

Application of Neutron Activation Analysis in the Determination of Trace Elements in Tourmalines

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ABSTRACT: The present work reports a methodology to determine trace elements in tourmaline by neutron activation analysis. The interference effect of ^{10}B was demonstrated by irradiating samples of different weight from the same tourmaline and plotting a graph of specific activity against the sample weight. The ideal weight with minimal interference effect was obtained in the straight line deviation. Instrumental neutron activation analysis can be applied to the ideal weight with minimal interference effect. Radionuclides ^{65}Zn , ^{59}Fe , ^{60}Co , ^{51}Cr , ^{46}Sc , ^{82}Br , ^{140}La , $^{24\text{m}}\text{Na}$, ^{42}K , ^{85}Sr , ^{182}Ta , ^{134}Cs , ^{124}Sb were detected.

1 INTRODUCTION

Trace elements studies are very important in modern petrology because they are more capable of discriminating between petrological processes than are major elements. Trace elements allow and are capable to understand the processes controlled by crystal-melt or crystal-fluid equilibria. Tourmalines are important as petrogenetic indicators because they can incorporate by total or partial substitution of a great variety of chemical elements depending on the mineralogical and metalogenetic history of the rock (Oliveira et al. 2002; Hawthorne et al. 1993; Hawthorne 1996; Hawthorne & Henry 1999; Slack 1996; Cleland et al. 1996; Henry & Dutrow 1996; Henry & Guidotti 1985; Koval et al. 1991).

Tourmalines are structurally and chemically complex borosilicate minerals that can be represented by the general formula $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$, where $\text{X} = \text{Na}^+$, Ca^{2+} , K^+ , and vacancy (); $\text{Y} = \text{Mg}^{2+}$, Fe^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Mn^{3+} , Cr^{3+} and Li^+ ; $\text{Z} = \text{Al}^{3+}$, Mg^{2+} , Fe^{3+} , Cr^{3+} , V^{3+} . The T site is occupied by Si or Al in fourfold coordination with oxygen and in threefold coordination with boron. These structurally distinct positions have been assigned to the W site, which is dominated by O^{2-} , OH^- , F, Cl, and the V site, which

is dominated by OH^- , or, more rarely, O^{2-} . In addition, several other trace elements can also be present in sites X, Y and Z (Hawthorne & Henry 1999).

This paper reports a methodology of determination of trace elements in boron rich minerals by instrumental neutron activation analysis (INAA) where tourmaline was the mineral investigated. INAA in samples containing boron is problematic due to the large neutron-capture cross section of ^{10}B (3838 barns in thermal energy 0.0253 eV). This results in different nuclear production rates in different parts of the samples and this is undesirable. As a consequence of the neutron-capture effect, the concentration of the elements determined by neutron activation is lower than it really. One of them is to use a graph of the specific activity against the sample weight and determine the smallest sample where interference effect is eliminated or minimum.

The determination of trace element in tourmalines by neutron activation analysis has been investigated by some authors (Koval et al. 1991; Laul & Lepel 1987; King et al. 1988; Jolliff et al. 1987). King et al. (1988) studied the REE distribution in tourmalines by INAA technique involving pretreatment by boron volatilization. Jolliff et al.

(1987) and Laul & Lepel (1987), studied the REE distribution in tourmalines by radiochemical neutron activation analysis (RNAA). The analytical methods described by these authors are very hard and/or contamination can occur.

2 METODOLOGY DESCRIPTION

The methodology used in this work is based on studies for determination of trace-element by INAA when during irradiation there is a suppression of the incident neutron flux in the target sample (Bowen & Gibbons 1963; Ehmann & Vance 1991). This interference effect can be demonstrated by irradiating the same sample of different weights and then, after determining the activity of each sample, plotting a graph of specific activity against sample weight. From the graph it is possible to determine the maximum weight where interference effect was eliminated or minimized and thus limit irradiation to the samples of that determined weight. This occur in the straight line deviation.

3 SAMPLING AND ANALYTICAL TECHNIQUES

Brazilian tourmalines from granitic pegmatites were carefully selected. Five tourmaline samples were selected from several hundreds of fragments based on quality and color homogeneity. Special care was taken to separate the different color zones from zone samples. The tourmalines from granitic pegmatites occur in northeastern Minas Gerais States, multi-colored tourmalines of the pegmatites belong to the Eastern Gemmological Province and were formed by partial melting of metasedimentary rocks during the granitogenic episode of the Neoproterozoic Araçuaí Belt (Pedrosa & Wiedemann-Leonardo 2000; Pinto & Pedrosa 2001). Firstly, electron microprobe and Mössbauer spectra have been acquired for tourmaline in study, Mössbauer spectra of the samples selected estimated the lower Fe^{3+}/Fe^{2+} ratio (Oliveira et al. 2002).

For INAA the irradiation was performed in the reactor TRIGA Mark I IPR-R1 at 100 kW_t with thermal neutron flux of 6.6×10^{11} n.cm⁻².s⁻¹. The acquisition parameters the gamma spectroscopy and the irradiation used were carefully defined in order to better sensitivity. The elements were determined through irradiation for 16 hours. Following a cooling time of about a week, samples were counted for one hour. After a further delay to permit shorter half-life activity to decay, about fifteen days, the samples were recounted for about one day (86000 s) to obtain the gamma activity for longer lived radioisotope. The gamma spectroscopy was performed using a hyperpure germanium detector (HPGe) with a

resolution (FWHM) 1.75 keV at 1332 keV peak of ⁶⁰Co, a relative efficiency of about 50%. All counting was performed at constant geometry in a position where the analyser dead-time registered about 0,1%. Thirty-three powdered samples of the same tourmaline of weight between 0,003-0,45 g were irradiated in order to approximate to the "no interference weight" condition. For radionuclides that showed an inadequate sensitivity it was necessary to tolerate higher degrees of interference. Reference certified material (Soil-7) was irradiated simultaneously with the tourmaline to provide reproducibility of results of the analysis and for the quality control. The results of three investigations for five tourmalines was realized and plotted for all radionuclides in order to provide reproducibility of method and check if the interference effect is lost.

4 RESULTS AND DISCUSSION

Table 1 presents the weight of samples, induced activity and specific activity for ⁶⁵Zn and ⁵¹Cr detected in the a tourmaline sample.

Table 1 - INAA experimental and acquisition parameters Weight activated (g); Induced activity (counts/s); Specific activity (counts/s/g)

Isotope	⁶⁵ Zn, E _γ = 1115 keV		⁵¹ Cr, E _γ = 320 keV	
	Weight activated	Induced activity	Specific activity	Specific activity
0,003	0,44	130,40	0,03	8,68
0,005	0,63	131,94	0,04	8,62
0,007	0,83	123,16	0,06	8,73
0,007	1,16	172,58	0,05	8,12
0,009	1,14	132,19	0,08	8,77
0,009	1,18	129,68	0,08	8,95
0,011	1,42	133,89	0,09	8,31
0,011	1,39	126,23	0,08	7,59
0,015	1,93	128,68	0,11	7,43
0,017	2,09	125,84	0,14	8,25
0,018	2,15	121,26	0,14	7,75
0,019	2,32	125,26	0,15	8,20
0,021	2,63	127,69	0,17	8,08
0,027	3,30	120,94	0,20	7,26
0,032	3,78	118,78	0,24	7,45
0,054	5,73	105,46	0,39	7,15
0,058	6,10	105,18	0,41	7,00
0,079	7,81	98,44	0,55	6,91
0,086	8,41	97,42	0,59	6,88
0,100	9,45	94,54	0,69	6,88
0,132	12,01	90,77	0,91	6,86
0,170	15,38	90,35	1,12	6,59
0,184	16,32	88,84	1,26	6,84
0,217	19,51	89,79	1,41	6,51
0,219	19,82	90,37	1,48	6,76
0,261	23,14	88,72	1,73	6,64
0,281	24,82	88,38	1,80	6,40
0,300	26,79	89,29	2,00	6,67
0,333	29,54	88,81	2,19	6,59
0,356	31,39	88,18	2,33	6,56
0,360	32,24	89,57	2,29	6,35
0,400	35,05	87,63	2,63	6,57
0,450	39,55	87,88	2,90	6,44

The graphs of specific activity against sample weight for some radionuclides are shown in Figure 1 and 2, where it is possible to observe the deviation from the straight line around 0,1g. In tourmaline samples weighing around 0,1g the interference effect does not occur, or occurs to a lesser extent.

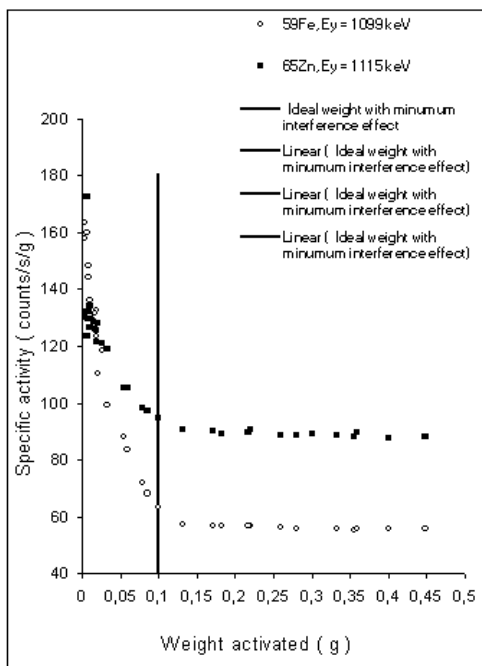


Figure 1 - Variation of induced specific activity with weight of tourmaline

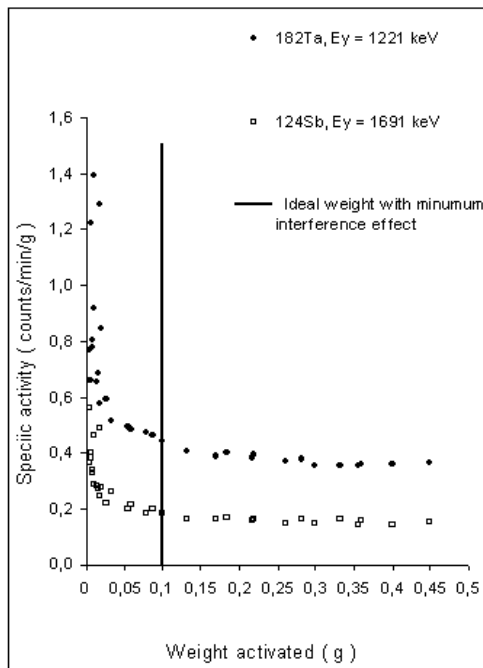


Figure 2. Variation of induced specific activity with weight of tourmaline

All radionuclides showed good agreement in the deviation from the straight line. Small systematic discrepancy was noted for ^{134}Cs , ^{182}Ta , ^{124}Sb , ^{46}Sc , due to their low concentration.

The isotopes investigated were: ^{187}W , ^{140}La , ^{199}Au , ^{72}Ga , ^{76}As , ^{42}K , ^{131}Ba , ^{75}Se , ^{203}Hg , ^{82}Br , ^{85}Sr , ^{51}Cr , ^{124}Sb , ^{134}Cs , ^{46}Sc , ^{86}Rb , ^{59}Fe , ^{60}Co , ^{182}Ta , ^{233}Pa , ^{65}Zn , $^{110\text{m}}\text{Ag}$, ^{152}Eu , ^{160}Tb , ^{175}Hf , $^{177\text{m}}\text{Lu}$, $^{24\text{m}}\text{Na}$. In the tourmaline samples, the radionuclides ^{65}Zn , ^{59}Fe , ^{60}Co , ^{51}Cr , ^{46}Sc , ^{82}Br , ^{140}La , $^{24\text{m}}\text{Na}$, ^{42}K , ^{85}Sr , ^{182}Ta , ^{134}Cs , ^{124}Sb were detected.

5 CONCLUSION

INAA has been used traditionally to determine trace element in mineral samples. Among the trace element analysis techniques, there are many advantages associated with the use of INAA when compared with other analytical methods. When interference effect of ^{10}B is eliminated, INAA can be used to determined trace element in tourmaline. However, special carefully in irradiation, experimental and acquisition parameters, since sensitivity can be affected by interference effect.

6 ACKNOWLEDGMENT

The authors are indebted to the FAPEMIG – Fundação de Amparo à Pesquisa do Estado de Minas Gerais, Brasil by financial support, in special mineral gems project development in CDTN/CNEN - Centro de Desenvolvimento da Tecnologia Nuclear/Comissão Nacional de Energia Nuclear.

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