Determination of Niobium and Tantalum in Geological Samples by ICP-AES After Preconcentration by Solid Phase Extraction on Activated Carbon or Chitin

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INTRODUCTION

Niobium (Nb) [earlier Columbium] and tantalum (Ta) are known as the “earth acid” elements because of the slightly acidic nature of their pentoxides. These elements are widely distributed in rocks and have never been found to occur as native metals (1,2,3). Niobium and tantalum compounds are used in several high technology fields, such as the aerospace, nuclear and electronic industries and in the manufacturing of superconductors, cutting tools, thermocouples, dielectrics, cryotrons and superalloys (2,3,4).

Because of its low thermal neutron capture cross-section, niobium finds use as a construction material in nuclear technology (4). It finds application as an end-plug in fuel elements in nuclear reactors and as protective covering (cladding) for uranium fuel elements in fast neutron and thermal neutron reactors. Tantalum is used as a construction material, particularly in vessels for chemical treatment of nuclear fuel. Further, Nb-Ta along with Zr-Hf forms two pairs of “twin” elements which are known as “high field strength elements”. They are used as tools for the study of geochemical processes in the earth's mantle, thereby necessitating their precise determination at extremely low concentrations in mantle rocks (5).

Due to the above-mentioned applications, development of precise and accurate, as well as selec-

ABSTRACT

Niobium and tantalum at low levels in geological samples have been determined by ICP-AES after preconcentration/separation by solid phase extraction using activated carbon or chitin as sorbents. Systematic investigations were carried out on the effect of various parameters on the sorption of niobium and tantalum on activated carbon and also on chitin and their quantitative desorption/recovery. Investigations were also carried out on interferences from other concomitant ions in the sorption process. Accuracy of the method was ascertained by applying it to certified reference materials. The method was then applied to selected rock samples and relative standard deviation (RSD) values ranging from 1.0 to 6.0% were obtained. The values obtained were in good agreement with those obtained by other techniques.

The method is simple, accurate, selective and eco-friendly as non-toxic/bio-compatible sorbents have been employed. The present method also leads to a significant reduction in the amount of total dissolved salts present in the sample solution arising from the fusion flux and the matrix for aspiration into the plasma.

tive and sensitive analytical methods for the determination of Nb and Ta in diverse matrices (like high purity materials, industrial and geological samples) has always been deemed very important by analysts. Analytical methodologies by wet procedures are particularly difficult for Nb-Ta since they

exhibit similar physicochemical characteristics, their minerals are highly complex in composition, and hence their analysis requires a large number of separations to be performed, leading to material losses (2,3,6). Further, Nb and Ta do not form simple soluble compounds in aqueous solutions. In neutral and acid solutions, they are hydrolyzed with the formation of hydrophyllic colloidal systems. In fact, hydrolysis in mineral acids results in a quantitative separation of Nb and Ta from many accompanying elements. Tartaric acid, oxalic acid, citric acid, fluoride and mixture of hydrogen peroxide and sulphuric acid are used to prevent hydrolysis. In most rock samples, the levels of niobium and tantalum are low, at ppm levels for niobium and at sub-ppm levels for tantalum. Therefore, one has to resort to highly sensitive techniques for the determination of these elements. ICP spectrometry (ICP-AES and ICP-MS) has emerged as the most advantageous and widely applied technique for the determination of these elements. Even with ICP spectrometry, direct determination of Nb and Ta in complex media such as geological materials is extremely difficult because of their low concentrations and the high levels of concomitant elements arising from the matrix and flux used which leads to various interferences and also blockage of instrumental components like cones, nebulizers etc. Hence, preconcentration/separation stages such as ion exchange, precipitation, co-precipitation, liquid-liquid extraction and solid phase extraction are usually employed prior to the determination of these elements at trace and

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ultra-trace levels in complex matrices so that the sensitivity and selectivity can be improved and the levels of total dissolved salts reduced.

For niobium-tantalum determination in geological samples, potassium bisulphate fusion followed by dissolution of the fused melt in tartaric acid solution is widely used. Lithium meta-borate fusions have also been reported (2,3,6,7). Evaluation of various sample preparation techniques for the determination of Nb and Ta by ICP-MS in geological materials has also been carried out (8,9,10). Hall and Pelchat have analyzed standard reference materials for Nb, Ta, along with Zr and Hf after lithium meta-borate fusion and cupferron separation (11). Preconcentration/separation steps like precipitation, extraction chromatography, etc., have been employed prior to the determination of these elements by ICP-AES and ICP-MS (12,13). Satyanarayana et al. (14) have employed acid hydrolysis separation for their estimation in niobate-tantalate and tin slag samples by ICP-AES.

Solid phase extraction is advantageous over other preconcentration methods because high enrichment factors are achievable and the methodology involved is simple (15). A variety of solid phase adsorbents like activated alumina, zeolites, silica gel, polyurethane foams, sawdust, yeast have been utilized, especially in the area of wastewater treatment for removal of toxic metals. Commercial activated carbons and synthetic ion-exchange resins have dominated the analytical scene so far, being applied to the separation/preconcentration of metals prior to their determination by FAAS, GFAAS, ICP-AES, and ICP-MS (10). Activated carbon has proved to be an excellent collector for numerous metal ions and has been used for selective preconcentration of trace elements in a variety of samples (16,17) ranging from

geological, biological, environmental, high purity materials, seawater and ground water. Sorption and preconcentration of some transition metals, rare earths, platinum group metals on activated carbon prior to determination by ICP-AES/ICP-MS have been reported (18-21). Zr, Hf, Mo and W in waters and geological materials have been determined after sorption preconcentration on activated charcoal prior to their determination by ICP-AES and ICP-MS (22-24).

Polysaccharide-based natural materials are now emerging as a new group of sorbents. Chitin is one such bio-sorbent which is tough, protective, semitransparent, non-toxic and biodegradable (25). It is extracted from the hard shells of crustaceans, such as crab, lobster, and shrimp. Chitin is primarily a nitrogen-containing polysaccharide (N-acetyl-D-glucos-2-amine) which is insoluble in water and alkali but soluble in strong mineral acids. It forms complexes with transition metal ions. Chitin also finds application in many fields such as agriculture, food, biotechnology, textiles, polymers and water treatment. However, only a few analytical applications have been reported so far. Chitin has been used as the adsorbent column for preconcentration/separation of Fe as its 1,10, phenanthroline complex in the presence of tetraphenyl borate as counter ion (26), Cr(VI) as its 1,5, diphenylcarbazide complex in the presence of dodecyl sulphate (27) and Mo(VI) as molybdate in water samples (28) prior to their determination by spectrophotometry. Elsewhere, chitin has been used for preconcentration/separation of rare earth elements and platinum group elements (29,30,31).

A survey of the literature as cited above shows that there are no studies published on preconcentration/separation of Nb and Ta in geological materials using activated carbon

and chitin as solid phase sorbents for their determination by ICP-AES or ICP-MS. The objective of this work was to develop a method for determining Nb and Ta at trace levels in different types of geological samples with preconcentration/separation using solid phase sorbents, namely, activated carbon and chitin. The authors are reporting for the first time the preconcentration/separation of Nb and Ta by solid phase extraction in general and on activated carbon/chitin in particular.

EXPERIMENTAL

Instrumentation

An ICP-AES Model Ultima 2 (Jobin-Yvon, France) was used for the determination of Nb and Ta. The instrumental parameters are listed in Table I.

Reagents and Standards

Activated carbon (AR grade, phosphorus-free) was procured from S.D.Finechem.Ltd, Mumbai, India. It was purified further by boiling with 1.2M HCl to remove trace impurities. The carbon after boiling with HCl was filtered, the carbon washed repeatedly with distilled water, dried in a hot air oven at 50 °C for one hour and stored in air-tight bottles for further use. Chitin obtained as flakes (from Loba Chemie Ltd., Mumbai, India) was finely powdered (200 mesh) in a shatter box, cleaned repeatedly by soaking in quartz double-distilled water and decanting to remove impurities. The cleaned chitin was finally dried in a hot air oven at 100 °C for one hour and stored in air-tight bottles for further use. All reagents used were of analytical grade.

Niobium pentoxide and tantalum pentoxide (SpecPure®) were obtained from Fluka AG, Buchs, SG (Switzerland). Niobium and tantalum standards (250 µg/mL of oxides) were prepared by fusing

25 mg each of niobium and tantalum pentoxide with 8 g of KHSO_4 to a red hot melt at 700 °C for 30–45 minutes in a silica crucible. The melt after cooling to room temperature was dissolved in 100 mL of 3% citric acid solution. Working standards were prepared by successive dilutions.

Recommended Procedure for Sample Dissolution

In neutral and acidic solutions, niobium and tantalum undergo hydrolysis. Tartaric acid, oxalic acid, citric acid, hydrofluoric acid or a mixture of hydrogen peroxide-sulphuric acid are used to prevent hydrolysis and keep them in solution. For Nb-Ta determination in geological samples, typically 0.5 g of the sample was accurately weighed in a Pt crucible. Silica in the samples was removed by volatilization as SiF_4 by fuming with 5 mL of 40% HF and 2 mL of 18N sulphuric acid on a sand bath. The dried residue was fused with potassium bisulphate to a red hot melt, followed by dissolution of the fused melt in sulphuric/citric/tartaric acid

solution. Since, citrate/tartrate/oxalate interferes in the sorption step, 3% (v/v) of 36N sulphuric acid containing 1–2 mL of 30% (w/v) hydrogen peroxide mixture was preferred for dissolving the material obtained after fusion.

Recommended Procedure for Preconcentration by Solid Phase Extraction on Activated Carbon/Chitin

To an appropriate aliquot of the sample solution taken in a 250 mL beaker, about 5 mL of 1% ascorbic acid was added, and the volume made up to 100 mL. Then the pH of the solution was adjusted to 3, and 0.5 g activated carbon/chitin was added, then the solution was allowed to stand for one hour with intermittent stirring. The solution was then filtered using Whatman 540 grade paper. The filter paper with carbon/chitin was dried thoroughly, taken in a Pt dish, and ignited at 650 °C for one hour. The residue obtained was dissolved in a mixture of 2 mL of 40% HF and 0.5 mL of 18N sulphuric acid on a water bath and evaporated to near

dryness. It was evaporated twice again to near dryness with few mL of distilled water. Finally, it was dissolved in 2 mL of 1% citric acid solution, made up to 10 mL volume and Nb-Ta determined by ICP-AES.

RESULTS AND DISCUSSION

Selection of Emission Lines for the Determination of Nb and Ta by ICP-AES

Detailed investigations on the interference of other concomitant elements on Nb and Ta emission lines have been already been carried out by other workers and results published (14). The most sensitive emission lines of niobium are 309.418 nm, 316.340 nm, and 313.079 nm; those of tantalum are 240.065 nm, 226.230 nm, and 268.517 nm. The present method involves a separation step with solid phase extraction on a sorbent and, hence, very low concentrations of matrix ions are present in the final solution along with Nb and Ta. Further, the instrument used in the present study has a very high resolution of 0.005 nm. Therefore, no interferences were observed by the authors from the residual matrix on both the Nb 309.418 nm and Ta 240.063 nm line (see Figures 1 and 2) and hence those lines were selected for this study.

Optimization of Experimental Parameters for Quantitative Sorption

The effects of several experimental parameters (such as pH, weight of carbon/chitin, initial metal ion concentration, sample volume) on the sorption of Nb and Ta on both activated carbon and chitin were first studied. Since chitin is a bio-material, high acid concentrations (especially of nitric acid) degraded chitin which may affect its surface properties.

TABLE I
ICP-AES Operating Conditions and Instrumental Parameters
(JY- Model ULTIMA-2)

Mounting	Czerny-Turner
Focal length	1 m
Grating	4320 grooves/mm and 2400 grooves/mm
Order of measurement	1st
1st order resolution	0.005
Type of generator	Solid state
Observation	Radial view
Frequency of generator	40.68 Mhz
Power	1000 W
Plasma gas flow rate	12 L/min
Sheath gas flow rate	0.2 L/min
Nebuliser gas flow rate	0.8 L/min
Nebuliser type	Meinhard
Type of spray chamber	Cyclonic
Injector tube diameter	1.8 mm, Alumina

Effect of pH

Double distilled water (100 mL) was spiked with 50 µg of Nb and Ta (both elements taken together) and the pH was adjusted to values ranging from 1 to 6. After adding 0.5 g of activated carbon, the solutions were allowed to stand for six hours with intermittent stirring. The amount of sorption at different pH values was determined from the residual Nb/Ta concentrations in the filtrate, and the results obtained are given in Figure 3. Quantitative adsorption was observed from pH 2 to 6 for both Nb and Ta. Hence, the pH of 3 was preferred as optimum for quantitative sorption for Nb and Ta. Similar experiments were carried out using 0.5 g of chitin and the results obtained are given in Figure 4. Quantitative adsorption was observed only from pH 2 to 4 for both Nb and Ta.

Hence, pH 3 was preferred as optimum for the quantitative sorption of Nb and Ta on chitin also.

Effect of Sample Volume

Different sample volumes ranging from 100 mL to 1000 mL of double distilled water were spiked with 50 µg of Nb and Ta (both elements taken together) and the pH was adjusted to 3. After adding

0.5 g of carbon, the solutions were allowed to stand for six hours with intermittent stirring and the amount of sorption was determined for the different sample volumes. The results obtained are given in Table II. It was observed that sorption was quantitative even up to a sample volume of 1000 mL for both elements. A maximum enrichment factor of 200 is feasible by the pre-

TABLE II
Effect of Sample Volume

Sample Volume	% Sorption on Carbon Nb	% Sorption on Carbon Ta	% Sorption on Chitin Nb	% Sorption on Chitin Ta
100 mL	> 98	>98	> 98	>98
200 mL	„	„	„	„
400 mL	„	„	„	„
500 mL	„	„	„	„
1 L	98	98	98	98

Fig. 1. Spectral profile of Nb 309.41 nm line.

Fig. 2. Spectral profile of Ta 240.06 nm line.

Fig. 3. Effect of pH on sorption of Nb and Ta on activated carbon.

Fig. 4. Effect of pH on sorption of Nb and Ta on Chitin.

sent preconcentration method for applications with aqueous samples (1000 mL initial volume to 5 mL final volume). Similar experiments were carried out separately using 0.5 g chitin. The results obtained are given in Table II. It was observed that sorption was quantitative up to a sample volume of 1000 mL for both elements and an enrichment factor of 200 is feasible by the present method using chitin also.

Effect of Amount of Carbon and Chitin

Varying amounts of carbon ranging from 25 mg to 1000 mg were added to 100 mL of double distilled water spiked with 50 µg of Nb and Ta (both elements taken together) maintained at pH 3. The solutions were allowed to stand for six hours with intermittent stirring and the amount of sorption was determined. The results obtained are given in Table III. It was observed that quantitative adsorption of Nb-Ta occurred even with 100 mg of carbon. However, 500 mg carbon was taken as optimum for real samples. The results obtained on chitin are given in Table III. It was observed that quantitative adsorption of Nb-Ta taken occurred with 100 mg of chitin and 500 mg chitin was deemed optimum for real samples.

TABLE III
Effect of Amount of Sorbent

Sorbent (mg)	% Sorption on Carbon		% Sorption on Chitin	
	Nb	Ta	Nb	Ta
25	85	85	84	76
50	90	90	94	92
100	>98	>98	98	95
200	>98	>98	>98	>98
300	>98	>98	>98	>98
500	>98	>98	>98	>98
1000	>98	>98	>98	>98

Effect of Contact Time

Carbon (0.5g) was added to 100 mL of double distilled water spiked with 50 µg of Nb and Ta (both elements taken together) maintained at pH 3 and allowed to stand for different contact times ranging from 15 minutes to six hours, with intermittent stirring. The amount of sorption was determined and it was observed from the results obtained (see Table IV) that adsorption is quantitative in 15 minutes for both Nb and Ta. Hence, contact time of one hour was deemed optimum for real samples. The above experiments were repeated with chitin also and it was observed from the results obtained (Table IV) that adsorption is quantitative in 30 minutes for both Nb and Ta. Hence, contact time of two hours was deemed optimum for real samples. It was observed that sorption on carbon was a much faster process than on chitin and becomes quantitative within 15 minutes.

Effect of Initial Metal Ion Concentration

Double distilled water (100 mL) was spiked with different amounts of Nb and Ta ranging from 2 µg to 500 µg (both elements taken separately), the pH adjusted to 3, and 0.5 g of carbon added; then the

solutions were allowed to stand for six hours with intermittent stirring. The amount of sorption was determined. From the results obtained (Table V) it was observed that 0.5 g of carbon was sufficient for quantitative adsorption of metals up to a maximum of 200 µg for both elements. The results of similar experiments carried out separately using chitin (Table V) showed that 0.5 g of chitin was sufficient for quantitative adsorption of the metals up to a maximum of 100 µg for both elements.

Desorption and Recovery of Nb and Ta from Carbon and Chitin

(a) Leaching with mineral acids

Nb and Ta do not form simple soluble compounds in aqueous solutions. In neutral and acid solutions, they are hydrolyzed and, hence, there is no option of recovering Nb-Ta quantitatively in soluble form by leaching with HCl. However, some studies were carried out with other reagents. An amount of 100 mL of distilled water was spiked with 50 µg of Nb-Ta, the pH adjusted to 3, and 0.5 g carbon was added; then the solutions were allowed to stand for one hour. The solutions were filtered, the filtrate discarded and the carbon transferred back into the beaker along with 25 mL of desorbing

TABLE IV
Effect of Contact Time

Contact Time	% Sorption on Carbon		% Sorption on Chitin	
	Nb	Ta	Nb	Ta
15 min.	>98	>98	98	95
30 min.	>98	>98	>98	>98
1 hour	>98	>98	>98	>98
2 hours	„	„	„	„
3 hours	„	„	„	„
4 hours	„	„	„	„

TABLE V
Effect of Initial Metal Ion Concentration

Metal Ion (ug)	% Sorption on Carbon		% Sorption on Chitin	
	Nb	Ta	Nb	Ta
2	>98	>98	>98	>98
10	>98	>98	>98	>98
50	>98	>98	>98	>98
100	>98	>98	>98	>98
200	98	98	87	88
500	<75	<75	<75	<75

reagents and leached for two hours on a hot plate. The solutions were filtered and Nb and Ta in the filtrate were determined by ICP-AES. The desorbing agents tried were 10% nitric acid, a mixture of 10% nitric acid, 20% hydrogen peroxide, and 1% citric acid. The results obtained are given in Table VI. There is total loss of tantalum but niobium could be recovered up to 32% with nitric acid. Citric acid was also not effective in leaching Nb-Ta from carbon. Similar leaching studies were carried out with chitin as well and the results obtained are given in Table VI. Niobium and tantalum could be recovered up to 22% with nitric acid. Citric acid was not effective in leaching Nb-Ta from chitin also.

(b) Ignition method of recovery

Since niobium and tantalum hydrolyze and could not be recovered with mineral acids, the feasibility of the ignition method for recovering the analytes was studied. After adsorption as per optimized conditions, the solution was filtered. The filter paper with carbon was transferred to a Pt dish, dried thoroughly, ignited at 650 °C for one hour; Different dissolution reagents were tried to recover Nb-Ta in soluble form from the carbon residue obtained after ignition. The residue was dissolved in different combination of the following acids: hydrofluoric acid, nitric acid, sulphuric acid and citric acid, and the recoveries determined. The results obtained are given in Table VII. Quantitative recovery was obtained using the combination of

HF, sulphuric acid and citric acid as follows: The residue obtained after ignition was dissolved in 2–3 mL of 40% HF and 0.5 mL of 18N sulphuric acid and evaporated to near dryness on a water bath. It was evaporated twice again to near dryness with a few mL of distilled water. Finally, it was dissolved in 2 mL of 1% citric acid solution, made up to 10 mL and Nb-Ta determined by ICP-AES. The above experiments when carried out with chitin yielding similar results as on carbon. It was observed that the hydrolyzing tendency of these ions can lead to significant losses during the desorption step, especially while recovering higher amounts of Nb and Ta, and utmost care is to be taken. Tantalum was found more susceptible to this problem than Nb.

Interference Studies

The effect of various anions on the sorption process was studied and the results obtained are given in Table VIII. Amongst the anions, sulphate, chloride and phosphate showed no interference. Fluoride, citrate and the complexing agent EDTA exhibited some degree of interference, whereas oxalate inhibited sorption quite severely. The effect of other cations present in geological samples on adsorption was also studied. It was observed that Fe showed slight interference, but Al and Mn showed significant

interference (Table IX). None of the trace elements (Cu, Co, Ni, Pb, Zn, Cd, Cr, V) showed any interference on sorption.

The results obtained on the effect of anions on sorption on chitin are also given in Table VIII. Sulphate and chloride did not interfere, but phosphate showed slight interference on Ta sorption. Fluoride interfered quite significantly, while complexing ions like EDTA and citrate interfered less severely. Similar to carbon, oxalate ion inhibited the sorption most severely. The effect of cations on sorption on chitin was also studied (Table IX). Amongst major ions, Al, Fe, and Mn interfered on sorption. However, it was observed that the interference from iron could be minimized with the addition of ascorbic acid for both carbon- as well as chitin-based methods. None of the trace cations showed any significant interference on sorption. Studies were also carried out to see whether interference on sorption would occur from the high levels of fusion flux and complexing acid used for sample dissolution which would invariably be present in the sample solution. For this, 100 mL of process blank solutions containing different levels of dissolved KHSO₄ flux and acids were doped with 50 micrograms of Nb-Ta and sorption was carried out at pH 3 with 0.5 g activated carbon for one hour. The results obtained

TABLE VI
Desorption Studies

Leachant Used	% Recovery on Carbon		% Recovery on Chitin	
	Nb	Ta	Nb	Ta
10% HNO ₃	32	<5	22	14
20% H ₂ O ₂ +10% HNO ₃	32	<5	23	15
1% Citric Acid	20	<5	<5	<5
0.2% Citric Acid	<5	<5	<5	<5

TABLE VII
Studies on Dissolution Procedures for Carbon/Chitin Residue

Dissolution Reagents for Recovery	% Recovery on Carbon		% Recovery on Chitin	
	Nb	Ta	Nb	Ta
HF/ HNO ₃	20	10	-	-
HF/H ₂ SO ₄	50	40	-	-
HF/H ₂ SO ₄ / HNO ₃	75	55	-	-
HF/HNO ₃ /H ₂ O ₂	60	5	-	-
HF/0.25% Citric Acid	85	50	-	-
HF/H ₂ SO ₄ /0.1–0.2% Citric Acid	>95	>95	>95	>95

are given in Table X. From the results obtained it was observed that sulphuric acid-H₂O₂ mixture is preferable for dissolution of the melt obtained after fusion with 4 g KHSO₄ since it causes no interference during the sorption step.

Choice of Medium for Sorption

Tartaric acid, citric acid, and oxalic acid are used as media for stabilization of niobate and tantalate solutions. Among the three, citric acid solutions have longer shelf life and stability. Hence, citric acid was used in the present investigations as medium for stabilizing niobate and tantalate solutions. Though 3% citric acid was chosen as the medium for preparing the standard stock solution, very minor quantities of the same were present in the working standards after successive dilution and, hence, the medium for

sorption studies also contained negligible amounts of citric acid.

Mechanisms of the Sorption Process

Niobium and tantalum do not form simple soluble compounds in aqueous solutions. In neutral and acid solutions, simple compounds of Nb and Ta are hydrolyzed with formation of hydrophilic colloidal systems. Literature data on the ionic states of Nb and Ta are very scarce (2,3,6,37). Niobium and tantalum complexes are stable in aqueous solutions only in the presence of high concentrations of ligands like citrate, tartrate, or oxalate. Otherwise, they readily hydrolyze with the formation of white gelatinous precipitates of Nb and Ta hydroxides (niobic and tantallic acids) of the composition M₂O₅.x.H₂O or (M₂O₅.x.H₂O)_n. These are insoluble in water but are readily peptized.

Quantitative sorption of niobium and tantalum was observed in the pH range of 2–6 in the present investigations on carbon. Hence, it is probably the ortho-niobate and tantalate species and also their isopoly ions which adsorb on activated carbon. The adsorption on carbon remains essentially constant from pH 2 to pH 6 and this suggests that ionic sites may not be involved in adsorption but adsorption is merely through overlap interaction between the “3d” and “4f” orbitals of niobium and tantalum, respectively, with the Π -orbitals of the carbon (32,33). Similar sorption behavior as a function of pH was observed in the case of Zr and Hf also (34). As in the case of Zr and Hf, the hydrophobic nature of the niobate and tantalate species formed could also play a role in their sorption on carbon surface.

Generally, two mechanisms are reported for sorption on chitin, namely, (a) electrostatic interaction between protonated chitin and the

TABLE VIII
Effect of Common Anions

Anion Added	% Sorption on Carbon		% Sorption on Chitin	
	Nb	Ta	Nb	Ta
1000 ppm Chloride	>95	>95	>95	>95
500 ppm Sulphate	>95	>95	>95	>95
100 ppm Phosphate	>95	>95	>95	90
100 ppm Fluoride	90	90	90	90
1% EDTA	90	85	95	70
0.2% Citrate	95	80	90	70
0.5% Citrate	95	75	90	75
1% Citrate	90	75	85	70
1% Tartrate	90	75	85	70
1% Oxalate	40	40	35	35

TABLE IX
Effect of Major Metal Ions

Major Ion Added	Sorption on Carbon		% Sorption on Chitin	
	Nb	Ta	Nb	Ta
20 mg Na	>95	>95	>95	>95
20 mg K	>95	>95	>95	>95
20 mg Ca	>95	>95	>95	>95
20 mg Mg	>95	>95	>95	>95
20 mg Al	95	95	65	55
20 mg Fe	90	80	95	85
2 mg Mn	85	85	75	70

TABLE X
Studies on Recovery of Nb/Ta in Presence of Complexants

Matrix	Nb			Ta		
	Spiked (µg)	Obtained (µg)	% Recovery	Spiked (µg)	Obtained (µg)	% Recovery
8 g KHSO ₄ +3% CA	50	22	44	50	20	40
4 g KHSO ₄ +3% CA	50	22.5	45	50	20	40
4 g KHSO ₄ +1% CA	50	42.5	85	50	40	80
4 g KHSO ₄ +3% H ₂ SO ₄ Acid - 0.5 mL of H ₂ O ₂	50	47.5	95	50	45	90

anion in solution and (b) coordinate covalent bonding between lone pair electrons of nitrogen and/or oxygen and metals in solution. The pH is the dominating parameter in determining the adsorption mechanism. On chitin, molybdenum and tungsten have been reported to be retained strongly from pH 3 to 4, whereas Zr and Hf were retained from pH 2 to 5 (31). Quantitative sorption of niobium and tantalum was observed in the pH range of 2–4 on chitin in the present investigations. Hence, it is probably the anionic ortho-niobate and tantalate species and also their iso-poly ions which adsorb on chitin. This is supported by the fact that chitin has been reported to act as a collector for anionic species in solution under weakly acidic conditions (35,36). So, it is probably the electrostatic interaction between

chitin and the anions which contributes to their sorption. With increasing pH, the extent of protonation of chitin decreases and hence there is a decrease in the electrostatic interaction with anions as well and other factors become dominating. This could probably be the reason for the fall in sorption beyond pH 4 which could also probably be attributed to higher solubility of the niobate and tantalate species in the aqueous phase under such pH conditions.

Procedural Blank

Procedural blanks were run concurrently along with the samples in order to assess any contribution arising from carbon, chitin and other reagents used. The values obtained were within experimentally found determination limits for all four elements by ICP-AES.

TABLE XI
Determination of Nb in Standard Reference Materials

Sample No.	Sample Type	Nb ($\mu\text{g g}^{-1}$) by Present Method Using Carbon	% RSD	Nb ($\mu\text{g g}^{-1}$) by Present Method Using Chitin	%RSD	Nb ($\mu\text{g g}^{-1}$) Recommended Value (38)
G-2	Granite	12.8	2.2	12.4	3.3	12
BHV0-1	Basalt	21.0	1.4	19.8	2.8	19
SDC-1	mica schist	17.8	1.6	17.6	3.2	18
SDO-1	ohio shale	11.7	2.1	11.9	2.1	11.4
SO-1	Soil	10.8	3.8	10.6	3.8	11.7
SO-2	Soil	20.8	1.0	21.2	2.2	22
W-2	Diabase	8.4	4.5	8.2	4.6	7.9
JG-2	Granite	14.2	2.5	14.4	2.5	15
SARM-1 (NIM-G)	Granite	51	1.8	52	1.6	54

TABLE XII
Determination of Ta in Standard Reference Materials

Sample No.	Sample Type	Ta ($\mu\text{g g}^{-1}$) by Present Method Using Carbon	% RSD	Ta ($\mu\text{g g}^{-1}$) by Present Method Using Chitin	%RSD	Ta ($\mu\text{g g}^{-1}$) Recommended Value (38)
SARM-1 (NIM-G)	Granite	5.2	5.8	5.1	6.0	4.5

Validation of the Present Method

The present method employing carbon and chitin as sorbents was validated by applying it to the determination of Nb and Ta in some standard reference materials. Both carbon- as well as chitin-based methods gave results which compare well with the certified values in the case of niobium (Table XI). The values tabulated were the average of four replicate determinations ($n=4$) and RSD values ranging from 1.0 to 4.6%. However, it was not possible to determine tantalum values in these SRMs as they were in the range of 1 ppm. Such low values of Ta could not be determined with the present methods owing to the sensitivity and precision constraints of the instrumental technique. But a slightly higher value of Ta could be determined as in the case of SARM-1 (Table XII). The value obtained by the present method agreed well with the certified value (Table XII).

Application of the Method for the Determination of Nb and Ta in Geological Samples

Alkali under-saturated rocks contain appreciable quantities of Nb but only small amounts of Ta. Basic rocks contain significantly less Nb than acidic rocks. In all silicate rocks, Nb is much greater than Ta, with ratios ranging from 4:1 in basic rocks to 400:1 in certain nepheline syenites. Some silicate rock samples were selected and the present method was applied to the determination of niobium and tantalum in those samples. The results obtained are given in Table XIII by both carbon- and chitin-based methods. The values tabulated were the average of four replicate determinations ($n=4$) and RSD values ranging from 2.8 to 6.0% were obtained. The values obtained by the present method agreed well with the values obtained by a reported method which employs $\text{HF/HClO}_4/\text{HNO}_3$

for sample decomposition followed by ICP-MS determination (10). Since samples containing significant

amounts of Ta were unavailable, some quartzite samples were spiked with known amounts of Ta.

TABLE XIII
Determination of Nb in Geological Samples

Sample No.	Sample Type	Nb ($\mu\text{g g}^{-1}$) by Present Method Using Carbon	% RSD	Nb ($\mu\text{g g}^{-1}$) by Present Method Using Chitin	%RSD	Nb ($\mu\text{g g}^{-1}$) Reported Method (10)
AMD-1B	1.5%Fe ₂ O ₃ , 32%Al ₂ O ₃ , 43%SiO ₂ , 3.2% X ₂ O, 13.9%YO	34	2.8	33	3.0	36
AMD-2B	5.5%Fe ₂ O ₃ , 12%Al ₂ O ₃ , 70%SiO ₂ , 5.1% X ₂ O, 3.0%YO	32	3.2	34	3.2	31
AMD-3B	4.8%Fe ₂ O ₃ , 11%Al ₂ O ₃ , 72%SiO ₂ , 4.2% X ₂ O, 5.5%YO	20	3.8	20	3.9	23
AMD-4B	2.2%Fe ₂ O ₃ , 16%Al ₂ O ₃ , 64%SiO ₂ , 7.0% X ₂ O, 5.0%YO	18	4.0	17	4.2	19
AMD-5B	1.8%Fe ₂ O ₃ , 13%Al ₂ O ₃ , 73%SiO ₂ , 7.2% X ₂ O, 1.7%YO	12	5.5	11.5	6.0	13

X= Na + K; Y= Ca + Mg

TABLE XIV
Determination of Ta in Geological Samples

Sample No.	Sample Type	Ta (Spiked) (μg)	By Carbon Method		By Chitin Method	
			Ta (Obtained) (μg)	% Recovery	Ta (Obtained) (μg)	% Recovery
AMD-1C	0.5%Fe ₂ O ₃ , 9%Al ₂ O ₃ , 84%SiO ₂ , 3.2% X ₂ O, 1.8%YO	20	19.2	96	19.0	95
AMD-2C	4.0%Fe ₂ O ₃ , 4.5%Al ₂ O ₃ , 85%SiO ₂ , 0.7%X ₂ O, 2.5%YO	50	47.5	95	48	96

X= Na + K; Y= Ca + Mg

The spiking procedure required a standard solution containing 10 $\mu\text{g/mL}$ tantalum which was taken in a platinum crucible, dried under an Infra-red lamp, 0.5 g of the sample was weighed accurately, and the sample solution prepared as described above under the heading "Procedure for Sample Dissolution" and analyzed by the present method. The results obtained are given in Table XIV. The present method gave good recoveries.

CONCLUSION

The preconcentration method developed for niobium and tantalum is simple in methodology {batch methods that can be applied in mobile geochemical vans stationed in field areas}, rapid, economical, and eco-friendly as non-toxic/bio-compatible sorbents are used. Further, the preconcentration method developed gives accurate and precise results when applied to geological samples.

These methods can be interfaced with not only ICP-AES but also with ICP-MS and other instrumental analytical techniques which require separation from matrix components (for minimization of interferences) and low levels of total dissolved salts (TDS) in solution (to prevent clogging of instrument components like nebulizers, cones. etc.).

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