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ANALYSIS FOR TRACE IMPURITIES BY NEUTRON ACTIVATION

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ABSTRACT

The application of radioactivation analysis to selected examples of trace element determinations is reported. The technique of the method of neutron radioactivation analysis and the sensitivities of detection of these elements in a variety of materials are discussed.

The limitations of existing conventional methods of analysis for trace elements have long been recognized. However, the recent applications of radioactivation analysis to certain of these problems have evoked an analytical method capable of being sensitive, specific, precise, and usually simple. This paper discusses and gives selected examples of trace element determinations by neutron activation analysis, one type of radioactivation analysis.

Boyd⁽⁴⁾ and Taylor and Havens⁽¹²⁾ have reviewed the principles of radioactivation analysis. Leddicotte and Reynolds⁽⁸⁾ have reported on the use of the Oak Ridge National Laboratory graphite reactor for the routine analytical determination of many trace elements by neutron activation analysis. Recent publications which have appeared deal with the application of activation analysis to specific problems, viz.: Brown and Goldberg's⁽³⁾ determination of gallium and palladium in meteorites; Smales and Pate's⁽¹¹⁾ determination of submicrogram quantities of arsenic in a variety of materials; Hudgens and Cali's⁽⁶⁾ determination of antimony in zirconium oxide; and Atchison and Beamer's⁽¹⁾ determinations of trace impurities in magnesium.

At present an analytical service by neutron activation analysis is offered by the United States Atomic Energy Commission. The work described in this paper was carried out on samples submitted to this program. The samples were irradiated in the ORNL graphite reactor and all of the chemical separations and radioactivity determinations were made by the Activation Analyses Group, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Method of Neutron Activation Analysis

Most elements when irradiated by the neutrons of a chain-reacting pile (the graphite reactor) become "activated" to form artificially radioactive species that have their own individual modes of decay and radiation spectra. The rate of

decay and the type of radiation emitted are characteristic of the radionuclide and are never exactly duplicated in any other radionuclide. This specificity makes activation analysis an unusual technique in that it is free from interference by other elements. Also, sample contamination with the element being determined, often encountered in conventional methods of analysis, is negligible unless the contamination is introduced into the sample before irradiation.

In a typical analysis, a weighed sample is exposed to the neutrons of the reactor for an appropriate length of time. A measurable amount of radioactivity from one or more radioisotopes of the element is produced when a stable isotope (or isotopes) of the element is bombarded. The radioactivity, A , present at a time, t , after the start of the bombardment, can be calculated from the expression:

$$A = Nf\sigma S$$

where A = the amount of radioactivity in disintegrations per second, N = the number of atoms of the target nuclide, f = the neutron flux per square centimeter per second, σ = the activation cross section (probability) for the reaction in square centimeters per atom, and S = the saturation factor, $1 - e^{-\lambda t}$, or the ratio of the amount of radioactivity produced in time, t , to that produced in infinite time. The decay constant, λ , is related to the half-life of the radionuclide produced ($\lambda = 0.693/\text{half-life}$).

In terms of the weight, W , of the element and on the assumption that the rate of production of the radioactivity given by $Nf\sigma$ is constant during the bombardment, the above equation may be written as

$$W = \frac{AM}{6.02 \times 10^{23} f \sigma S}$$

where M = the chemical atomic weight of the element being determined.

Quantitative analysis by radioactivation techniques follows a procedure in which the specimen and a standard sample containing a known weight of the element

being determined are bombarded under the same reactor conditions and processed in the same manner after the analysis has been completed. The use of the comparison method of analysis eliminates the necessity of monitoring the flux of neutrons (or other nuclear particles) which is usually a difficult quantity to measure accurately or control. Similarly, the per cent isotopic abundance may be neglected so long as the natural ratios are present. However, variance from the natural ratios of isotopes will give bias results and must be taken into account. Also, by this procedure the concentration of the element in the unknown is calculated as a simple ratio of the radioactivity of the element of interest produced in the sample to the radioactivity produced in the standard under the same conditions. The radioactivity produced can usually be measured with great sensitivity by means of counters or other instruments for detecting ionizing radiations.

The radioactivity of the samples and standards can be determined by one of two methods. The simplest determination is a direct measurement of the radioactivity in the irradiated material shortly after the irradiation has been completed. This method is one in which the irradiated material is suitably mounted on either a watch glass or a metal plate, or an aliquot placed in a small culture tube. The mount is then placed into some type of counter and its radioactivity measured by recording the number of counts per unit time. The analysis is then completed by a resolution of the data obtained. This method of analysis is applicable to those samples where the contaminant can be appreciably activated in the presence of the major sample constituent which gives either practically no radioactivity or only a very short-lived radioactive isotope when irradiated by a source of nuclear particles.

However, it cannot always be assumed that the major constituent of the sample will not become activated during irradiation, so a chemical separation of the desired element and its induced radioactivity is generally made. After the

irradiation, a known amount of the inactive element as an "isotopic carrier" is added to the solutions of both the specimen and standard samples. This "carrier" is then chemically processed to isolate it and the desired radioactivity from other elements and contaminating radioactivities. Since the procedures used in these chemical separations usually give less than quantitative yield, a correction for "chemical yield" must be made. After the separation, the carrier and the isolated radioactivity are placed into some type of counter and the radioactivity measured. The purity of the separated radioactivity may be checked by absorption techniques and a measurement of its half-life.

Nuclear Data for the Elements of Interest

This investigation reports on the analysis of vanadium in motor oil, manganese in alloys, cadmium in resins, strontium in animal tissue, gallium in aluminum, and cobalt in crude biological materials. The radioactive isotopes and other nuclear data for the elements considered in this work are listed in Table I. It has been compiled from information appearing in the National Bureau of Standards' Circular 499(13).

Sample Preparation for Irradiation

All sample materials were carefully handled to avoid contamination of the material with the elements to be determined. The precautions include handling of the material in an area of the laboratory kept clean and without access to the comparative sample material. The equipment used to contain the materials for bombardment has been cleaned with special care.

In the determination of vanadium in motor oil and cobalt in crude biological materials, ~1.0 gram portions of the specimens were transferred from the sample container to quartz ampoules. After the irradiation, weighed aliquots were taken for analysis. In the determinations of manganese in alloys, strontium in animal tissue and gallium in aluminum, 0.1 - 0.2 gram samples were weighed and placed in

individual small quartz tubes, which were sealed with a cork stopper wrapped in aluminum foil. The tube and its contents were then placed in an irradiation container. In the determination of cadmium in resin, 1.0 - 2.0 gram portions were weighed and transferred to an aluminum foil capsule which in turn was placed in an irradiation container. For the comparative standards, milligram amounts of pure vanadium metal, cobalt metal, manganese metal, strontium carbonate, gallium metal and cadmium metal respectively were weighed into small quartz tubes and placed in the respective irradiation containers.

Length of Irradiation and Determination of Radioactivity After Irradiation

The time intervals used in the respective element irradiation are given in Table II. The length of irradiation time is usually about one half-life. The only exceptions in the examples given are the irradiation times for cobalt and vanadium. These materials were irradiated for two weeks and seven minutes respectively.

In the determination of vanadium in motor oil and manganese in alloys, the simple and direct method of measuring the induced radioactivity was used. In determining the radioactivity due to vanadium, both the specimen and the standard samples were alternately counted on counting equipment that is continuously recording and of instantaneous response. The present equipment used is a proportional type counter having a tube with a gold covered mica window of 1.85 mg/cm² thickness. The tube is mounted in a standard counting shield. The ionization current pulses are fed to an A-1 linear amplifier through a preamplifier. The output from the A-1 feeds into a logarithmic counter rate meter and is recorded as counts per minute on a Brown single-pen recorder of 0 -to 10 mv range. The concentration of vanadium was calculated by resolving the decay curves recorded on the Brown strip chart. Figure A illustrates a typical analysis for vanadium by this method.

Similarly, the manganese-radioactivity in the alloys was determined by alternately counting the specimen and standard in a high pressure ionization chamber of the type described by Borkowski(2). In this analysis, the major component of the sample matrix did not become activated. The concentration of manganese was calculated by a resolution of the decay data. Figure B illustrates a typical determination of manganese by the direct measurement.

The radioactivity induced in strontium, cobalt, cadmium, and gallium was measured in a gamma scintillation counter after a chemical separation of the isotopic "carrier" and the radioactivity. This counter has also been described by Borkowski(2) and contains a thallium-activated sodium iodide crystal. The chemical separation procedures are described below.

Chemical Procedures

The Determination of Cobalt. A weighed portion of irradiated crude biological material was wet ashed with $\text{H}_2\text{SO}_4\text{-HNO}_3$ in a 50 ml beaker. Standardized cobalt carrier and copper, iron, nickel, zinc, strontium, sodium holdback carriers were added. The strontium was separated as SrSO_4 , the copper as CuS and the iron as $\text{Fe}(\text{OH})_3$. The cobalt, nickel and zinc were precipitated as basic sulfides and the cobalt separated from nickel and zinc as the hydroxide in 1 M potassium hydroxide. The final precipitate of potassium cobaltinitrite, $\text{K}_3\text{Co}(\text{NO}_2)_6\cdot\text{H}_2\text{O}$, (5, p.324) was washed with water, alcohol, ether, dried 5 minutes at 110° , weighed, mounted and counted.

The Determination of Strontium. An appropriate sized sample of irradiated animal tissue was dissolved in concentrated nitric acid. Standardized strontium carrier and barium, iron, copper holdback carriers were added. Strontium and barium were twice precipitated as barium and strontium nitrates from a strong acid solution(9). The precipitate was dissolved in water, additional iron holdback carrier added and the iron precipitated with ammonium hydroxide. The barium was separated from strontium as the chromate in buffered acetic acid solution (pH-5).

FIGURE B
ALLOY SAMPLE - GAMMA DECAY IONIZATION CHAMBER

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The filtrate was then made slightly ammonical and the strontium precipitated with ammonium oxalate(5, p. 504). The precipitate of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was dried for 10 minutes at 110°C , cooled, weighed, mounted and counted.

The Determination of Gallium. The irradiated sample was put into solution by the addition of small amount of concentrated hydrochloric acid. Standardized gallium carrier and concentrated hydrobromic acid were added to the solution. After evaporation of the solution to dryness, the residue was dissolved in 6 N hydrochloric acid and the solution extracted three times with equal volumes of diethyl ether(5, p.96). The combined extracts were washed with 6 N hydrochloric acid and the gallium extracted into an equal volume of water. At this point, copper, iron and barium holdback carriers were added to the solution. The copper was removed by a hydrogen sulfide precipitation, while the iron and barium were removed by precipitation with sodium hydroxide and sodium carbonate. After filtration the solution was made 6 N hydrochloric acid and the gallium extracted with an equal volume of diethyl ether. The gallium was re-extracted into water and the water layer was heated to near boiling to expel equilibrated ether. Then a few milliliters of 8-hydroxyquinoline solution (50 g per liter in 2 M acetic acid) was added and the gallium 8-hydroxyquinolate was precipitated by the dropwise addition of 6 M ammonium acetate(14, p. 293). After filtration, the precipitate was washed with water, dried for 15 minutes at 110°C , cooled, weighed, mounted, and counted.

The Determination of Cadmium. The irradiated sample of resin was ignited at 600°C and the residue treated with a mixture of $\text{H}_2\text{SO}_4\text{-HNO}_3$. Standardized cadmium carrier and iron, barium and sodium holdback carriers added and the solution evaporated to strong fumes of sulfuric acid. The solution was diluted with water to 0.5 N sulfuric acid and saturated with hydrogen sulfide. The cadmium sulfide precipitate was dissolved in 6 M hydrochloric acid, additional iron holdback carrier

added and removed by a basic ferric acetate precipitation(10, p.88). The solution was then made acid with 6 M hydrochloric acid and CdS precipitated. The sulfide precipitate was dissolved, the hydrogen sulfide expelled and Cd $\text{NH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ precipitated by addition of the 3 M NH_4Cl and 1.5 M $(\text{NH}_4)_2 \text{HPO}_4$ (7, p.350). After boiling for 15 minutes, the solution was filtered and the collected precipitate washed in water, dried for 10 minutes at 110°C, cooled, weighed, mounted, and counted.

Results

The results obtained by the neutron activation analysis of four (4) samples of motor oil are reported in Table III. Spectrographic analysis of these oils reported 1.0 ppm.

Table IV shows the analysis of a series of manganese alloys. The activation analysis results are compared with the spectrographic results from two different laboratories.

Tables V and VI report on the analysis of cobalt in crude biological materials and strontium in animal tissues. No comparative data was available.

Table VII shows activation and spectrographic analysis results on gallium in aluminum.

Table VIII reports on the determination of cadmium in a series of vinylite resins. Polarographic and spectrographic data is also reported.

Summary

From the results reported, it is felt that the method of neutron radioactivation analysis is quite capable of being a specific, sensitive and precise method of analysis. Its specificity is graphically illustrated in Figures A and B. Although these determinations were made by the simplest method of analysis, i.e., direct measurement immediately after irradiation, the results show that the method's specificity is truly significant since the radioactivity measured was primarily associated with the radioactivity of V^{52} and Mn^{56} , respectively. Table II also gives the sensitivity of detection for the selected examples used in

this paper. Here, the limits of detection were obtained by assuming the minimum useful counting rate to be 40 disintegrations of beta, or equivalent, per second, a pile flux of 5×10^{11} neutrons/cm²/second, and a given irradiation time period. Samples which are irradiated for different time intervals or at a different neutron flux will produce different sensitivity values. Comparison of the activation analysis results with the results obtained by conventional methods, such as spectrographic or polarographic analysis, lend reliability to the precision of this method of analysis. This precision has been arbitrarily set at $\pm 10\%$ and in practice it has been found to be much better than this value.

TABLE I

Nuclear Characteristics of the Elements Determined

<u>Stable Isotope</u>	<u>% Abundance</u>	<u>Radioactive Nuclide</u>	<u>Thermal Neutron Activation Cross Section</u>	<u>Half-Life</u>	<u>Radiations</u>
V ⁵⁰	0.2	-----	-----	-----	
V ⁵¹	99.8	V ⁵²	4.5	3.9 Min.	β^- , γ
Mn ⁵⁵	100.0	Mn ⁵⁶	12.0	2.6 Hrs.	β^- , γ
Co ⁵⁹	100.0	Co ⁶⁰	20	5.3 Yr.	β^- , γ
		Co ^{60m*}	0.66	10.7 Min.	β^- , γ
Ga ⁶⁹	60.2	Ga ⁷⁰	1.4	20 Min.	β^- , γ
Ga ⁷¹	39.8	Ga ⁷²	3.4	14 Hrs.	β^- , γ
Sr ⁸⁴	0.52	-----	-----	-----	-----
Sr ⁸⁶	9.8	Sr ^{87m*}	1.3	2.7 Hrs.	γ
Sr ⁸⁷	7.0	-----	-----	-----	-----
Sr ⁸⁸	82.7	Sr ⁸⁹	0.005	53 d	β^- , γ
Cd ¹⁰⁶	1.22	Cd ¹⁰⁷	1.0	6.7 Hrs.	β^+ , γ , K
Cd ¹⁰⁸	0.98	-----	-----	-----	-----
Cd ¹¹⁰	12.4	Cd ¹¹¹	0.2	49 Min.	β^- , γ
Cd ¹¹¹	12.8	-----	-----	-----	-----
Cd ¹¹²	24.0	Cd ¹¹³	0.020	5 Yr.	β^-
Cd ¹¹³	12.3	-----	-----	-----	-----
Cd ¹¹⁴	28.8	Cd ¹¹⁵	0.14	43 d	β^- , γ
		Cd ¹¹⁵	1.1	2.3 d	β^- , γ
Cd ¹¹⁶	7.6	Cd ¹¹⁷	1.4	2.7 Hrs.	β^-

*Metastable state.

TABLE II

Length of Irradiation and Sensitivity of Detection

<u>Element</u>	<u>Irradiation Time</u>	<u>Sensitivity of Detection, μg (Calc.)</u>
V	7.0 minutes	0.003
Mn	3.0 hours	0.001
Sr	3.0 hours	0.00
Co	2.0 weeks	0.04
Ga	16.0 hours	0.01
Cd	3.0 days	0.10

TABLE IIIVanadium Content of Motor Oils

<u>Sample</u>	<u>Vanadium</u>
1	0.7; 0.7 ppm
2	1.0; 0.9 "
3	0.7; 0.7 "
4	1.0; 0.9 "

TABLE IVManganese Content of Alloys

<u>Sample</u>	<u>Activation Analysis</u>	<u>Spectrographic Analysis(*)</u>
1	193 ppm	150 - 236 ppm
2	170 "	180 - 205 "
3	115 "	88 - 100 "
4	152 "	120 - 154 "
5	111 "	100 - 152 "
6	120 "	96 - 160 "
7	125 "	110 - 192 "
8	116 "	99 - 135 "

(*)Spectrographic results from two different laboratories.

TABLE VCobalt Content of Crude Biological Materials

<u>Sample</u>	<u>Activation Analysis</u>
1	2.30; 2.30 ppm
2	2.00; 2.10 "
3	0.01; 0.01 "

TABLE VIStrontium Content of Animal Tissues

<u>Sample</u>	<u>Activation Analysis</u>
1	5.6; 5.9; 6.1; 6.1 ppm
2	14.4; 13.6; 14.4; 13.0 ppm
3	33.2; 34.1; 31.0; 31.1 ppm
4	44.8; 45.6; 45.9; 45.4 ppm
5	56.1; 58.5; 55.8 ppm
6	42.2; 45.7; 44.3 ppm

TABLE VIIGallium Content of Aluminum

<u>Sample</u>	<u>Activation Analysis</u>	<u>Spectrographic Analysis</u>
1	140 ppm	130 ppm
2	120 "	130 "
3	100 "	120 "
4	120 "	140 "
5	130 "	130 "

TABLE VIIICadmium Content of Vinylite Resins

<u>Sample</u>	<u>Activation</u>	<u>Polarography</u>	<u>Spectrographic</u>
1	220 ppm	228 ppm	---- ppm
2	449 "	452 "	958 "
3	214 "	---	225 "
4	38 "	15 "	45 "
5	128 "	142 "	175 "

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