



A RAPID ANALYTICAL TECHNIQUE FOR THE DETERMINATION OF NIOBIUM IN GEOCHEMICAL SAMPLES BY ABSORPTION SPECTROSCOPY

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ABSTRACT

A simple and economic method has been developed for the determination of niobium from geochemical matrix sample. The sample is attacked by potassium pyrosulphate fusion followed by hydrochloric acid. Silica is removed in the first stage by hydrofluorisation. Ammonium thiocyanate selectively forms complex with Nb and Fe (III), where the Fe (III) is subsequently reduced to Fe (II), whose thiocyanate complex is not only colourless but also preferentially soluble in aqueous phase. The stable niobium–thiocyanate complex is extracted with ethyl acetate and niobium content has been estimated by spectrophotometry.

Key words: Niobium, Ammonium thiocyanate, Ethyl acetate, Complexation

INTRODUCTION

A number of procedures have been suggested for the determination of niobium, yet only a few have found general application to the analysis of ores and rocks. The procedure so far followed involves colour development with specific reagent by forming niobium–reagent complexes. It is well known that niobium occurs in association with tantalum and titanium and but a serious interference from titanium is there that it forms similar complexes as that of niobium under similar conditions^{1,2}. Moreover, the problem arising from the analysis of rock samples with high silica contents have not been solved by the existing procedures. This leads to serious errors in the determination of niobium. The existing procedures are very tedious to follow and it involves too many steps with costly chemicals^{3,4}. The absorption of niobium in atomic absorption spectrophotometer at trace levels (ppm) is very weak⁵ and hence, the determination of niobium is found to be difficult. The method described here is very simple to follow, economic, rapid and avoids interfering matrix elements.

EXPERIMENTAL

Apparatus

A Systronic spectrophotometer 106 was used for the determination of niobium at 385 nm.

Reagents

All the reagents used were of analytical reagent grade where otherwise not mentioned. Distilled water was used to prepare all solutions. Freshly prepared solutions were always employed.

Stannous chloride solution : 20.0 g of SnCl_2 is dissolved in 17.0 mL of concentrated HCl and made up to 100 mL with DI water.

Ammonium thiocyanate solution : (NH_4SCN) 20% – 20.0 g of NH_4SCN is dissolved in 100.0 mL of DI water.

Hydrochloric acid–tartaric acid : 15.0 g tartaric acid is dissolved in 100.0 mL of 9M HCl.

Standard niobium solution

0.0286 g of niobium pentoxide is fused with 1.5 g of $\text{K}_2\text{S}_2\text{O}_7$ in platinum crucible and the fused mass is dissolved in 1M tartaric acid and made up to 100.0 mL of 1M tartaric acid. 10.0 mL of the above solution is diluted to 100.0 mL with tartaric acid and mixed thoroughly.

Recommended procedure

0.5 g of sample is weighed accurately in a platinum crucible and fused with 4.0 to 5.0 g of potassium pyrosulphate ($\text{K}_2\text{S}_2\text{O}_7$) and the fused mass is leached with 6M HCl. The residue is filtered through Whatmann 42 filter paper and ignited at 900°C in a furnace. The ignited mass is again fused with potassium pyrosulphate and leached with 6M HCl and filtered as above. The two filtrates are combined and stored. Again the residue is ignited and hydrofluorised with HF and the remaining mass is dissolved in HCl and combined with earlier filtrates and made up to a known volume.

10.0 mL aliquot of the solution is pipetted out into a 250.0 mL separating funnel, 5.0 mL of hydrochloric acid–tartaric acid reagent is added and the contents are thoroughly mixed. 5.0 mL of ammonium thiocyanate solution and 5.0 mL of ethyl acetate is added to separating funnel and the mixture is shaken for 30 seconds. When the phases are separated, the aqueous phase is shaken for 20 seconds. The aqueous layer is again discarded and again stannous chloride is added and separation is repeated. Now the ethyl acetate phase is transferred to a 10.0 mL volumetric flask and made up to volume with ethyl acetate. The solution is transferred to cuvette and the absorbance is taken on a spectrophotometer at 385 nm and the number of micrograms of Nb present is ascertained by reference to a standard curve.

RESULTS AND DISCUSSION

In the present investigation, the sample containing niobium is fused with potassium pyrosulphate and the mass is digested with 6M HCl.



Sulphur trioxide is the effective attacking agent acting in a medium of molten potassium sulphate. This is the most convenient reagent for decomposition of sample containing niobium. Since an insignificant amount of acid remains after fusion and the sulphate ion can be tolerated by most colorimetric procedures. Fusion by potassium pyrosulphate is a convenient means of simple attack for sample containing niobium when the melt is leached with HCl. Complete decomposition of sample is observed with the combination of potassium pyrosulphate/HCl.

The major interfering radical silica (SiO_2) is removed from the sample solution by hydrofluorisation. Tartaric acid extracts niobium completely from the solution by forming a complex along with iron and certain other radicals. Ammonium thiocyanate selectively forms complex with niobium and iron (III) giving red coloured solution.

Vanadium, if present in the solution goes into the aqueous layer when ethyl acetate extracts niobium complex. The addition of stannous chloride reduces Fe (III) to Fe (II) whose thiocyanate complex is not only colourless but is also preferentially soluble in the aqueous phase. If stannous chloride is added directly to the HCl-tartaric acid solution before the ethyl acetate extraction, vanadium is reduced and forms a yellow coloured thiocyanate that is extracted along with niobium. Hence, the proposed procedure avoids all the interfering radicals in the determination of niobium from geochemical matrix sample.

Known amounts of pure niobium solution, where processed by the proposed extraction procedure and the recovery were found to be satisfactory and the results are presented in Table 1.

Table 1. Efficiency of the ethyl acetate extraction procedure for the recovery of niobium from pure solution

Sample No.	Niobium taken $\mu\text{g g}^{-1}$	Niobium found $\mu\text{g g}^{-1}$	Percentage of recovery
1	2.0	1.98	99.00
2	4.0	3.99	99.75
3	6.0	5.99	99.83
4	8.0	8.00	100.0
5	10.0	9.99	99.90

The niobium contents of two international standards and 3 in-house standards were determined by the proposed extraction procedure and by the internationally followed procedure that is presented in Table 2. Good agreement was observed between the proposed method and the internationally followed procedure.

Table 2. Comparison of results obtained by known method and the proposed method

Sample	Certified niobium content $\mu\text{g g}^{-1}$	Values obtained $\mu\text{g g}^{-1}$	
		Known method	Proposed method
CRPG BIOTITE	270.0	268.28	269.10
CRPG R5	19.0	18.21	18.52
GR 1	56.0	55.41	56.17
GR 2	84.0	83.22	84.61
GR 3	148.0	147.53	148.34

Eight individual niobium determinations for each of three rock samples and two in-house standards were performed to evaluate the reproducibility for a 0.5 g sample weight. Good precision was obtained for all the sample and standards (Table 3).

Table 3. Reproducibility of values for 0.5 g of samples analysed by the proposed method (in $\mu\text{g g}^{-1}$)

Determination number	Sample A	Sample B	Sample C	GR 1	GR 2
1	109.00	59.71	31.80	56.19	84.61
2	108.71	59.01	31.01	55.02	85.53
3	107.12	58.90	30.92	54.81	86.74
4	107.04	59.55	32.97	55.34	85.15
5	106.76	60.01	30.71	54.16	85.00
6	105.59	60.10	31.80	56.17	84.71
7	106.10	59.97	32.69	55.09	84.08
8	106.91	59.89	30.11	55.30	85.01
Mean	107.15	59.64	31.50	55.26	85.10
Standard deviation	1.17	0.459	0.994	0.676	0.786

Linearity of niobium determination was carried out from $29.6 \mu\text{g g}^{-1}$ to $148 \mu\text{g g}^{-1}$. In GR-3 in-house standard, a straight line graph is obtained showing good linearity conforming the proposed method to international requirements (Table 4).

Table 4. Linearity of the niobium in silicate rock sample

Amount of reference sample (GR 3) in g	Quantity of niobium present ($\mu\text{g g}^{-1}$)	Quantity of niobium determined using the proposed method ($\mu\text{g g}^{-1}$)
0.1	29.6	29.61
0.2	59.2	59.19
0.3	88.8	88.80
0.4	118.4	118.35
0.5	148.0	147.11

Based on the results of the tests of linearity, comparison, reproducibility etc., the proposed method is found to be very effective and sensitive for batch analysis of samples containing niobium.

CONCLUSION

The proposed method is simple, economic and precise with higher accuracy than the existing method. Moreover, the reproducibility of the results is comparable with the existing methods. Hence, this method can be used for bulk analysis of niobium in geochemical samples.

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