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DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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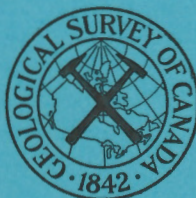
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NEUTRON ACTIVATION ANALYSIS OF SILICATE ROCKS

1. Preliminary Report on Cadmium Determination in Keno Hill Samples

BY

R. A. WASHINGTON



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I. Introduction

Neutron activation analysis has been used to determine various trace elements in rocks and minerals. Vincent et al. (1, 2) have reported the analysis of rocks of the Skaergaard intrusion for Au and Cd, and the analysis of stone meteorites for Au. Schroeder and Winchester (3) have determined the Na content of silicate minerals and rocks. Huizenga et al. (5, 6) have analysed stone meteorites for Bi, Tl, Hg, Sc, Cr, and Eu. Smales et. al. (7, 8) have determined Ta, W, V, and Sc in rocks and meteorites, and Morris and Killick (9) have determined Ag, and Tl in rocks.

Charged particles have also been used in activation analysis, but not so widely. Sipple and Glover (4) employed this technique to determine light elements in sedimentary rocks.

The present study has been undertaken in order to determine the cadmium content of a number of rock samples collected by Dr. R.W. Boyle in the Keno Hill area of Yukon Territory. The samples have been analysed spectrographically for Cd, and were found to be below the detection limit, which varies from 2 to 5 ppm. depending on the sample (10).

Preliminary calculations of the sensitivity limit of the activation method were based chiefly on data published by Koch (12) and Meinke (13).

Assuming a minimum detectable disintegration rate of 2 sec.^{-1} using the available counting equipment, a neutron flux of $5 \times 10^{12} \text{ cm.}^{-2}\text{-sec.}^{-1}$, and an irradiation time of 100 hours, the detectable concentration of Cd in a 100 mg. sample was found to be ca. 0.01 ppm. The sensitivity could be increased by using a higher flux, or a larger sample, but this was considered unnecessary.

II. Procedure

The experimental procedure adopted in the preliminary experiments was as follows:

Portions of 100 mg. of the samples (as received) were accurately weighed into Vycor vials and sealed. Standards containing 1.0 μ of Cd as the chloride in aqueous solution were sealed into similar vials. Six samples and one standard were irradiated under the predetermined conditions (see above) in the NRX reactor at Chalk River. Irradiated samples were received in the laboratory about 30 hours after removal from the reactor, and chemical treatment was started at once.

Each vial was opened and the contents transferred to a Pt crucible. The sample was attacked by $\text{HF-H}_2\text{SO}_4\text{-HNO}_3$ in the presence of 10 mg. Cd carrier and 1 mg. each of Cu, Mn, Mg, Na, and K as holdback carriers. The mixture was evaporated to fumes of SO_3 to destroy fluorides and remove Si. The treatment was repeated, and the residue digested with a little 6M HCl to dissolve all soluble material. The insoluble residue (chiefly CaSO_4 , together with a little C and resistant minerals such as zircon and rutile) was centrifuged off. (It has been assumed that the Cd remaining in

this residue is negligible. This point must be confirmed by later tests.) Cd was precipitated with brucine and KBr, (11) and the precipitate dissolved in a mixture of 70% HClO_4 and 18M. H_2SO_4 (3:17), with heating and addition of small amounts of 15M. HNO_3 to complete solution. Contaminating activities were scavenged out by precipitating iron, manganese and magnesium hydroxides, using an excess of NH_4OH to keep Cd in solution. (The hydroxide precipitate carries In, which would otherwise follow the Cd closely.) The solution containing Cd was acidified slightly, KCN added, and CdS was precipitated using tank H_2S . The CdS was dissolved in the minimum amount of 6M. HCl , and boiled to expel H_2S . This solution can be recycled if desired for radiochemical purity. Two or three cycles were considered sufficient.

The final solution of Cd was evaporated to dryness to remove excess acid, the residue dissolved in H_2O , and diluted to a known volume. Aliquots were taken for counting and chemical yield determination.

Chemical yield was determined by addition to the aliquot of 10 ml. of buffer (pH 10), 5.00 ml. 0.01M. disodium EDTA (for an aliquot of 0.2) and a little eriochrome black T indicator. (If sufficient EDTA has been added, the colour will be blue. If the colour is reddish-purple, more EDTA must be added.) The excess EDTA was back-titrated using 0.01M. MgSO_4 solution to a distinctly reddish-purple end-point. The observed chemical yield varied from 60 to 90%.

Samples were counted on Cu planchets in a thin end-window gas flow proportional counter.

Standards were treated in the same way, except that the initial attack was, of course, omitted. Carrier Cd and holdback carriers were added, the brucinate precipitated, an iron hydroxide scavenge was made and the sulphide precipitated. The final sample was recycled if necessary.

III. Results and Discussion

Preliminary trial runs have been carried out, using this procedure, on four of the samples and on the standard rocks G1 and W-1. The samples used were a graphitic schist, a calcareous quartzite, an aplite, and a granite. If it is assumed that the Cd values given by Bilefield and Vincent (14) are correct for G-1 and W-1, the observed values are:

Graphitic Schist	0.88 ppm
Quartzite	0.35 ppm
Aplite	1.2 ppm
Granite	0.80 ppm

The estimated error in these results is less than 25% in each case.

The results cannot be regarded as conclusive for several reasons. First, it will be necessary to check the published values for G-1 and W-1 using prepared standards. Second, additional checks are necessary on the irradiation procedure and on the mounting and counting technique, and on other details of the procedure. In addition, some modifications to the procedure are required in order to approach the theoretical sensitivity of 0.01 ppm.

Suggested improvements in the technique include:

1. Decreasing the elapsed time from the end of irradiation to receipt of the sample in the laboratory, in order to increase the amount of activity available.
2. Modification of the chemical yield determination in order to permit the use of a larger aliquot for counting.
3. Possible additional steps in the chemical separation to improve the radiochemical purity. The presence of some contamination is suspected using the present technique, but the total amount of activity observed is so slight (a few tens of counts per minute above background) that accurate half-lives are difficult to obtain, and observation of the gamma-ray spectrum cannot be accomplished with the available equipment. Positive identification of the impurity and estimation of its amount are therefore impossible, and a trial-and-error process will probably be necessary to achieve greater radiochemical purity.

IV. Summary

Preliminary results have shown that the activation method is capable of greater sensitivity than the spectrographic method in determining Cd in silicate rocks. The experimental sensitivity limit for the technique used is estimated to be 0.1 - 0.2 ppm, but the suggested improvements are expected to reduce this by about an order of magnitude. Greater accuracy will probably also be achieved in the final results.

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