The Re-activation Analysis of Aluminum—The Activation Analysis of Aluminum with Special Reference to Yield Determination

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In an activation analysis using short-lived nuclides with radiochemical separation, the chemical yield has been determined by, for instance, the gravimetry, volumetry, photometry, polarography and tracer method. The yield determination by these methods requires a long period of time, however; therefore, these methods cannot be used in rapid determination. A method in which the chemical yield is determined by re-irradiating the counted sample and which can be completed in a short time is suitable for rapid determination.

On the other hand, it is not desirable, from the standpoint of the precise determination of the chemical yield, that other methods, such as the gravimetry, volumetry, photometry and polarography, be applied to the yield determination of elements being analyzed after their activity has been counted.

When the correction factor of chemical yield is previously determined by a radioisotope tracer under the same conditions as the practical and is used for the correction of chemical yield in each separation, there is the disadvantage that an error is produced by the difference between the chemical yields obtained in the individual separations.

The present authors have devised an activation analysis in which the chemical yield is easily corrected by the re-activation of the counted sample; they have designated this method "re-activation analysis".[1]

After the addition of a carrier to the irradiated sample solution, the element to be determined is isolated in a radiochemically pure form by solvent extraction, transferred into a polyethylene tube, and its γ-ray spectrum measured. It is then allowed to decay to a negligible activity level and sealed again in a polyethylene tube. This sample is re-activated with neutrons and counted. The element is determined by the induced activity from the first irradiation, which is corrected for the chemical yield calculated from the induced activity from the second irradiation. In other words, the technique of non-destructive activation analysis is applied to determine the yield of radiochemical separation in normal destructive activation analysis. This method has the advantage of determining the chemical yield without loss of the counted sample.

This method has been satisfactorily applied to the determination of aluminum.

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[1] Y. Kamemoto and S. Yamagishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 291 (1963).

Theoretical

This re-activation technique consists of these steps: the first irradiation of a sample, the addition of a carrier, radiochemical separation, the counting of the induced activity from the first irradiation, the sealing of the counted sample in a polyethylene tube, cooling, a second irradiation, and the counting of the induced activity from the second irradiation. For rapid radiochemical separation, a solvent extraction method was adopted. In this method the carrier to be added is sometimes limited to a rather small amount. Therefore, the amount of the element to be determined cannot be disregarded in the calculation of the chemical yield. From these considerations, an equation for determining the element in the sample from the induced activities from the first and the second irradiation was derived as follows:

$$\text{Chemical yield} = \frac{W_c'}{W_c + W} \tag{1}$$

where

W: weight of the aluminum in the sample (g.),
W_c: weight of the aluminum carrier added to the first irradiated sample (g.),
W_c': weight of the aluminum isolated from the sample after the addition of the carrier (g.).

When the chemical yield is 100%, the induced activity, A, from the first irradiation is:

$$A = A_{\text{sam}} \times \frac{W_c + W}{W_c'} \tag{2}$$

where A_{sam} is activity of the ^{28}Al isolated from the first irradiated sample.

The specific activity in the first irradiation is the same in unknown and the standard samples.

Therefore,

$$A/W = A_{\text{st}}/W_{\text{st}} \tag{3}$$

where

A_{st}: the induced activity of the standard aluminum from the first irradiation,
W_{st}: the amount of the standard aluminum for the first irradiation.

From Eqs. 2 and 3,

$$W = \frac{A_{\text{sam}} \times W_c \times W_{\text{st}}}{A_{\text{st}} \times W_c' - A_{\text{sam}} \times W_{\text{st}}} \tag{4}$$

The specific activity in the second irradiation is also the same in the unknown and the standard samples.

Therfore,

$$A_{\text{sam}}'/W_c' = A_{\text{st}}'/W_{\text{st}}' \tag{5}$$

where

A_{sam}': the induced activity of the ^{28}Al isolated from the second irradiation,
A_{st}': the induced activity of the ^{28}Al of the standard aluminum from the second irradiation,
W_{st}': the amount of standard aluminum for the second irradiation.

From Eqs. 4 and 5,

$$W = \frac{A_{\text{sam}} \times W_c \times W_{\text{st}}}{(A_{\text{st}} \times A_{\text{sam}}' \times W_{\text{st}}'/A_{\text{st}}') - A_{\text{sam}} \times W_{\text{st}}} \tag{6}$$

Experimental

Standard Sample.—4.7 mg. of a spectrographically pure aluminum rod made by Johnson Matthey Co., Ltd., was dissolved in 1 ml. of sulfuric acid. After evaporation, the residue was dissolved in water and diluted to 50 ml. This solution was further diluted to give several solutions of different aluminum concentration. Each 1 ml. of the standard solution was sealed in a polyethylene tube and placed in the center of a capsule packed with soft paper.

Sample. — Samples containing different amounts of aluminum, manganese, sodium and magnesium were prepared in the same way as the aluminum standard.

Apparatus. — The JRR-1 reactor was used as a neutron source, while the RCL-256 channel pulse-height analyzer with a 1.75×2 inch NaI (Tl) crystal (well type) attached was used as a counter.

Neutron Irradiation.—All irradiations were made in the No. 16 experimental hole (pneumatic tube) at a neutron flux of about 3×10^{11} n/cm^2/sec. The first irradiation was continued for 3 min., and the second irradiation, for 10 sec.

Procedure. — This method consists of the first irradiation, the addition of the carrier, solvent extraction, counting, the second irradiation, cooling, and counting. The above procedure was repeated for each sample with the reactor always in the same stationary state.

The sample solution irradiated in the reactor for 3 min. was transferred into a separating funnel. An aluminum carrier solution (94.0 μg. Al) was added to this solution. After the further addition of 50 ml. of an oxine solution containing 30 mg. of oxine, 1.5 ml. of an acetic acid solution and 2.5 g. of sodium acetate, aluminum was extracted with 5 ml. of benzene.[2-4] The organic phase was transferred into a polyethylene tube, which was then mounted in the NaI (Tl) crystal 5 min. after the end of the irradiation; it was counted for 2 min., and the resultant γ-ray spectrum was measured. The polyethylene tube containing the benzene phase was sealed again and was kept sufficiently long to allow the aluminum-28 activity decay. It was then irradiated again for 10 sec. and cooled for 2 min., and the γ-ray spectrum was measured for one minute.

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[2] E. Sudo, ibid., 72, 718 (1951).
[3] H. Nishida, *Japan Analyst* (*Bunseki Kagaku*), 4, 39 (1955).
[4] S. Yokosuka, ibid., 5, 71 (1956).

In the first irradiation, the standard sample was irradiated for 3 min. and measured for the γ-ray spectra 5 min. after irradiation in the same manner as for the unknown sample. In the second irradiation, the standard sample was irradiated for 10 sec., cooled for 2 min., and counted for one minute.

In each of the resultant gamma spectra, the height of the photopeak due to the 1.78 MeV. γ-ray from the ^{28}Al was measured.

Results and Discussion

γ-Ray Spectrum.—An example of the γ-ray spectrum of ^{28}Al, which was measured after irradiation and extraction, is shown in Fig. 1.

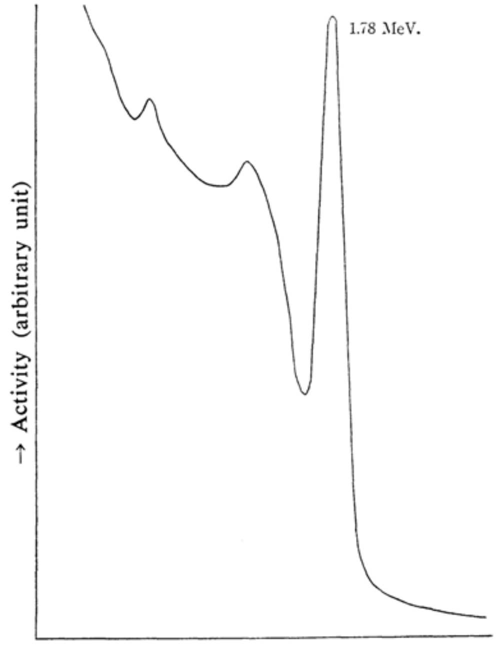

Fig. 1. γ-Ray spectrum of ^{28}Al of sample No. 10.

Calibration Curve. — The calibration curves of aluminum for the first and the second irradiation are shown in Figs. 2 and 3 respectively.

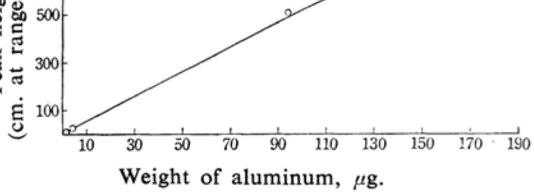

Fig. 2. Calibration curve of aluminum for the first irradiation.

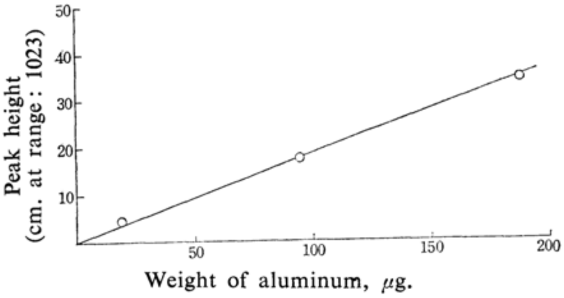

Fig. 3. Calibration curve of aluminum for the second irradiation.

In the concentration ranges of aluminum of 0∼100 and 0∼190 μg. for the first and the second irradiation respectively, the relation between activity and concentration was linear. Therefore, in these concentration ranges aluminum could be determined with each standard sample in the first and the second irradiation.

Result.—The determination results of aluminum by this method are shown in Table I.

TABLE I. ANALYTICAL RESULTS BY THIS METHOD

Sample No.	Sample Al added μg.	 Other element added, mg.	Al found μg.
1	3.76	0	3.34
2	3.76	0	3.97
3	3.76	0	3.73
4	3.76	0	3.81
5	3.76	0	3.72
6	1.88	0	1.92
7	0.94	0	0.99
8	3.76	Mn, 1	4.64
9	3.76	Mn, 0.1	4.45
10	3.76	Mg, 1	3.69
11	3.76	Mg, 0.1	3.80
12	3.76	Na, 1	3.78

The coefficient of the variation was 1.22% for the determination of 3.76 μg. of aluminum. This value is the total error produced in this method, including the error due to the neutron flux variation in the reactor.

Interference.—The γ-rays which may be confounded with the γ-ray of aluminum at 1.78 MeV. are that at 1.734 MeV. of ^{90}Y, at 1.81 MeV. of ^{56}Mn, and at 1.853 MeV. of ^{88}Rb. The interefence by ^{56}Mn, ^{24}Na and ^{166}Ho must also be taken into account because of their high activation cross sections and saturation factors.[5]

The present authors also examined the interference by sodium and manganese which

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[5] T. Nakai, S. Yajima, M. Okada, K. Shiba and T. Moki, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **81**, 104 (1960).

was sometimes observed in the non-destructive determination of aluminum.

Since sodium and rubidium were not extracted with an oxine-benzene solution, these elements did not affect the determination of aluminum in the present method. It could be considered that manganese did not affect it either because of its non-extractability with an oxine-benzene solution. However, some interference by manganese was found. This interference may be due to some precipitation of manganese hydroxide at the pH value of the extraction step.

The induced activities of sodium and manganese obstruct the photopeak of aluminum or cause a pile-up phenomena in the γ-ray spectrum when the amount of these elements in the sample material is 25～250 times as much as that of the aluminum. In such cases, the non-destructive determination of aluminum is not practicable. In the proposed method, sodium does not affect the determination of aluminum. Manganese causes an error of about 18% in the determination of aluminum, but a semi-quantitative determination is possible. These results show the advantages of the present method over other non-destructive methods.

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