the reagent. We have subsequently synthesised several furylacrylo- analogues of MPFA.[17] As expected, the increased conjugation at the coordination site in the furylacrylo analogues (Figure 1, A) resulted in enhanced colour of the metal complexes of these reagents relative to the complexes of the furo analogues (Figure 1, B). The binary complexes of niobium with N-phenyl-2-furylacrylohydroxamic acid and its analogues in chloroform have maximum absorbance in the region 360–390 nm with molar absorptivities at λmax in the range 0.25×10^4 to 1.6×10^4 $1\,mol^{-1}\,cm^{-1}$. To further enhance the sensitivity, ternary complexes were formed in the chloroform extracts by adding pyridylazo reagents. PAR, 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-pyridylazo)-*p*-cresol (PAC), 5-(ethylamino)-2-(2-pyridylazo)-*p*-cresol (EAPAC), 5-bromo-EAPAC and 3,5-dibromo-EAPAC were tried for this purpose; the best results with respect to precision, stability and sensitivity of absorbance

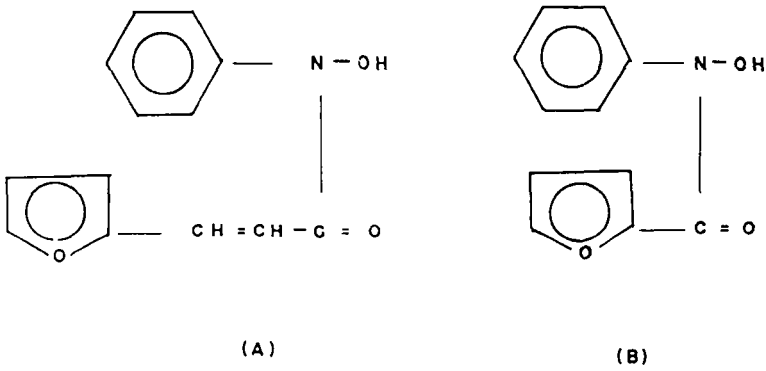

Figure 1 (A) N-Phenyl-2-furylacrylohydroxamic acid and (B) N-phenyl-2-furohydroxamic acid.

measurements were obtained using PAR as the reagent. Table 2 gives the sensitivities of colour systems involving niobium, MFHA, and pyridylazo reagents. Similar trends were observed with hydroxamic acids other than MFHA, except that the sensitivities were always lower than the ones obtained with MFHA. The trend is illustrated with niobium-hydroxamic acid-PAR systems in Table 3.

Table 2 Spectral characteristics of ternary systems involving niobium(V), MFHA and pyridylazo reagents in chloroform

Pyridylazo reagent	λ_{max}		*Molar absorptivity of the ternary system at* λ_{max}, $l\ mol^{-1}\ cm^{-1}$
	Reagent	*Ternary system*	
PAN	450	555	1.4×10^4
PAC	435	565	1.9×10^4
5-Bromo-EAPAC	445	580	2.2×10^4
3,5-Dibromo-EAPAC	440	590	2.3×10^4
EAPAC	440	600	3.1×10^4
PAR	430	550	3.8×10^4

Table 3 Spectral characteristics of ternary systems involving Niobium(V), PAR and the furylacrylohydroxamic acids

Hydroxamic acid	*Wavelength of maximum absorbance of the ternary system,* λ_{max}, *nm*[a]	*Molar absorptivity at* λ_{max}, $l\ mol^{-1}\ cm^{-1}$[a]
N-*p*-Methoxyphenyl-2-furylacrylo-	550	3.8×10^4
N-*m*-Methoxyphenyl-2-furylacrylo-	550	3.4×10^4
N-*p*-Tolyl-2-furylacrylo-	545	3.1×10^4
N-*m*-Tolyl-2-furylacrylo-	545	3.0×10^4
N-Phenyl-2-furylacrylo-	542	2.8×10^4
N-*p*-Chlorophenyl-2-furylacrylo-	540	2.2×10^4
N-*p*-Bromophenyl-2-furylacrylo-	535	2.0×10^4
N-*p*-Iodophenyl-2-furylacrylo-	535	1.9×10^4
N-*p*-Nitrophenyl-2-furylacrylo-	525	0.9×10^4

[a]Against the reagent blank.

EXPERIMENTAL

Apparatus

The molecular absorption spectra were recorded on Perkin–Elmer 402 and Hitachi 220 spectrophotometers. Instrumentation Laboratory 551/951 instruments were used for atomic absorption spectrometric studies. The pH measurements were done on Radiometer PHM-29 and Industrial Electronics Corporation 092 pH meters. Corning all-glass stills were used throughout.

Reagents and solutions

All chemicals used were of analytical-reagent grade, unless otherwise specified. Deionised and double distilled water was used throughout.

Stock solution of niobium(V) was prepared from niobium(V) oxide by fusion with $KHSO_4$ in a platinum crucible and dilution to measured volume with 200 g l^{-1} tartaric acid solution. The standard solutions of niobium(V) were prepared by appropriate dilution of the stock solution with 20% tartaric acid immediately before use.

N-*o*-Methoxyphenyl-2-furylacrylohydroxamic acid (MFHA) and its analogues were used as 4 g l^{-1} solution in ethanol, prepared daily.

4-(2-Pyridylazo) resorcinol (PAR) was used as 0.1 g l^{-1} solution of its disodium salt in dimethyl sulfooxide (DMF). It was also prepared daily. Other reagents used were: pyridine 500 ml l^{-1} in DMF; tartaric acid 20 g l^{-1} in water; ascorbic acid 10 g l^{-1} in water; PAN and other pyridylazo reagents (Table 1) 0.05 g l^{-1} in DMF.

Procedure

To a 20–50 ml portion of the sample solution containing up to 35 μg of niobium(V) in a separating funnel, were added 2 ml of ascorbic acid solution, 2 ml of MFHA solution and sufficient concentrated hydrochloric acid to make the mixture 5 M in HCl. Ten ml of chloroform was added and the contents were equilibrated by mechanical shaking for 5 minutes. The phases were allowed to separate and the chloroform extract was filtered through dry cotton wool. From the filtrate 2 ml of the chloroform solution was pipetted into a 20 ml test tube and 2 ml of pyridine-DMF solution and 3 ml of PAR

solution were added. The liquid was warmed at 65 ± 2 °C in a thermostated bath for 10 minutes and was allowed to cool at room temperature. It was diluted to 10 ml in a calibrated flask with DMF and its absorbance was measured at 550 nm against a reagent blank prepared in the same way but free from niobium(V). For samples very low in niobium (< 0.25 ppb) it is desirable to pipette 5 ml of the niobium-MFHA extract and heat it at 65 ± 2 °C for 30 minutes after the addition of 1.5 ml of pyridine-DMF (750 ml l^{-1}) and 1 ml of PAR (0.3 g l^{-1}). This enables achievement of higher sensitivity in analysis but makes the method more time consuming.

RESULTS AND DISCUSSION

Development of colour

The reaction between the Nb(V)-MFHA complex and PAR in DMF was slow at room temperature. Addition of organic bases *n*-butylamine, tert-butylamine or pyridine in DMF at several concentrations was tried for expediting the colour development and several alternatives of temperature and time of warming were studied. Optimum results were obtained by heating the Nb-MFHA extract at 65 ± 2 °C for 10 minutes with 2 ml of pyridine-DMF (50%) solution. For samples containing less than 0.25 ppb of niobium it was desirable to employ 5 ml of niobium-MFHA extract and develop the colour by heating it for 30 minutes with 1.5 ml of pyridine-DMF (750 mg l^{-1}) and 1 ml of PAN (0.3 g l^{-1}). The absorbance maxima appeared at 550 nm and the absorbance remained constant for over 2 hours. The absorption spectra of the ternary system is presented in Figure 2.

Enrichment potential

A fixed quantity (5 μg) of niobium was extracted from 10 to 250 ml aqueous solutions into a set volume, 10 ml, of organic phase, and was determined spectrophotometrically. It was found that a change in the ratio of volumes of aqueous phase to organic phase from 1 to 20 does not cause any adverse influence on the complete recovery of niobium. When the ratio is increased beyond 20, longer equilibration times are required to effect complete extraction of niobium.

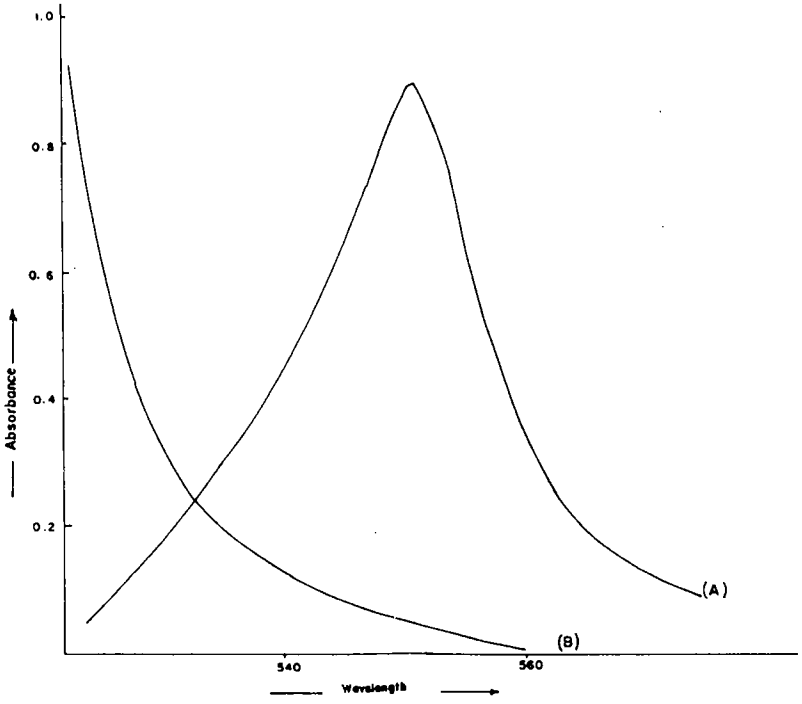

Figure 2 Absorption Spectra (A) of niobium(V)-MFHA-PAR system against reagent blank and (B) of reagent blank against chloroform.

Calibration graph, sensitivity, accuracy and precision

Beer's law was obeyed over the range 0.05–1.5 $\mu g\,ml^{-1}$ of niobium(V) in the extract. The molar absorptivity was 3.6×10^4 1 $mol^{-1}\,cm^{-1}$ at 550 nm. The sensitivity of the method according to Sandell's definition[18] is 0.0026 $mg\,l^{-1}$. As niobium can be enriched by extraction into organic phase up to 1/20 the volume of aqueous phase, the effective sensitivity can be enhanced 20-fold and by using cells with path length 10 cm for optical measurements, niobium levels as low as 10^{-4} ppm (0.1 ppb) can be determined by the present method. The detection limit, within a relative error of $\pm 2\%$ was 0.05 ppb.

Analytical data, generated from replicate determinations of different levels of niobium (Table 4) indicates the precision of the method; the maximum relative error is 1.5%.

Table 4 Analytical data on the extraction and determination of niobium(V) with MFHA and PAR. Number of replicates: 10

Niobium in in aqueous solution		*Niobium in the MFHA-$CHCl_3$ extract (expected)*[3]		*Niobium found, ppm ($mg\ l^{-1}$)*	*Relative error %*	*Standard deviation*
Volume of the sample, ml	*Concentration of Nb(V), ppm ($mg\ l^{-1}$)*	*Volume of the extract, ml*	*Nb(V), expected in the extract, ppm ($mg\ l^{-1}$)*			
200	0.101	10	0.200	0.197	1.5%	0.005
200	0.050	10	1.000	0.989	1.1%	0.005
100	0.100	10	1.000	0.991	0.9%	0.004
50	0.500	10	2.500	2.517	0.7%	0.03
10	1.000	10	5.000	4.981	0.4%	0.08

Interference study

The effect of several elements most frequently associated or likely to be associated with niobium(V) in waters, rocks, ores, soils, plants, animal tissues, alloys, industrial effluents and other environmental samples were studied. The tolerance limit was set at the amount of foreign species, higher than which would cause more than $\pm 2\%$ error in niobium recovery. The tolerance limits in the determination of 10 μg of Nb(V) in 10 ml samples are shown in Table 5. Most of the alkali, alkaline earth and lanthanide metals are tolerated at Nb: metal ion ratios of 1:250 and higher. Fe(III) at levels greater than 100 mg may interfere but is easily masked with ascorbic acid. If Fe(III) is present in concentrations exceeding 1000 times the Nb concentration it may be removed prior to the determination of Nb by extraction with methyl isobutyl ketone (MIBK) from 5 M HCl solution without loss of Nb. Vanadium(V) and tin(II) are tolerated at concentrations 5 times the Nb concentration but the tolerance can be enhanced 500 times the Nb concentration in the presence of

Table 5 Tolerance limits for the determination of 10 μg of Nb(V) in 10 ml samples with MFHA and PAR

Interferent	*Tolerance limit, μg*
Ascorbate, chloride, fluoride	$\gg$100,000
Li, Na, K, Ca, Ba, Sr, Mg, Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II), As(III), Bi(III), La(IV), Ce(III), Fe(II)	10,000
Th(IV), Cr(III), BO_3^{3-}	5,000
Cu(II), Po_3^{3-}	2,500
Sb(III)	750
Fe(III)	100
	10,000[a]
	400,000[b]
Ta(V), U(VI), Mo(VI), W(VI)	100
V(V), Sn(II)	50
	5,000[c]
Ti(IV), Zr(VI)	10
	60[d]

[a]In presence of 100 g l^{-1} ascorbic acid (10%).
[b]Removable to below 5,000 μg by MIBK extraction.
[c]In presence of 10 g l^{-1} hydroxylammonium chloride.
[d]In presence of 5 g l^{-1} fluoride.

hydroxylammonium chloride ($10\,g\,l^{-1}$). Similarly the tolerance for Ti(IV) and Zr(VI) can be enhanced by using fluoride as masking agent.

Composition of the niobium(V)-MFHA-PAR complex

The modified Job's method of continuous variation and the molar ratio method[19] were applied to study the stoichiometry of the ternary complex; both indicated that niobium, MFHA and PAR exist in the ratio 1:2:2 in the ternary system.

ANALYSIS OF NIOBIUM IN ALLOYS AND ENVIRONMENTAL SAMPLES

Analysis of niobium in alloys

To the alloy sample (1 g) taken in a beaker, 35 ml of 20% ($200\,ml\,l^{-1}$) aqueous concentrated sulfuric acid and 1.5 ml of concentrated orthophosphoric acid were added. The mixture was heated gently and 1 ml of concentrated nitric acid was added. The mixture was evaporated carefully to the paste form and then 2.5 ml of concentrated sulfuric acid were added twice, evaporating the mixture nearly to dryness after each addition. The mixture was cooled and dissolved in 10 ml of $200\,g\,l^{-1}$ tartaric acid solution, warming gently to assist dissolution. The solution was cooled and made up to the mark in a 100 ml calibrated flask. A portion of the sample containing up to 35 μg of niobium was taken into a 100 ml separating funnel. To it sufficient concentrated HCl was added to make the solution 5 M in HCl, followed by 10 ml of MIBK. The mixture was shaken vigorously for 5 minutes to extract Fe(III) into MIBK and after phase separation, the MIBK layer was discarded. Niobium was then determined as described earlier. The results of the analysis of standard alloy samples (BCS—458), presented in Table 6, indicate the accuracy and precision of the present method.

Analysis of niobium in ores

To the finely grounded niobium ore (0.2–0.4 g) taken in a platinum crucible, 40 fold excess of $KHSO_4$ was added and the mixture was

fused. After cooling, it was dissolved in 10 ml of 200 g l^{-1} tartaric acid and was subjected to MIBK extraction followed by niobium determination as described above. The results of niobium recovery from a certified ore sample (IGS—33) are presented in Table 6.

Analysis of niobium in plant and animal tissues

The plant samples were washed with 50 g l^{-1} EDTA solution and then with deionised water to ensure removal of dust particles absorbed on the plant surface. The animal tissue samples were washed with physiological saline solution before washing with deionised water to remove any clotted blood.

The samples were dried at 120 °C to a constant weight (referred as "dry weight") and were mixed carefully to achieve homogeneity. Weighed quantities (100 mg) were heated with concentrated sulfuric acid (5 ml) on a hot plate at 70 °C for 5 minutes and nitric acid was

Table 6 Analysis of niobium(V) in alloys, ores, biological matrices and waters

Sample	*Niobium present (certified value)*	*Niobium added*	*Niobium found (average of eight determinations)*	*Standard deviation*
Alloy steel (BCS—458)	0.05%	nil	0.049%	0.006
Culombite ore (IGS—33)	47.93%	nil	47.87%	0.41
Leaves of olive, *Olea europaea* (BCR:CRM—062)	nil	5.000 ppm	4.989 ppm	0.07
Leaves of legume *Mimosa pudica*	—	nil	0.117 ppm[a]	0.003
	—	2.000 ppm	2.121 ppm[a]	0.013
Liver of quail, *Coturnix sp*	—	nil	0.198 ppm[a]	0.004
	—	1.000	1.202 ppm[a]	0.006
Pond water	—	nil	nil[b]	—
	—	0.500 ppm	0.493 ppm	0.009
Lake water	—	nil	nil[b]	—
	—	2.500 ppm	2.494	0.012

[a]Dry weight basis.
[b]Less than 0.5×10^{-4} ppm.

added dropwise till all visible reaction ceased. The temperature was raised to 100 °C and the heating was continued for 15 minutes. The reactants were taken off the hot plate, about 25 ml of water was added and the resultant solutions were cooled. If the solutions were cloudy, a few drops of hydrogen peroxide were added and gentle heat was applied till the digests were clear. They were finally made up to fixed volumes with water in calibrated flasks.

The results of analysis of certified olive leaf samples, and tissues of legume and quail liver, with and without standard addition of niobium (Table 6), indicate the reliability of the present method.

Analysis of water samples

The water samples were filtered on site through 0.45 μm membrane filter and acidified to pH $\sim$ 1.8 with nitric acid as per standard methods.[20] The results of analysis of pond water (total dissolved solids 137 ppm) and lake water (total dissolved solids 310 ppm) with and without standard addition of niobium indicate the suitability of the method in the analysis of niobium in unpolluted or polluted natural waters.

ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF NIOBIUM

For the atomic absorption spectrometric (AAS) determination, niobium was extracted with MFHA using methyl isobutyl ketone (MIBK) as the solvent instead of chloroform. The latter solvent produced pungent gases in the AAS flame and was a potential health hazard. MIBK was also preferred over other organic solvents because it allows increased aspiration rate and improved nebulization efficiency, so that a greater percentage of the sample reaches the flame, giving increased sensitivity.[21,22] The optimum conditions of acidity of the aqueous phase, ascorbic acid and MFHA concentrations, and extraction time when MIBK was used as solvent were similar to the ones when chloroform was used. The extract was aspirated directly into a nitrous oxide-acetylene flame (reducing conditions) and absorbance measurements were made using the 406 nm resonance line. The concentration-absorbance curve was

linear in the range 0.3–15 ppm of niobium. The minimum accurately determinable concentration was 0.3 ppm (relative error ±2%) which was more than 3 times higher than the limit of 1 ppm achieved so far with flame AAS or atomic fluorescence spectroscopy.[10,11] The sensitivity of the direct determination of niobium by AAS is marred by the formation of highly stable oxide species in the flame, as is the case with vanadium, molybdenum and titanium.[11] Aspiration as MFHA chelate in MIBK obviously facilitates atomisation of niobium, enhancing the sensitivity of the method. Similar beneficial effects of chelation-extraction on the sensitivity of AAS methods have been observed in case of other metals.[21,22] However, the spectrophotometric method is by far the more sensitive.

The analysis of ore samples (Table 6) by AAS yielded the value, 48.1% for niobium. The analysis of olive leaves and lake water samples spiked with 5.00 and 2.50 ppm of niobium respectively (Table 4) yielded the values 4.95 ppm and 2.47 ppm. These results show the excellent recovery achievable by this method and the agreement with the results obtained spectrophotometrically (Table 6).

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