in the sample, is now subtracted (No. 3). Comparison of Nos. 3 and 6 proves the remainder to be a spectrum of vanadium. The amount of vanadium is determined as above by summing under the photopeak and comparing with the standard.

There are some imperfections in the vanadium spectrum of No. 3, especially in the ranges where the manganese photopeaks had been subtracted. These "shadow peaks" result from slight drifts of the energy scale of the γ-ray spectrometer. While the sum of the channel contents in the photopeak range is reproducible within the counting error, the differential curves may not match exactly.

The total computer time required for correction, normalization, and peeling of the three constituents was of the order of 2 hours The same procedure carried out with a desk calculator would have required the better part of 2 weeks.

Sample 2 of Table I contains sodium, bromine, and silver. The gamma spectrum of the irradiated sample is seen in No. 7 of Figure 2. Sodium is readily identified by its long-lived peaks at 1.37 and 2.7 m.e.v. The sodium content is determined as above by comparison of the peak area of the most energetic peak with the equivalent of the standard sodium spectrum (No. 10). The adjusted sodium spectrum is subtracted and the resulting difference spectum obtained (No. 8).

There is a superposition of peaks in the energy range 0.5 to 0.7 m.e.v., with one component decaying more rapidly than the other. The spectrum taken 26 minutes after the end of the irradiation (No. 8) contains two clearly resolved peaks at 0.54 and 0.64 m.e.v. This spectrum is identified as a bromine spectrum by comparison with No. 11. Comparison of the peak areas in the 26-minute spectrum with the equivalent in the bromine standard yields the value of the bromine content.

Subtraction of the bromine contribution from No. 8 leaves the spectrum of No. 9. The result of this second subtraction is a spectrum of silver (No. 12).

Several additional samples and their analyses are given in Table I.

DISCUSSION OF PEELING PROCEDURE

The examples show the method of peeling the spectra and indicate that there are various approaches in cases of overlaps and interferences. Contribution of a little-activated known matrix can be peeled by approximate estimation of the impurities and subtraction from 100%.

Peeling is generally started by identifying the most energetic and Compton-interference-free peak of the spectrum. Identification is done both by energy and half life. The area of the peak is determined and compared with the equivalent of the standard. The standard spectrum, normalized to the area of the maximum-energy peak of the unknown, is then subtracted, leaving the spectrum of the unknown-minus-one component. The same operation is repeated until only noise remains.

When the most significant peaks of two elements overlap, other peaks are used to estimate the contents.

If a component has only the peak which is suffering interference, the amount of interference is determined by measuring another peak of the interfering element and peeling this element first.

Interference of two elements giving rise to products of great differences in their half lives may be resolved by identifying first the longer-lived activity. Its contribution may be clearly resolved in the spectra taken after the short-lived component has decayed out. This was done in the second example.

Difficulties are encountered in peeling spectra with large bremsstrahlen contributions, as these can vary the shape of a spectrum depending on the size and average atomic weight of the counting sample. In general, one will try not to peel the element giving rise to the bremsstrahlen, but rather determine it last, as was done in the case of silver in the second example.

CONCLUSION

The time schedule of the data collection is arbitrary, but fixed for a given set of standards. A rapid chemical group separation may precede the spectra taking in order to reduce the number of components in the counting sample. The chemical yield of the separation has to be known, however. The method described can thus be used alone or as a time-saving component of a more elaborate analysis scheme employing chemical separations.

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Neutron Activation Method for the Determination of Traces of Cadmium in Aluminum

ENZO RICCI and W. D. MACKINTOSH

Chemistry and Metallurgy Division, Atomic Energy of Canada Ltd., Chalk River, Ontario

▶ **Cadmium in high purity aluminum can be determined in the 1-p.p.b. range by neutron activation analysis. The method was developed specifically for the analysis of aluminum intended for use in reactor cores. Simultaneous irradiations of samples and comparative standards were carried out in the NRX reactor, Chalk River. The induced radioactivity derived from the cadmium impurity was separated from the matrix by ion exchange and purified by precipitation using carriers. The purified radioisotopes of cadmium were then counted to determine the amount of induced radioactivity and the concentration of cadmium in the sample was calculated from the counting results. A sensitivity of 17 p.p.b. was readily obtained. The relative standard deviation was ±9.4%. As the half life of the radioactivity involved is moderately long (53 hours), the analysis need not be made at a reactor site.**

CADMIUM has a high absorption cross section for neutrons, hence its concentration in aluminum which is to be used in reactor cores must be carefully controlled.

Karabash *et al.* (*8*) have determined cadmium spectrographically in alu-

minum with a maximum sensitivity of 10^{-6}%.

Neutron activation can provide a simple and extremely sensitive method for the determination of 1-p.p.b. amounts of cadmium in high purity aluminum. Neutron activation analysis possesses a number of desirable features. No elaborate sample preparation is necessary; interferences from other elements and contamination of the samples are easily avoided. Many papers have described the general technique and its application to chemical analysis (*5, 7, 9, 15*). This journal has provided excellent reviews of activation analysis with comprehensive bibliographies (*10*).

Yakovlev *et al.* (*15*) have reported the detection of cadmium in zone-refined aluminum by neutron activation and Gaittet and Albert (*1*) have determined cadmium as part of a systematic procedure for analyzing impurities in very pure aluminum. This paper describes a rapid, direct, and precise method for determining trace amounts of cadmium in high purity aluminum.

PROCEDURE

Although a number of radiosiotopes are formed by neutron activation of naturally occurring cadmium, 53-hour cadmium-115 and its daughter 4.5-hour indium-115m are dominant when the metal is irradiated for a maximum of 64 hours and subsequently allowed to decay for 24 hours. These isotopes were, therefore, counted as a measure of the natural cadmium present as an impurity, after irradiation and chemical separation of cadmium from the matrix.

Irradiation. Samples and comparative standards were irradiated simultaneously. The samples were rectangular pieces which weighed from 300 to 500 mg. The standards consisted of 1 to 3-μl. aliquots of a solution containing 0.2074 mg. of spectroscopically pure cadmium per milliliter. The aliquots were introduced into thin-walled (0.3 mm.) quartz vials 1 mm. in internal diameter and 2 cm. long, which were then sealed by heating the open end. The volume of the aliquots was determined by weighing. Standards and samples were wrapped in thin aluminum foil and placed side by side in the iron irradiation capsule. They were irradiated in a pneumatic carrier facility located in the lattice of the NRX reactor, Chalk River (*14*). The flux was 6.3×10^{13} neutrons per square centimeter per second, and the times of the irradiations were 16 to 64 hours.

Chemical Separation. After irradiation, the surface of each sample was cleaned by treating with acetone, water, and concentrated HCl, successively, followed by further washes with water. Twenty milligrams of cadmium carrier in solution were added and the sample dissolved in concentrated HCl. A few drops of 30% hydrogen peroxide were added to oxidize other impurities, then the excess was boiled off. The solution was cooled and made 1*M* in HCl. It was passed through a 10 cm. $\times$ 4 mm. column of Dowex 1 – X8, 100-to 200-mesh, in the chloride form. A flow rate of 3 to 5 ml. per minute was achieved by applying slight pressure to the top of the column. When the solution had passed through, 30 ml. of 1*M* HCl were used to elute the remainder of aluminum and some associated impurities (manganese, copper, gallium, iron, molybdenum) (*7*). The cadmium was then eluted with 50 ml. of distilled water.

Zinc and the remainder of the molybdenum were eluted at the same time. To eliminate these, holdback carriers of zinc and molybdenum were added and then cadmium was precipitated with concentrated NaOH. The precipitate of cadmium hydroxide was separated by centrifuging, then washed twice with water. To completely decontaminate the cadmium it was necessary to redissolve the precipitate in a few drops of concentrated HCl and repeat the hydroxide precipitation twice in the presence of holdback carriers. The final cadmium hydroxide precipitate was dissolved in 20 ml. of hot 0.5*M* H_2SO_4, then cooled. The cadmium was precipitated as the sulfide by passing H_2S through the solution. The precipitate was washed, mounted for counting, dried under an infrared lamp, and weighed.

Each quartz vial containing the irradiated standard solution was washed with concentrated HCl and water. It was placed in a beaker and covered with 1 ml. of solution containing the same amount of cadmium carrier as used for the sample. The vial was carefully crushed with a glass rod and, after thorough mixing, the pieces of quartz were removed by filtering and the cadmium precipitated with concentrated NaOH. The precipitate was washed twice with water and then dissolved in 0.5*M* H_2SO_4. The cadmium was reprecipitated as the sulfide with H_2S, washed, mounted, dried, and weighed in the same manner as for the sample.

Counting. The precipitates were allowed to decay for 24 hours before any counting was attempted. The delay allowed the short-lived cadmium isotopes to decay to insignificance and the indium-115m to reach equilibrium with its parent cadmium-115.

Both γ-ray spectrometry and β-counting were used to ascertain the radiochemical purity of the separated nuclides and to determine the amount of radioactivity.

The γ-ray spectrometer consisted of a Chalk River 100-channel pulse-height analyzer, described by Goulding (*2*), with a 3 $\times$ 3 inch NaI (Tl activated) crystal mounted in a closure described by Hawkings and Edwards (*3*). Complete scans from zero to 1.77 m.e.v. were obtained so that the presence of a contaminating radioisotope could be detected. The intensity of the 0.335-m.e.v. photopeak of indium-115m was taken as a measure of the amount of radioactivity derived from the cadmium in the samples and in the standards.

The β-counting was carried out with a continuous flow methane proportional counter.

The weight of cadmium in the sample was then calculated from the following expression:

$$Wa = \frac{Aa}{As} \times \frac{Ys}{Ya} \times Ws$$

where: Wa = weight of cadmium in the sample
Aa = β-counts or γ-ray photopeak area of the radioactivity derived from the sample at any given time
As = β-counts or γ-ray photopeak area of the radioactivity derived from the standard at the same time as the sample
Ys = weight of precipitate separated from the standard
Ya = weight of precipitate separated from the sample
Ws = weight of cadmium in the standard

RESULTS AND DISCUSSION

Table I shows some typical results for the determination of cadmium in high purity aluminum samples which represent material intended for use in a reactor core.

Table I. Cadmium Contents of Samples of Reactor Grade Aluminum Obtained by Neutron Activation Analysis

Sample No.	Cadmium Content (P.P.B.)
1	71
2	65
3	145
4	86
5	17
6	19
7	40
8	19

These results were obtained by γ-counting of the indium-115m photopeak. The relative standard deviation of sample 8 for nine determinations was ± 9.4%. Part of this spread could be due to a nonuniform distribution of the cadmium metal throughout the piece of metal from which the samples were cut.

Sample 5, containing 17 p.p.b. or 8.5×10^{-9} gram of cadmium in a 0.5-gram specimen was the sample with the lowest content of cadmium available to us, but does not necessarily represent the ultimate sensitivity. It has been estimated that 10^{-10} gram or 0.2 p.p.b. of cadmium in a 0.5-gram sample of aluminum, irradiated for 64 hours at a flux of 6.3×10^{13} neutrons per square centimeter per second, would

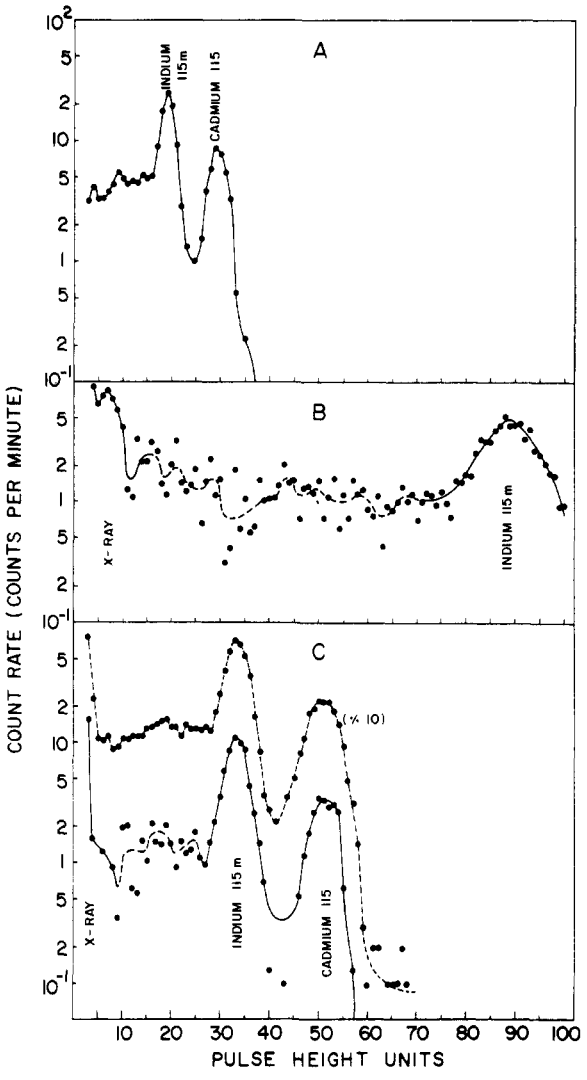

Figure 1. γ-Ray spectra of cadmium, separated from aluminum sample with background subtracted

A. 17.7 k.e.v. per pulse-height unit
B. 3.60 k.e.v. per pulse-height unit
C. 10.1 k.e.v. per pulse-height unit (dotted line, standard)

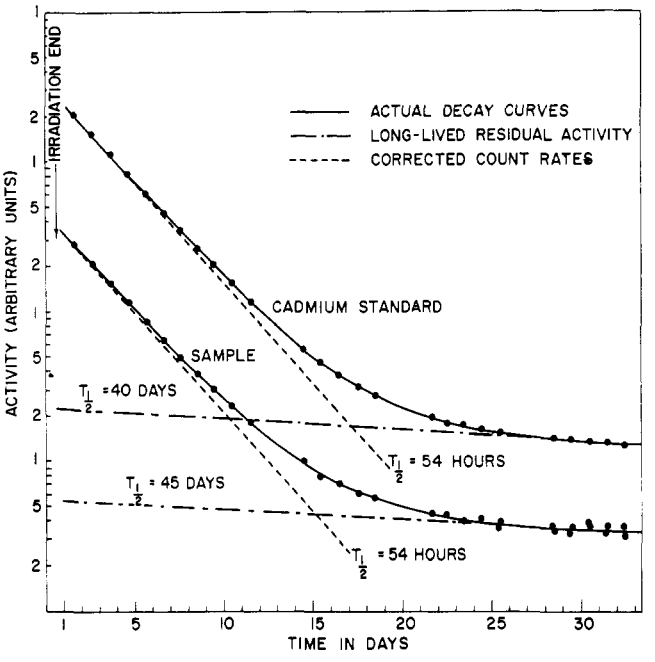

Figure 2. Typical decay curves of sample and standard, obtained by β-counting

yield a suitable photopeak for measurement.

Figure 1 shows several γ-ray spectra of the final precipitate of a specimen of sample 8 which was irradiated for 16 hours. In *A*, no photopeaks other than those due to cadmium-115 and its daughter indium-115m (*4*) are apparent up to an energy of 1.77 m.e.v.; these photopeaks also exhibited the correct half life, indicating that radiochemical purity had been achieved.

Cadmium-115 in equilibrium with indium-115m shows a sharp x-ray photopeak at 24 k.e.v. (*4*); however, at the level of radioactivity obtained in these experiments, this photopeak is not suitable for measurement, as is shown in *B*.

Usually the γ-ray spectrum over the range zero to 1.0 m.e.v. was recorded. Typical curves for sample and standard are shown in *C*. Results were most precise when the area of the indium-115m photopeak was determined rather than that of cadmium-115 (0.523 m.e.v.), possibly because the area of the former was more than twice that of the latter. If elimination of the decay period between separation and counting were desirable, the area of the cadmium-115 photopeak could be measured providing some loss in precision was acceptable.

In Figure 2, the decay curves obtained by β-counting at intervals over a period of 32 days show the correct half life for cadmium-115 after a long-lived component has been subtracted. The long-lived component was identified as cadmium-115m [which decays to nearly stable indium-115 (*11*)] from its half life of 43 days and the fact that it also occurs in the standard. Radiochemical purity was, therefore, achieved, and the initial count rates could be used to calculate the concentration of cadmium in the sample. The results obtained by β-counting were in agreement, within the observed precision, with those obtained by γ-counting of indium-115m.

The sensitivity for β-counting has been estimated to be 10^{-10} gram or 0.2 p.p.b. of cadmium in a 0.5-gram sample of aluminum, irradiated for 64 hours at a flux of 6.3×10^{13} neutrons per square centimeter per second, assuming that a count rate twice that of the background is sufficient.

The time required for the chemical separation was 4 to 5 hours for duplicate samples. The chemical yields obtained ranged from 80 to 90%.

During the analysis, care was taken to avoid potential sources of error of the type discussed by Plumb and Lewis (*12*). The neutron flux was known to be constant throughout the volume occupied by sample and standard, from previous experiments with cobalt wires (*6*). It was calculated by the method of Stewart and Zweifel (*13*) that self-shadowing is insignificant for the concentration and dimensions used for the standards. The quartz vials that contained the standards were free of high neutron cross-section impurities. The neutron absorption cross section of the aluminum samples is too low to cause any significant shielding of the impurities during activation. The samples were cleaned after irradiation to eliminate surface contamination. It was also ascertained, by reference to the relevant data in the literature, that under these irradiation conditions, significant amounts of cadmium-115 or

indium-115m could not have been produced by nuclear reactions on other elements.

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Separation of Radioactive Zinc from Reactor Cooling Water by an Isotope Exchange Method

W. B. SILKER

Hanford Atomic Products Operation, General Electric Co., Richland, Wash.

▶ **A method was developed to separate radioactive zinc from reactor cooling water by isotope exchange with inert zinc in the form of zinc amalgam. The radioactive zinc is recovered in high yield and free from all other activities except Cu^{64} and traces of Mn^{56} by a single contact with zinc amalgam. The Cu^{64} interference can be removed quantitatively by a pre-extraction into cadmium amalgam. The procedure is rapid, and simple enough to warrant application to an automatic analyzer for continuous measurement of radioactive zinc in waste streams.**

THE HANFORD PRODUCTION REACTORS use treated Columbia River water to remove the heat formed by the fission process. In the reactor, the impurities in the water are exposed to a high neutron flux, where a fraction absorb neutrons and become radioactive. These radioactive materials are discharged with the water to retention basins where the short-lived radioisotopes are allowed to decay. The water from these basins is then returned to the river.

A long-lived radioisotope introduced to the river in this manner is Zn^{65}, which is useful as a tracer in the study of biological systems that are dependent on the Columbia River. Perkins and Nielsen measured the Zn^{65} concentrations in farm produce and livestock from land which was irrigated with Columbia River water, and measured the resultant accumulation of individuals who obtained their food from these sources (*4*). Certain marine organisms in the Columbia River estuary achieve a high concentration factor for zinc; oysters, for example, concentrate Zn^{65} by a factor of about 2×10^5 from their environment (*1, 5*). The interpretation of data from these studies requires an accurate measurement of the amount of radioactive zinc continually discharged to the river.

Zinc-65 in reactor cooling water is currently determined by gamma spectrometric analysis of an evaporated sample which is allowed to decay for more than 5 days. If an analysis is required prior to this time for Zn^{65}, or for Zn^{69m}, a short-lived isotope, a more complicated chemical separation is required to obtain radiochemically pure isotopes of zinc. The possibilities for a simple one-step procedure that could be adapted for automatic analysis of Zn^{65} were investigated. The radioisotopes in reactor cooling water that are present in amounts that would interfere with a γ-spectral analysis for Zn^{65} are Na^{24}, Mn^{56}, As^{76}, Ba^{140}, and several of the rare earth isotopes. Copper-64, in addition to the previously mentioned isotopes, would interfere with the measurement of the gamma photons from Zn^{69m}, and exclusion of these isotopes from the final product is required.

Preliminary studies by DeVoe (*2*) suggested that isotope exchange on amalgams might find application in radiochemical analysis where a high decontamination factor is required. This paper presents a procedure using zinc amalgam exchange to separate radioactive zinc from a complex mixture of other radioactive isotopes. This procedure can be used for the automatic determination of Zn^{65} in waste streams, and is suitable for routine determination of radioactive zinc isotopes by laboratory personnel.

EXPERIMENTAL

The zinc amalgam used in this work was prepared by the method of Morse and Burton (*3*), in which granular zinc and mercury in the ratio of 1 gram to 5 ml. were mixed in the presence of 0.1*M* tartaric acid. Simultaneous amalgamation and isotope exchange were equally effective in recovering radioactive zinc; consequently the use of 0.1*M* tartaric acid was adopted as the electrolyte for this procedure.

A reasonable aliquot of reactor cooling water that could be used for the radiochemical determination of Zn^{65} was 100 ml. To determine the optimum amount of zinc amalgam for use with this volume of sample, 100 ml. of 0.1*M* tartaric acid was spiked with Zn^{65} tracer and shaken for 5 minutes with various amounts of amalgam. The two phases were separated and the amounts of radiozinc in each phase measured by conventional γ-ray spectrometric methods. The results, presented in Table I, indicate that 6 ml. of amalgam was the minimum quantity to be used.

Since the removal reaction is based on the interchange of atoms between the