

DETERMINATION OF MINOR AND TRACE ELEMENTS IN
CASSITERITE BY NEUTRON ACTIVATION ANALYSIS^{*}

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Mn, Sc, Ta and W present in cassiterite were determined by non-destructive neutron activation analysis using γ -ray spectrometry. Lanthanides, U, As and Sb were determined after radiochemical separation. Experiments with radioactive tracers for checking radiochemical separation yields were carried out. A discussion on the precision, accuracy and sensitivity of the method is also included.

INTRODUCTION

As it has been observed by Bowen¹, neutron activation had not been extensively used for analysis of tin ores. Bowen¹ and Djojosebroto et al.² applied this technique to analyse tin ores from Indonesia, the main source of tin in the world. Bowen¹, by using nondestructive activation analysis determined W and La quantitatively. As, Fe, Gd, Sb, Ta and Tb were only detected qualitatively. Djojosebroto et al.² determined V by non-destructive activation analysis, and Zr, Hf, and Ta after chemical separation.

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Even though these authors^{1,2} applied both, non-destructive and destructive techniques, some elements present in cassiterite at trace level were not quantitatively analysed.

This paper presents a radiochemical separation method based on the works of Maenhaut et al.^{3,4} for the analysis of metallic tin. The main difference in the analytical procedure carried out here is the sample dissolution, because tin is easily dissolved in acids, but cassiterite needs fusion.

The scope of this paper was to develop an analytical method for the determination of minor and trace elements in cassiterite, and that would allow geochemical comparison among samples from different sources.

EXPERIMENTAL

Sample preparation

The white particles (quartz) of the ore samples were handpicked. After sample homogenization about 10 g was washed with 4M HCl solution, deionised water and then dried at 110°C. The dried samples were ground in an agate mortar and wrapped in an aluminium foil for irradiation.

Apparatus and reagents

The counting equipment used for γ -ray spectrometry was:

- 1) TMC Model 406-2, 400-channel analyzer coupled to a well-type 3" x 3" NaI(Tl) scintillation detector.
- 2) Hewlett-Packard 4096-channel analyzer coupled to a coaxial 27.8 cm³ Ge-Li detector, ORTEC, Model 8001-0521. The energy resolution of the system was 3 keV fwhm for the 1332 keV ⁶⁰Co line.

A distillation apparatus like that described by Maenhaut et al.³ was used for the separation of As, Sb and Sn.

Preparation of stock and standard solutions

Stock solutions with 10 mg/ml of elements to be analysed were prepared by dissolution of the elements or their oxides in suitable reagents. Alternatively, when it was possible, the solutions were dried and the residues were dissolved in deionised water. Standard solutions were prepared by dilution of stock solutions. From these solutions, aliquots were taken in order to prepare standards for irradiation, as well as to be used as tracer solutions.

Qualitative analyses

Irradiations (about 100 mg of sample) were carried out at a thermal neutron flux of $3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ for 15 seconds to one minute periods. Activities of the short-lived ^{52}V , $^{94\text{m}}\text{Nb}$ and ^{51}Ti were not detected. Irradiations of 30 minutes and a decay period of about 3 hours allowed the 846 keV ^{56}Mn photopeak identification in the γ -spectrum. After 15-20 hours decay, identification of ^{182}Ta , ^{187}W , ^{46}Sc and ^{140}La (in 2 samples) was possible. ^{76}As and ^{122}Sb activities were detected after radiochemical separations were carried out in samples irradiated for 8 hours. The non-volatile elements were identified in the bromides' distillation residue. The complexity of the ^{182}Ta spectrum would make detection of the lanthanide radioisotopes, ^{239}Np and ^{233}Pa rather difficult. However, after precipitation of the lanthanides as fluorides, the detection of ^{153}Sm , ^{141}Ce , ^{143}Ce , ^{169}Yb , ^{140}La , ^{239}Np and ^{233}Pa was made possible.

Procedure1) Non-destructive activation analysis

Standards of Mn, Ta, W, Sc, La, and 100 mg ore sample were irradiated for 30 minutes with a thermal neutron flux of $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. After 2-3 hours decay period (determination of Mn) and 15-20 hours decay periods the γ -ray spectrum was recorded using the Ge-Li detector. Results are shown in Table 1.

TABLE 1
Results for non-destructive activation analyses

Sample	Mn (%)	Ta (%)	W (%)	Sc (ppm)	La (ppm)
I	0.018 ± 0.001	0.28 ± 0.01	0.058 ± 0.003	128 ± 5	91 ± 9
II	0.105 ± 0.007	0.16 ± 0.01	0.34 ± 0.01	217 ± 4	35 ± 3
III	0.82 ± 0.002	0.70 ± 0.01	0.0062 ± 0.0005	77 ± 8	
IV	0.019 ± 0.005	0.48 ± 0.02	0.0018 ± 0.0001	59 ± 2	

Means and standard deviations for 8 determinations.

2) Activation analysis with chemical separation

About 100 mg of tin ore were sealed in a polyethylene envelope and activated for 8 hours. Standards of each element to be analysed were also placed in a heat-sealed polyethylene envelope and were activated simultaneously with the sample in a flux of $3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$.

The irradiated sample, after a 20 hours cooling period, was transferred into an iron crucible containing 2 g of Na_2O_2 and 1 mg carrier of the elements Sb, As and La (as oxides). The mixture was melted, cooled and leached with water and transferred to a distillation flask. The crucible was washed with 1M H_2SO_4 and the solution was also transferred into the distillation flask.

Distillation was carried out as described by Maenhaut et al.³. Two traps were connected in series with the apparatus, the first one with 25 ml of concentrated HCl and the second containing 25 ml of 6M HCl solution.

Distillate analysis

After adding 20 mg carrier of As and Sb to the solution, As was precipitated as As_2S_3 using thioacetamide. Sb was separated from Sn in the As_2S_3 filtrate, by reduction with iron, as described by Maenhaut et al.³. Arsenic activity in the precipitate was compared with the activity of the standard. Reduced Sb and iron were dissolved in 6M HCl solution. Sb standard was also dissolved in an equal volume of 6M HCl solution. The activities of both sample and standard were determined and compared.

Analysis of distillation residue

Before removing the residue from the distillation flask, 10 mg of hydroxylamine and 20 ml of water were added. The mixture was heated and, after dissolution, it was transferred to a teflon beaker. Lanthanide fluorides were precipitated by adding HF and NH_4OH until pH = 5. In this way, co-

precipitation of Sc as fluoride was prevented. After standing overnight, the precipitate was filtered and the gamma spectrum was recorded with a Ge-L detector.

Determination of chemical separation yields

The procedure was tested with inactive ore samples and radioactive tracers. To the iron crucible containing the ore sample and Na_2O_2 , radioactive tracers of each element analysed were added; $^{152-154}\text{Eu}$ was used

TABLE 2
Chemical yields of the elements

Element	Yields
As	95.1 ± 2.2
Sb	86.0 ± 3.2
Lanthanides	96.7 ± 1.7
Uranium (^{239}Np)	91.7 ± 2.6

Means and standard deviations for 8 determinations

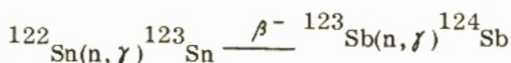
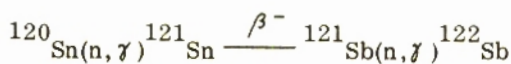
TABLE 3
Analysis of artificial sample

Elements	Added (ug)	Found (ug)
As	0.17	0.16
Sb	5.0×10^{-3}	5.1×10^{-3}
La	8.60	8.43
Ce	45.2	47.3
Yb	2.1	2.1
Sm	1.8	1.7
U	0.04	0.04

as tracer for the lanthanides. The yields of chemical separation were computed by comparing the added and recovered activities. Table 2 shows the separation yields. In order to verify the accuracy that may be expected with the correction introduced by means of separation yields, an artificial sample was prepared and analysed. Added and found values are shown in Table 3.

Interferences

The following nuclear reaction must be taken into account when Sb is determined in tin ores by neutron activation analysis:



Corrections were made to the ^{122}Sb activity by using the values obtained by Op de Beeck⁵, since irradiation time, thermal neutron flux and thermal to epithermal neutrons ratio, in the present work, were the same ones as used by Op de Beeck⁵. Results for the elements analysed with chemical separation are shown in Table 4.

DISCUSSION

The main difficulty of cassiterite analyses, in this work, came from the high Ta content. The complexity of the ^{182}Ta γ -spectrum hindered the detection of elements probably present in cassiterite samples, like Fe, for instance. ^{182}Ta also restricted the possibilities of non-destructive analysis, since only Mn, W, Sc and La (samples I and II), besides Ta, could be determined with a good precision (Table 1).

Chemical separation yields, determined with radioactive tracers, showed a good precision, as may be seen from Table 2. However, determination of thorium was not possible by using the chemical separation scheme present-

TABLE 4
Results of analysis with chemical separations

Sample	As (ppm)	Sb (ppb)	Sm (ppm)	Ce (ppm)	Yb (ppm)	La (ppm)	U (ppm)
I	2.7 ± 0.6	4.5 ± 1.4	37 ± 13	223 ± 13	11 ± 1	90 ± 11	0.22 ± 0.05
II	184 ± 33	13.7 ± 0.8	9.0 ± 0.5	83 ± 12	26 ± 3	31 ± 2	0.58 ± 0.05
III	2.7 ± 0.4	3.0 ± 0.6	0.92 ± 0.08	18 ± 3	2.0 ± 0.2	4.4 ± 0.3	0.20 ± 0.03
IV	0.7 ± 0.3	2.9 ± 0.6	0.18 ± 0.06	3 ± 1	1.2 ± 0.2	1.3 ± 0.3	0.04 ± 0.01

Means and standard deviations for 8 determinations.

ed in this paper, because ^{233}Pa is only partially coprecipitated with lanthanide fluorides and the results showed a poor precision. Artificial sample analysis (Table 3) pointed out the accuracy of results for the elements determined with chemical separation. Good precision and accuracy were also shown by the values obtained for La in samples I and II, since there is a good agreement between results from analyses without chemical separation (Table 1) and with chemical separation (Table 4).

Determination limits, calculated by Currie's criterion⁶, depended on sample composition when non-destructive analysis was used. In the case of separated fluoride group, determination limits depended also on the group composition as well as on the proportions of the various lanthanides

TABLE 5

Determination limits in cassiterite samples

Element	Determination limit (ppm)
Mn	0.1 — 6.0
Ta	16 — 21
W	0.1 — 1.4
Sc	0.4 — 0.7
As	0.001
Sb	0.001
Sm	0.03 — 0.30
Ce	0.6 — 10
Yb	1 — 4
La	0.1 — 20
U	0.01 — 0.08

Cooling times at which elements were determined: 3h (Mn); 20h (Ta, W, Sc); 48h (As, Sb); 70h (Sm, Ce, Yb, La, U)

Counting time: 4 min (Mn); 50 min (Ta, W, Sc, Sm, Ce, Yb, La, U); 100 min (As, Sb)

that were present. The detection limits found for a 100 mg sample are presented in Table 5, where the minimum and maximum values, when there was not individual separation, are shown.

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