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Determination of Niobium in Geological Materials by Activation Analysis with Pre-Irradiation Separation

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The solvent extraction of Nb from geological materials in the presence of carrier-free ^{95}Nb tracer prior to neutron irradiation is described. The possibilities of contamination and interferences are discussed. Dissolution of samples and the solvent extraction of Nb are relatively simple and can be made simultaneously on a large number of samples and the subsequent activation procedure allows more efficient use of the reactor. For the measurement of 10^{-6} g of Nb, the uncertainty due to counting statistics is ±2% and the limit of detection or of contamination is of the order of 5×10^{-9} g. This technique was used to measure the Nb content in 15 U.S. Geological Survey standard rocks.

The determination of niobium by neutron activation analysis is not common because of the time restrictions imposed by the short half life ($t_{1/2}$ = 6.6 min) of the ^{94m}Nb formed from this monoisotopic element. Another problem with this measurement is the high degree of internal conversion in the decay of ^{94m}Nb, which makes the 16.7-keV Nb x-ray the only practical peak to use in γ spectrometry. In order to gain resolution and efficiency for measuring these x-rays, it is advantageous to use low energy photon detectors (e.g., *1*). Nevertheless, the Compton and bremsstrahlung background from other elements in a sample limit the sensitivity and force one to resort to a rapid radiochemical separation (e.g., *2, 3*). One of the advantages of these procedures over other techniques is the relatively small risk of contamination and/or loss of Nb because the pre-irradiation treatment of the sample is minimized. The chemical separations are carried out after the activation of the sample and in the presence of carrier to determine any losses. However, rapid separations on very radioactive samples (like activated geological materials) are difficult, inefficient, as well as a hazard to the analysts' health. While a pre-irradiation separation of Nb or any other element does risk contamination and/or loss, this approach can improve the sensitivity and efficiency of some neutron activation measurements. In this work the dissolution of geological samples and the separation of Nb was made in the presence of carrier-free ^{95}Nb tracer which eliminated the need for a quantitative recovery of the Nb. The separation procedures did not need to be as complex

and selective as those used for some spectrophotometric methods (*4–7*) because interferences by elements like Ta are not a problem in the neutron activation measurement. The simple separation procedures helped eliminate some of the possible sources of contamination and the contamination levels were below the detection limit of the method.

EXPERIMENTAL

Procedure. Samples of the U.S. Geological Survey standard rock samples were weighed into 100-mL Teflon beakers which had previously been washed with HF. The sample size was not critical although for most of the geological standards a 0.1-g sample was sufficient to ensure an uncertainty due to counting statistics of less than 2%. To each beaker a measured amount (0.5 μCi) of ^{95}Nb tracer (carrier free ^{95}Nb in 0.5% oxalic acid; Radiochemical Center, Amersham, U.K.) was added. The tracer was also added to several irradiation vials which were to contain the Nb standards. Sample dissolution was carried out by adding 10 mL of concentrated HF and 1 mL of concentrated HNO$_3$ (both reagent grade) to each beaker. In addition to dissolving the matrix, the presence of fluoride ion helped ensure dissolution and exchange of the Nb which is strongly complexed by fluoride. The beakers were placed on a hot plate until the acid was evaporated. Then 10 mL of aqua regia was added to dissolve any phases not soluble in HF, and this too was evaporated to dryness. The residue was dissolved in 15 mL of an aqueous solution which was 5.6 N in HF and 9 N in H$_2$SO$_4$. Nb was extracted from this solution into 10 mL of methyl isobutyl ketone (hexone) and the aqueous phase was removed. The hexone was then washed with a fresh 15-mL portion of the HF/H$_2$SO$_4$ solution. Care was taken in each separation to prevent any physical carry-over of the aqueous solutions as the same separatory funnel was used for the back extraction. The Nb was extracted into 4 mL of a 1.5% H$_2$O$_2$ solution, and then transferred into a clean polyethylene irradiation vial. Standards were prepared by measuring 4 mL of a Nb standard solution (1 ppm Nb in 0.5% oxalic acid) into the irradiation vials containing the ^{95}Nb tracer.

Irradiations. After all samples and standards had been prepared, they were irradiated sequentially in the "rabbit" facility of the JEEP II reactor (Kjeller, Norway) for 5 min each (flux = 1.5×10^{13} n cm^{-2} s^{-1}). The samples arrived in the isotope laboratory 30 s after the end of irradiation and the dominant activity was the ^{19}O ($t_{1/2}$ = 27 s) from the water. After inserting the next sample into the reactor, the irradiated sample was opened and transferred to a clean polyethylene counting bottle. The irradiation vial was washed with 1 mL of water bringing the total volume of the counting solution to 8 mL which was sufficient to cover the bottom of the counting bottle in a reproducible manner.

Radioassay. The samples were counted exactly 3 min after the end of the irradiation on a planar, intrinsic germanium detector (200 mm^2 surface area and 7 mm active depth) coupled to a

Table I. Activation Analysis of USGS Standard Rocks for Niobium

| Standard Rock | Nb concentration (ppm), this work | | Nb Concentration (ppm), literature[a] |
	Individual samples	Average	
W-1	6.3 ± 0.1,[b] 6.8 ± 0.2	6.5	7.1 (E)
G-2	9.4 ± 0.3, 10.1 ± 0.1	9.8	7.0 (E), 13.3 (S)
GSP-1	20.0 ± 0.3, 20.2 ± 0.2	20.1	20.5 (E), 29.4 (S)
AGV-1	12.6 ± 0.1, 12.0 ± 0.2	12.3	9.4 (E), 15.0 (S)
PCC-1	0.04 ± 0.01, 0.02 ± 0.02	0.03	<2.2 (E)
DTS-1	0.04 ± 0.02, 0.03 ± 0.02	0.04	<2.2 (E)
BCR-1	10.3 ± 0.1, 10.9 ± 0.1	10.6	12.2 (E), 13.5 (S)
STM-1	See Table II	262	189 (E), 298 (E)
RGM-1	7.5 ± 0.1, 8.5 ± 0.3	8.0	5.4 (E), 9.4 (S)
QLO-1	See Table II	9.3	6.1 (E), 11.7 (S)
SDC-1	16.0 ± 0.1, 16.0 ± 0.1	16.0	14.4 (E), 21.1 (S)
SCO-1	9.0 ± 0.1, 8.1 ± 0.3	8.6	7.3 (E)
SGR-1	5.0 ± 0.7, 5.5 ± 0.2	5.3	5.3 (E)
MAG-1	9.7 ± 0.7, 9.5 ± 0.3	9.6	7.7 (E)
BHVO-1	See Table II	16.3	15.2 (E), 21.0 (S)

[a] Values followed by (E) are computerized emission spectrographic data from Walthall et al. (10) and in the case of STM-1 from Snavely et al. (11). Values followed by (S) are spectrophotometric measurements by Greenland and Campbell (4, 5). [b] The mean of two counts on the same sample and half the difference between these two calculated values. The differences are due in part to counting statistics and in part to differences in counting geometries for the two counts.

multichannel analyzer (Canberra 8100). This 1-min count was made with the sample 10 mm above the Be window of the detector and through a 3-mm thick Plexiglas absorber. The x-ray peaks due to ^{94}Nb decay Kα = 16.6 keV, Kβ = 18.7 keV) were integrated internally in the multichannel analyzer along with background areas on either side of the peaks. A second 1-min count on the sample (without the Plexiglas absorber) was made exactly 5 min after the end of the irradiation. At about the time this count was started, the irradiation of the next sample ended so that it could be prepared for counting. This sequential procedure was easily within the capabilities of a single person and gave maximum utilization of the time during which the reactor was in operation. In order to achieve better sensitivity, low Nb samples were irradiated for 10 min and counted twice for 5-min periods (3 and 9 min after the irradiation). Standards were irradiated and treated in the same manner.

At some convenient time after the irradiation, each solution was recounted on a coaxial Ge(Li) detector (although a NaI detector would suffice) to measure the intensity of the 765 keV γ-ray from the ^{95}Nb tracer in order to determine the relative recoveries of samples and standards.

RESULTS AND DISCUSSION

This procedure for the separation of Nb is simple and gives good yields (80–90%). Most of the losses result from the loss of some hexone in the effort to avoid having any of the original sample solution left in the separatory funnel. The extraction is quite selective although Ta is also extracted (7–9). Activity induced from any elements which are extracted should not interfere with the measurements, since the resolution of the detector (FWHM at 16 keV is about 0.4 keV) helps eliminate most of the possible spectral interferences. The possibility of spectral interferences in the region integrated for the Kα and Kβ x-rays of Nb (15.7–19.4 keV) was considered. This would include K x-rays from Zr, Mo, Tc, and Ru as well as L x-rays for elements above Z = 90 (Th, U). Some of these elements are not activated to form an isotope whose decay is accompanied by emission of its characteristic x-ray. For instance, Mantel and Amiel have shown that for a sample with a Nb/Zr ratio of $1/10^4$ there was no spectral interference from Zr in the region of the Nb x-rays (1). The activation of Mo would give rise to some Mo and Tc x-rays, but the much smaller decay constants for the Mo isotopes as compared to ^{94m}Nb limit the importance of this interference. In addition, the extraction efficiency for Mo is less than 1% of that for Nb in these solvent extractions (9). Thus Mo in the sample would have to be over 10^5 times that of Nb in order to be a problem. Likewise, while activation of U and Th would give rise to Pa and Np x-rays (1), the solvent extraction procedure

is very effective in removing them from the solution (9). In fact a HF/H$_2$SO$_4$ extraction into hexone has been used in the separation of Nb from U alloys (7). It therefore appears that a combination of the selectivity of the extraction and the use of high resolution detectors eliminates all interferences that might be encountered in geological materials. The Ta which is extracted along with the Nb could be measured simultaneously. The 172-keV γ-ray from ^{182m}Ta ($t_{1/2}$ = 15.8 min) was observed in many of the samples, but since no carrier free tracers are available for Ta, the recovery of Ta would have to be shown to be related to that of Nb.

Since only a limited number of reagents are used in this procedure, there should be little or no problem with contamination. This was shown by measuring blanks prepared in the same manner as the samples. Since these blanks included an aliquot of the ^{95}Nb tracer, they also provide a measure of how much Nb carrier was present in the "carrier-free" tracer. After 10-min irradiation, the two 5-min counts of the blanks showed a significant amount of Compton and bremsstrahlung background in the energy range of the Nb x-rays. In the first count, this was due primarily to ^{19}O, and in the later count to some ^{24}Na, ^{33}Cl, and ^{80}Br. Although there were no visible peaks due to ^{94m}Nb, the uncertainties in the background of the blanks set an upper limit to the possible blank of 2×10^{-8} g of Nb in the case of the first 5-min count. The lower background in the second count limited the Nb blank to less than 5×10^{-9} g. Blank corrections did not therefore appear to be necessary and only the background activity limited the sensitivity. In cases where the limit of detection is approached, it is obviously better to use only the results of the second count as was done in the case of the U.S. Geological Survey standards DTS-1 and PCC-1. For each of these two samples, the uncertainty due to counting statistics was on the order of 25% (for the second count) when the absolute amount of Nb measured was about 3×10^{-8} g.

The procedure was tested on 15 U.S. Geological Survey standard rocks which differed considerably in composition. The results are shown in Table I. The individual results of measurements on replicate samples of three of the rocks are shown in Table II. The individual values given in Table II as well as Table I are the mean concentrations based upon the two counts made after each irradiation, and the uncertainty given is half the difference between these two counts. The actual uncertainty due to counting statistics is usually lower than indicated by the differences calculated for the two counts. When the Nb present is of the order of 10^{-6} g the statistical uncertainties are about ±2%. For most of these

Table II. Results for the Determination of Niobium in
Replicate Samples of Some USGS Standard Rocks

Rock	Sample weight, mg	Nb concentration, ppm
STM-1	45	282 ± 6^a
	54	254 ± 2
	68	262 ± 1
	72	255 ± 2
	108	259 ± 7
	119	257 ± 8
	Av.	$\overline{262 \pm 10^b}$
BHVO-1	100	16.4 ± 0.1
	111	17.6 ± 0.4
	130	15.0 ± 0.1
	131	17.1 ± 0.1
	207	16.4
	251	16.6 ± 0.3
	270	15.2 ± 0.1
	Av.	$\overline{16.3 \pm 0.9^b}$
QLO-1	97	8.8 ± 0.2
	168	9.7 ± 0.1
	170	9.5 ± 0.4
	178	9.5 ± 0.2
	204	9.9 ± 0.1
	285	8.6
	Av.	$\overline{9.3 \pm 0.5}$

[a] The mean of two counts on the same sample and half the difference between the two calculated values. [b] Mean value for the replicate determinations and the standard deviation.

samples, the counting statistics were even better than ±2%. The source of the variations between the two counts probably resulted from geometry effects. Slight variations in the thickness of the counting vials were more critical for the second count since the vials were the only absorbers. Unevenness of the bottom of the counting vials could have some effect upon the comparison between two different samples as the distance between the detector and samples was so small. These effects were investigated using 8 mL of ^{57}Co tracer in five different bottles. The variation between bottles was about 4% with an uncertainty due to counting statistics of about 1%. As expected, the greatest variations were for the 14-keV γ ray measured without an absorber. The 122-keV γ ray intensities were less variable and could be accounted for in terms of the counting statistics. For those samples (BHVO-1, STM-1, and QLO-1) where six or more individual samples were analyzed, the mean and the standard deviation of the measurements are given in Table I. In all three cases the relative standard deviations are of the order of 5%. Based upon the ^{57}Co experiments, these variations between individual samples could be due to differences in the counting vials or to slight inhomogeneities in the samples themselves.

The accuracy of this technique depends upon the exchange of the ^{95}Nb tracer and the Nb from the sample. While solutions of Nb at the 1-ppm level were analyzed with great accuracy (within the 1% statistical uncertainty), this was not clear evidence for exchange in the geological materials. In the samples of BHVO-1, STM-1, and QLO-1, the sizes of the samples analyzed were varied by nearly a factor of three in each case. The calculated concentrations for each sample showed no correlation to sample size (Table II) which suggests that incomplete exchange was not a problem. The results for all of the USGS standard rocks compare favorably with results obtained by other techniques (5, 10–13) which are capable of measuring Nb at the 10-ppm level (Table I). It is important to note that the sensitivity of this neutron activation technique is in fact better than these other techniques. For instance, while x-ray fluorescence (12, 13), emission spectrographic (10), and isotope dilution spectrophotometric techniques (4) have place limits of from <5 ppm to <1 ppm on the Nb contents of DTS-1 and PCC-1, much lower concentrations (<0.04 ppm) are measured by this procedure. The use of <0.7-g samples of these two rocks results in an uncertainty due to counting statistics of about 25% and makes the choice of the background area to be subtracted quite critical.

The use of this method on a wide variety of geological materials indicates that a pre-irradiation separation of an element can be used to improve both the sensitivity and the convenience of neutron activation analysis when short lived isotopes are involved. Such procedures are also useful in avoiding high radiation exposure to the analyst resulting from some radiochemical procedures. Where the appropriate carrier free tracers are available, the idea of pre-irradiation separations should be considered for routine neutron activation measurements.

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