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APPLICATION OF EPITHERMAL NEUTRON ACTIVATION ANALYSIS FOR THE DETERMINATION OF INDIUM AND CADMIUM IN BLENDES, INTERFERENCE OF MANGANESE

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Received 24 October 1973
Accepted 31 October 1973

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RADIOCHEM.RADIOANAL.LETTERS 15/6/ 379-385 /1973/

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The advantage of using epithermal irradiation for the determination of indium and cadmium, when large manganese contents are present is discussed. Application to instrumental analysis of blendes is shown. Results for manganese, indium and cadmium in twenty samples are included.

INTRODUCTION

The epithermal neutron analysis of elements with important resonances in this region of the spectrum has been applied successfully in several cases. With this method it is possible to carry out the instrumental determination of some elements in presence of others which have large interfering effects mainly in the thermal zone. Brune and Jirlow[1] have expressed the feasibility of using epithermal activation with an "advantage factor" defined as $/RCd/_d/ \ /RCd/_D$, where RCd is the cadmium ratio, d is the interfering element and D is the element to determine. The expression of RCd is:

$$RCd = 1 + \frac{\phi th \ \sigma th}{\phi epi \ I}$$

$\phi th = nv_o$ is the thermal flux, ϕepi is the parameter which defines the flux in the epithermal region, I is the resonance integral above the cadmium cut-off energy ECd, including the $^1/v$ contribution, and σth is defined with the formula

$$\sigma th = g\sigma o + \frac{\phi epi}{\phi th} \int_{\mu kT}^{ECd} \sigma/E/ \frac{dE}{E}$$

where g corrects the departure of the cross section from the $^1/v$ law in the thermal zone, σ_o is the 2.200 m/s cross section and μkT is the equivalent cut-off of the 1/E spectrum.

The ratio $\phi th/\phi epi$ can be calculated from the cadmium ratio of a well-characterised standard /indium or gold, for instance/. The calculation of approximate values of σth is possible with the assumption that cross sections are 1/v below the cadmium cut-off, so g = 1 and

$$\int_{\mu kT}^{ECd} \sigma/E/ \frac{dE}{E} = \sigma_o \int_{\mu kT}^{ECd} \frac{E_o^{1/2}}{E^{3/2}} dE$$

which can be easily solved. A value of 0,56 σ_o was found for this integral in our experimental conditions.

Under the precedent considerations it is feasible to find cadmium ratios and therefore the advantage factor for any element in the presence of any interference, if cross sections and resonance integrals are known.

APPLICATION TO THE CASE OF BLENDES

As part of a general study on blendes /ZnS minerals/, analyses were made of manganese, indium and cadmium in samples from several parts of the Argentine Republic.

Different possibilities are open for these elements through analysis by γ spectrometry. The simplest case is that of manganese, where ^{56}Mn is the only alternative. The high thermal cross section and the generally large concentrations in which it is present in these blendes make its determination quite simple. For indium and cadmium analyses the situation is more difficult. When 1-2 hours or 3-4 days irradiations were made with measurements 1 and 15 days respectively after the end of irradiation, which were necessary for the determination of other elements in the same matrix, interferences of other nuclides were found. These interferences can be avoided irradiating the samples during short periods, so that long-lived nuclides are minimized. ^{111m}Cd and ^{116m1}In are then the most favourable nuclides for the determination, because of their half-lives

TABLE 1

Nuclide	σth/I	Cadmium ratio	Advantage factor*
^{116m1}In	0.065	4.56	11.8
^{111m}Cd	0.050	3.73**	14.4
^{56}Mn	0.964	53.74	

*Referring to ^{56}Mn as interference
**Data obtained considering ^{110}Cd/n,γ/^{111m}Cd as the only re-

of 48,6 min. and 54 min. respectively. In this case however ^{56}Mn interferes when a predominantly thermal flux is used. The convenience of using epithermal activation can be seen when the advantage factors are calculated. Data are given in the Table 1. $^{111}Cd/n,n'/^{111m}Cd$ can also be produced with fast neutrons, but this reaction is not included in the calculation due to the lack of data about the fast flux. Approximate values for this show that it is small related to the thermal flux, so that the error in the value for the advantage factor is not high.

EXPERIMENTAL

Irradiations were performed in one of the pneumatic tubes of the RA-3 reactor /thermal flux: $1{,}7 \times 10^{13}$ n cm^{-2} sec^{-1}; $\phi th/\phi epi = 54{,}7$/. Samples were ground in an agate mortar, weighed in polyethylene vials and irradiated. Mixed flux was used to find the manganese contents of the samples, and also to provide preliminary information about concentrations of indium and cadmium. The former could be calculated only in half of the cases, and it was impossible to obtain any information on the latter. Irradiations under cadmium cover were performed for the determination of these two elements, with different irradiation and counting times, depending on data obtained during the first assays. After irradiation the vials were washed with 50 % NO_3H, then with distilled water and finaly dried. This treatment was made with the purpose of assuring complete removal of possible cadmium contamination from the cover.

A Ge/Li/ detector of 27 cm^3 and resolution of 3.2 keV cou - pled to a multichannel analyzer Packard model 46, of 4096 channels, was used for the measurements.

TABLE 2

Nuclide	Half-life /min/	Energy measured /keV/	Flux type	Irradiation time /min/	Counting time /min/
$^{116m_1}In$	54	1097.1*	epithermal	1-2	60-120
^{111m}Cd	48.6	245.4	epithermal	1-2	60-120
^{56}Mn	154.6	846.7	mixed	0,5	30

* The $^{116m_1}In$ 1293.4 keV peak, which is the most intense, could not be used for the determination of this element, because of the interference of the 1293.8 keV peak of ^{41}Ar, which appeared as background of the measurement room and from activation of the air enclosed in the capsules

The characteristics of the nuclides, times of irradiation and measurement and the selected γ energy peaks for calculation are shown in Table 2.

Results were obtained by means of a program prepared for use in a table computer[2]. The parts of this program are: smoothing of the raw data, evaluation of the peak area with Wasson's method, correction for decay during the time of measurement and the interval between measurement of sample and standard, and then calculation of the concentration.

RESULTS AND DISCUSSION

Data about concentration of indium, cadmium and manganese in twenty samples of blendes were obtained /Table 3/.

The results show that epithermal neutron irradiation improves significantly the possibilities of determining indium and cadmium in these samples.

TABLE 3

Sample No	Procedence	In /ppm/	Cd /%/	Mn /%/
1	Jujuy	0.51 ± 0.03	0.33 ± 0.01	0.116 ± 0.004
2	San Juan	5.5 ± 0.1	0.33 ± 0.02	0.305 ± 0.008
3	San Juan	16.4 ± 0.3	0.31 ± 0.02	0.121 ± 0.003
4	Chubut	188 ± 3	0.38 ± 0.03	0.114 ± 0.002
5	Catamarca	0.42 ± 0.07	0.32 ± 0.02	0.532 ± 0.009
6	Córdoba	220 ± 2	0.30 ± 0.05	0.009 ± 0.001
7	San Juan	4.5 ± 0.1	0.13 ± 0.01	1.77 ± 0.03
8	San Juan	21.7 ± 0.4	0.13 ± 0.01	0.065 ± 0.001
9	Jujuy	2.5 ± 0.1	0.159 ± 0.009	1.80 ± 0.05
10	Jujuy	0.14 ± 0.06	0.13 ± 0.01	1.51 ± 0.04
11	San Luis	33.9 ± 0.7	0.22 ± 0.01	0.57 ± 0.01
12	Neuquén	0.88 ± 0.08	0.38 ± 0.01	0.0097 ± 0.0004
13	Mendoza	154 ± 3	0.31 ± 0.04	0.358 ± 0.009
14	San Juan	0.26 ± 0.02	0.154 ± 0.002	0.067 ± 0.002
15	Rio Negro	0.15 ± 0.07	0.30 ± 0.01	0.283 ± 0.007
16	La Rioja	5.0 ± 0.1	0.43 ± 0.03	0.49 ± 0.01
17	Chubut	4.19 ± 0.07	0.429 ± 0.009	0.0346 ± 0.0006
18	La Rioja	0.08 ± 0.02	0.344 ± 0.005	0.00113 ± 0.00007
19	Mendoza	11.5 ± 0.2	0.20 ± 0.01	0.241 ± 0.003
20	Catamarca	136.3 ± 1.3	0.27 ± 0.03	0.0080 ± 0.0005

Small concentrations of indium /tenths of parts per million/ can be determined in the presence of relatively large quantities of manganese. On the other hand cadmium can be determined by instrumental analysis only when it is present in high concentrations, because of the low sensitivity of the method.

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