

EVALUATION OF REACTOR INDUCED (n, p) REACTIONS FOR ACTIVATION ANALYSIS OF TITANIUM IN GEOLOGICAL MATERIALS

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The possibilities of reactor induced (n, p) reactions as a tool for neutron activation analysis of titanium in geological samples are discussed. The interference of calcium and scandium is experimentally evaluated. Results for Ti, Ca and Sc in GSP-1 and PCC-1 standard rocks are presented. On the basis of the experimental values, it is concluded that the $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ reaction is the most favourable for titanium determination.

Introduction

Titanium is the ninth most abundant element of the earth crust; practically all crystalline rocks, soils and sediments contain this element in concentration levels of minor component. The industrial applications of titanium are numerous, so that there is a real need to rely on methods for its analysis. As titanium minerals are sometimes more resistant to chemical attack than the silicate matrix, destructive methods of determination are tedious and time-consuming, therefore, purely instrumental techniques, like X-ray fluorescence or neutron activation analysis have been tried.^{1,2} However, activation analysis of titanium in nuclear reactors appears to be somewhat difficult task: the only nuclear reaction induced by thermal neutrons leads to ^{51}Ti , which is a short-lived nuclide ($T = 5.8$ min) so that precautions must be taken to avoid errors in the application of the necessary correction factors for decay and differences in dead times. In addition, Compton distribution from the main components of the gamma spectrum (^{28}Al , ^{56}Mn , ^{24}Na , ^{27}Mg) often masks its 320.0 keV peak. The interference of the 320.1 keV radiation from ^{51}Cr is not so noticeable but it should be considered in minerals with high chromium contents.

Different authors³⁻⁵ have determined titanium by ^{51}Ti in multielemental analysis of geological samples, but with low sensitivity and poor precision, due to

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the mentioned drawbacks. An alternative procedure is the use of threshold reactions induced by the fast component of the reactor neutron spectrum, to accomplish the analysis. The (n, p) reactions seem to be the most adequate, as suggested by GLADNEY and PERRIN.⁶ The aim of the present work is the experimental evaluation of the (n, p) reactions on titanium as a method for its determination in geological samples.

Review of the (n, p) reactions of titanium

Only three of the five (n, p) reactions on titanium may be used with certain possibilities of successful determination. The reactions on ^{49}Ti and ^{50}Ti should be discarded, because of the unfavourable characteristics of their products: ^{49}Sc , having very low gamma-intensities (0.01% for the main radiation), and the short-lived ^{50}Sc ($T = 1.7$ min). Nuclear data for the remaining reactions are indicated in Table 1; the interfering reactions are also included.

On the basis of Ti/V concentration ratios generally found in geological samples, and the nuclear data of vanadium isotopes, it can be demonstrated that less than 1% of the total activity originates from this interference.⁶ Both calcium and scandium interferences should be examined more carefully: calcium is abundant in most of the geological materials, although the thermal cross-section, the resonance integral and especially the isotopic abundance of ^{46}Ca are not favourable for ^{47}Sc production; on the other hand, scandium is currently present at trace levels, but high activities of ^{46}Sc can be formed via this element, due to its good nuclear constants. In relation to both interferences, the authors have performed experimental assays in order to find the ratio of concentrations titanium/interfering element which are compatible with the requirements of precision in analysis.

Experimental

Materials and methods

Specpure chemicals of Ti and Sc (Johnson, Matthey and Co., London) and CaCO_3 (analytical grade) were used for the study of interferences. Standard solutions were prepared by dissolving metallic Ti in dilute H_2SO_4 , Sc_2O_3 in conc. HNO_3 , and CaCO_3 in dilute HCl.

For the investigation of Ca interference on Ti determination, solutions of both elements, simultaneously irradiated, were diluted, and several aliquots were mixed

Table 1
Nuclear data for reactions concerning titanium determination

Reaction	Precursor			Product			Precursor		
	Θ , %	σ , mb	T	E_γ (keV) and intensity (%)	Interfering reaction	Θ , %	σ , mb	I, mb	
$^{46}\text{Ti}(n, p)^{46}\text{Sc}$	8.2	12.5	84 d.	889.3 (100)	$^{45}\text{Sc}(n, \gamma)^{46}\text{Sc}$	100	35000*	11000	
$^{47}\text{Ti}(n, p)^{47}\text{Sc}$	7.4	20	3.35 d.	160.0 (100)	$^{50}\text{V}(n, \alpha)^{47}\text{Sc}$ $^{46}\text{Ca}(n, \gamma)^{47}\text{Ca}(\beta)^{47}\text{Sc}$	0.250 0.0033	1.5** 700*	320	
$^{48}\text{Ti}(n, p)^{48}\text{Sc}$	73.8	0.315	43.67 d.	983.3 (100) 1037.1 (100) 1311.4 (100)	$^{51}\text{V}(n, \alpha)^{48}\text{Sc}$	99.75	0.022**		

* Thermal cross-section.

**Averaged over a fission spectrum. (Cross-section data taken from Ref. 7.)

in order to obtain Ti:Ca mass ratios within 0 and 0.015. The mixtures were transferred to small aluminium cans and dried by gentle heating; the residues were mounted for measurement. A similar procedure was used to investigate mutual interference between Ti and Sc; the range of Ti:Sc masses was 0–794. In both experiments some ratios were included which were more unfavourable than those found in most geological samples. All the mixtures contained the same mass of the interfering element and variable quantities of titanium.

Solid Ti and Sc standards were prepared for analysis of the reference materials GSP–1 and PCC–1 (U.S. Geological Survey) by depositing aliquots of standard solutions on high purity SiO_2 , then drying and homogenizing; CaCO_3 was used as standard for calcium. Masses of samples and standard irradiated were within 10–20 mg. After irradiation, they were weighed and mounted for measurement in standard polyethylene vials.

Irradiations and measurements

Two positions of the RA–3 reactor (Centro Atómico Ezeiza) were used for irradiation of bare and cadmium covered samples, having respectively: thermal flux: $1.1 \cdot 10^{13} \pm 10\% \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and $2.2 \cdot 10^{13} \pm 10\% \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; ephitermal to thermal flux ratio: $0.018 \pm 10\%$ and $0.040 \pm 10\%$; fast to thermal flux ratio: $0.10 \pm 10\%$ and $0.30 \pm 10\%$.

The samples were sealed in quartz ampoules which were conditioned in aluminium irradiation capsules; for epicadmium irradiations a 0.6 mm cadmium cover was added. The analysis of reference materials was carried out by a combination of both types of irradiation, while only epicadmium irradiations were used for the study of interferences.

The irradiation time was always 8 hrs; the following decay times were selected: 5 days, 5–9 days and 20–35 days, for ^{48}Sc , ^{47}Sc and ^{46}Sc , respectively. Measurements were performed with a 70 cm^3 Ge(Li) detector (Princeton Gamma Tech, 2.4 keV resolution for the ^{60}Co 1332.5 keV peak) coupled to a 4096 multichannel analyzer (Canberra, Serie 80) with digital output by teletype. The measured energies were: 889.3 keV (^{46}Sc); 160.0 keV (^{47}Sc); 983.3 keV, 1037.1 keV, 1311.4 keV (^{48}Sc).

Method of evaluation

Peak areas were calculated by Covell's method; the data were corrected for decay in each experiment.

The activity of the peaks was plotted as a function of concentration ratios for the study of interferences. The titanium concentrations in the standard rocks were calculated from the following equations:

$$A_s = A_{Ti} |Ti| + A_{in} |int|$$

$$A'_s = A'_{Ti} |Ti| + A'_{int} |int|$$

where A and A' are the specific activities of the peaks, induced after thermal and epithermal irradiation, in $\text{counts} \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ for samples (subscript s) and $\text{counts} \cdot \text{s}^{-1} \cdot \mu\text{g}^{-1}$ for standards of titanium and interferences (subscripts Ti and int); $|Ti|$ and $|int|$ are the concentrations of titanium and interferences, in $\mu\text{g/g}$.

Results

Interference of calcium in titanium determination by the $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ reaction

The ^{47}Sc activity obtained for different Ti/Ca concentration ratios is indicated in Fig. 1. It can be seen that the activity induced by calcium is 22% of the total activity for a Ti/Ca ratio equal to 0.015. An additional point was studied, corresponding to a Ti/Ca ratio of 0.05; the results showed that this point fell on the curve, and 7% of the total activity originated from calcium.

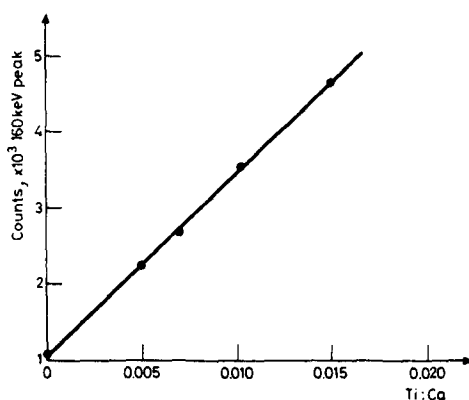


Fig. 1. Activity of ^{47}Sc for different $Ti:Ca$ concentration ratios

Table 2
Concentration ratios Ti:Ca and Ti:Sc for different USGS rock standards

	W-1	G-1	G-2	GSP-1	AGV-1	PCC-1	DTS-1	BCR-1
Ti:Ca	0.082	0.157	0.200	0.276	0.178	0.019	0.066	0.258
Ti:Sc	183	537	751	562	462	10	20	286

The Ti/Ca concentration ratios in some of the U.S. Geological Survey standard rocks are shown in Table 2, calculated on the basis of data recommended by FLANAGAN.⁸ With the only exception of the peridotite PCC-1, the ratios were higher than the ones studied; the ^{47}Sc activity formed by episcandium irradiation in these standard rocks is almost entirely titanium induced.

Interference of scandium in titanium determination by the $^{46}\text{Ti}(n, p)^{46}\text{Sc}$ reaction

Fig. 2 represents ^{46}Sc activity as a function of Ti/Sc concentration ratio. The contribution of scandium to the total activity reaches 79% for a Ti/Sc ratio as high as 794. An additional point of this curve, at a ratio of 1588, showed that 66% of the whole activity was formed by scandium. Since the Ti/Sc concentration ratios for standard rocks (Table 2) are similar in magnitude to the ones studied, the scandium interference must be always taken into account, even in episcandium irradiation.

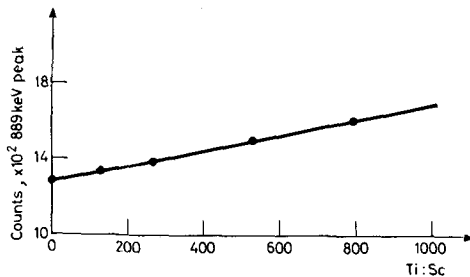


Fig. 2. Activity of ^{46}Sc for different Ti:Sc concentration ratios

Analysis of reference materials

The results for Ti, Ca and Sc in a single analysis of two standard rocks (GSP-1 and PCC-1) are indicated in Tables 3 and 4, together with the recommended values.⁸

The above method of evaluation was used to calculate the concentrations from ^{46}Sc and ^{47}Sc . The results quoted for titanium via ^{48}Sc are the average of three values obtained from the measurement of each peak. The errors were calculated on the basis of counting statistics and theory of error propagation.

Table 3
Results of titanium determination in reference materials

Standard	$^{46}\text{Ti}(\text{n}, \text{p})^{46}\text{Sc}$	$^{47}\text{Ti}(\text{n}, \text{p})^{47}\text{Sc}$	$^{48}\text{Ti}(\text{n}, \text{p})^{48}\text{Sc}$	Recommended value
GSP-1	2610 \pm 730	4180 \pm 150	4190 \pm 750	3990
PCC-1	n.d.	89 \pm 38	n.d.	70

n.d.: not detected.

(These results show the better precision and accuracy which are obtained by the $^{47}\text{Ti}(\text{n}, \text{p})^{47}\text{Sc}$ reaction.)

Table 4
Results for calcium and scandium in reference materials

Standard	Calcium		Scandium	
	this work p.p.m.	recommended p.p.m.	this work p.p.m.	recommended p.p.m.
GSP-1	16700 \pm 5400	14443	5.84 \pm 0.25	7.1
PCC-1	5300 \pm 2600	3647	7.40 \pm 0.34	6.9

Discussion

The previous experimental assays were confined to the verification and evaluation of the interferences produced by nuclear reactions in titanium determination. Some spectral interferences can also occur in the analysis of complex matrices like those of geological origin. Whereas ^{48}Sc peaks can be considered as interference-free, the situation is different in relation with ^{46}Sc and ^{47}Sc . The ^{46}Sc peak at 1120.5 keV can be interfered by a 1121.2 keV peak from ^{182}Ta , which is currently present in activated geological

materials. This interference has been experimentally confirmed by the authors; consequently, the 889.3 keV peak was exclusively used for calculations. A possible spectral interference for ^{47}Sc is the 158.4 keV peak from $^{117\text{m}}\text{Sn}$; however, tin is usually present at low concentrations in geological samples, and its nuclear characteristics do not favour the activation.

The determination of titanium from the $^{46}\text{Ti}(n, p)^{46}\text{Sc}$ reaction is severely affected by the scandium activation, which forms most of the total activity; low contents like those present in the peridotite PCC-1 cannot be detected. On the other hand, the presence of titanium leads to errors in epithermal neutron activation analysis of scandium, as observed by other authors.^{9,10}

There is a significant difference between the value found for scandium concentration in the granodiorite GSP-1 and the one recommended by FLANAGAN; the authors checked the former by thermal activation with different scandium standards, finding results similar to the previous one, within the limits of statistical errors.

A result close to the recommended value for titanium in the GSP-1 rock is obtained by ^{48}Sc , but the precision is poor, because of the relatively long decay time necessary to allow the measurement of its three peaks; this fact also limits the sensitivity, and the analysis is not possible in the PCC-1 standard.

The determination from the $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ reaction leads to a value for the GSP-1 standard that is in good agreement with the recommended one; the precision is good, the error being less than 5%. Titanium is determinable even at such a low concentration as that existing in the PCC-1 rock, but the precision obtained is, of course, poorer. It should be noted that the value quoted by FLANAGAN in his compilation is informative, since the titanium determination in his standard at that time had been carried out by only one author,¹¹ whose individual results were 78 ppm and 83 ppm; a more recent value⁶ coincides with the present result. Both the low contents of titanium and the unfavourable Ti/Ca concentration ratio are the reasons for the poor precision in the analysis of the PCC-1 standard rock. A possible alternative to improve it is to effect both irradiations (with and without cadmium cover) in less thermalized positions of the reactor, so as to increase the relative contribution of titanium. Simultaneous determination of calcium should be discarded in these conditions. The complementary alternative is to carry out the irradiations in more thermalized positions to determine calcium, but even in this case the contribution of this element to ^{47}Sc activity is low, as has been demonstrated.

Some authors have proposed the determination of calcium by ^{47}Sc after epithermal neutron activation.^{5,9} The present results prove that subtraction of titanium contribution is mandatory in most geological materials for the correct application of this method. A short irradiation and subsequent measurement of ^{49}Ca is probably a better method for calcium assay.

Conclusions

Threshold reactions offer an applicable alternative for neutron activation analysis of titanium in geological samples. Furthermore, the reaction: ${}^47\text{Ti}(n, p){}^47\text{Sc}$ is more convenient than the (n, γ) reaction, although the minor contribution of calcium should be considered and subtracted. The determination can be accomplished with adequate accuracy and precision, even at low Ti/Ca concentration ratios. The sensitivity is sufficient for the range of titanium concentrations normally found in geological materials.

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