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ABSTRACT

The nuclear reactions which take place in the Oak Ridge National Laboratory graphite reactor now form the basis of an analytical service for the determination of trace elements in many different materials. This paper discusses the techniques of the method, its sensitivities and applications. Special attention is directed to the determination of trace amounts of the alkali metals by neutron activation analysis.

INTRODUCTION

Nuclear science has created a new analytical procedure for the determination of trace quantities of many elements. This procedure, called "Activation Analysis," is a method in which the nuclear reactions in a chain-reacting pile (or a charged particle accelerator) produce an artificially-radioactive isotope of the element to be determined.

The use of characteristic nuclear reactions as a technique for solving otherwise difficult analytical problems was conceived shortly after the discovery of artificial radioactivity by Joliot-Curie in 1934[8]. Hevesy and Levi[5,6] first used activation analysis to determine trace rare earth elements in rare earth mixtures. As interest grew in this unusual method, other researchers applied it to the determination of trace impurities in a variety of materials, and it has now developed to such an extent that a special analytical service is offered by the Oak Ridge National Laboratory. Using the principles reviewed by Boyd[3] and Taylor and Havens[13], this analytical service has been used in the determination of about 65 of the elements as trace impurities in many different types of samples[11].

Method of Neutron Activation Analysis

Neutron activation analysis is accomplished by exposing a specimen containing a small quantity of the element to be determined to neutrons in a graphite reactor ("pile"). One (or more) of the stable isotopes of the element captures neutrons (is "activated") to produce a measurable amount of a radioisotope of the element.

In terms of the weight, W, of the element sought, and assuming that the rate of production of the radioactivity is constant during irradiation, the equation may be written as

$$W = \frac{AM}{6.02 \times 10^{23}\ fos}$$

In this equation, A = the activity in distintegrations per second, M = the chemical atomic weight of the element sought, 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 activity produced in time t to that produced in infinite time. The decay constant, λ, is related to the half-life of the radionuclide produced by $\lambda = 0.693/\text{half-life}$.

The analysis is made quantitative by following a procedure in which the specimen and a comparison sample, containing a known weight of the element being determined, are irradiated under the same reactor conditions. The use of a comparison sample eliminates the necessity of monitoring the flux of neutrons, which is usually a difficult quantity to measure or control. By this procedure it is only necessary to measure the activity produced in the sample under the same conditions as the activity produced in the standard and to calculate the amount of the element in the unknown by a simple ratio. The radioactivity can be measured with great sensitivity by means of counters or other instruments for detecting ionizing radiations.

In some instances, it is possible to determine a trace element in a sample by simply measuring the induced radioactivity by some type of a radiation counter immediately following the irradiation. Such a procedure is used in assaying samples which have only a single trace element that can be activated and in which the major constituent of the sample is either an element in which practically no radioactivity is induced or is an element which activates to only a very short-lived radioactivity. For example, this direct-measurement technique has been applied to the determination of manganese in aluminum. The aluminum isotope has a half-life of 2.3 minutes, while manganese has a half-life of 2.59 hours. Following irradiation, the aluminum activity was allowed to decay completely (at least 10 half-lives) before measuring the activity due to the

manganese. If a sample contains a second contaminant of different half-life, it can be measured after the decay of the shorter lived activities. The direct-measurement technique can also be used when there is a difference in the types, or energies, of radiation emitted.

In general, however, a chemical separation of the element sought is made after the irradiation. In this technique, a known amount of the element as an inactive isotopic carrier is added to the solutions of both the specimen and comparative sample. The "carrier element" is then chemically processed to separate and isolate it from the other elements. Since the reactions usually used give less than quantitative yield, correction for chemical yield must be made. A comparison of the activity of the element produced in the unknown is made against the activity of the element produced in the standard. The purity of each activity may be checked by a measurement of half-lives and by absorption techniques.

Sensitivity of the Method

The sensitivity for different elements ranges from about 0.00003 microgram for europium to about 100 micrograms for niobium[10]. Here the term sensitivity is used to indicate the amount of an element that would produce a sufficient activity to be measured after it had been irradiated at a predetermined neutron flux for a given time interval. The sensitivity with which the element sought may be detected is also dependent upon its cross section. Likewise the radiation emitted from the radionuclide produced must be sufficiently energetic and the half-life must be long enough so that the measurements can be made readily.

Radioisotopes with half-lives greater than 10 minutes and not longer than several days are best to use in these measurements. Those emitting beta rays or positrons of sufficient energy can be determined with reasonable accuracy

using ordinary counting equipment such as Geiger-Mueller counters. If the energy of the particles emitted is low, or if the radioisotope emits only conversion electrons or X-rays, special measurement techniques are necessary and are not very satisfactory in activation analysis. Difficulty arises if the sample contains large amounts of high cross-section material or interfering substances.

Application of the Method to the Determination of Trace Quantities of the Alkali Metals

With specific reference to the alkali metals, Table I shows the products of slow-neutron bombardment(14). It is evident that Na^{24} and K^{42} are desirable nuclides. Rb^{88} is too short-lived for most work, while Rb^{86} and Cs^{134} are rather long-lived, but the high Cs cross-section partially compensates for this. The sensitivity is the amount of the element producing in ten half-lives, or in one month, whichever is shorter, a readily measurable amount of the radionuclide (in this case, 40 disintegrations per second). The flux, 5×10^{11} neutron/cm^2/sec, is that flux normally obtained in the ORNL Graphite Reactor.

TABLE I

Neutron Activation Analysis: The Products and Sensitivity of Detection By Slow-Neutron Irradiation of the Alkali Metals

Target	Product	t-1/2	Radiation	Sensitivity (μg)
Li (6)	H (3)	12.1 y	β^-	*
	He (4)	Stable		
Li (7)	Li (8)	0.9 s	β^-, 2α	*
Na (23)	Na (24)	15.0 h	β^-, γ	0.007
K (41)	K (42)	12.4 h	β^-, γ	0.08
Rb (85)	Rb (86)	19 d	β^-, γ	0.03
Rb (87)	Rb (88)	17 m	β^-, γ	0.3
Cs (133)	Cs (134)	3 h	I.T., e^-	ca 1.0
	Cs (134)	2 y	β^-, γ	0.03

*Detection requires special counting apparatus.

To lend further interpretation of the information appearing in Table I and to establish the application of radioactivation analysis to the alkali metals, reference is made to the characteristic reaction used in the determination of sodium. The reaction is as follows:

$$Na^{23} + n \longrightarrow Na^{24} + \gamma$$

It is more commonly written as Na^{23} (n,γ) Na^{24}, which means that the stable isotope of sodium of weight 23, "captures" a neutron to give an isotope of sodium of weight 24 plus a quantum of energy which is emitted as a gamma ray. Na^{24} is radioactive and undergoes a second change as follows:

$$Na^{24} \longrightarrow Mg^{24} + \beta^- + \gamma$$

(T-1/2 = 15 hours)
β^- = 1.40 Mev
γ = 1.38 Mev
= 2.76 Mev.

This rate of decay (a half-life of 15 hours) and the energy with which the beta particles and the gamma photons are emitted are characteristic of this nuclide and will not be duplicated exactly in any other nuclide.

Determination of Sodium, Potassium, Rubidium, and Cesium By Neutron Activation Analysis

Radioactivation analysis has been applied routinely to the determination of trace quantities of sodium and potassium in a variety of materials. Rubidium and cesium have been determined less extensively and are reviewed briefly in the discussion that follows. The simple method of direct-reading after irradiation, as well as the method of measurement after separation and isolation by such techniques as precipitation or ion exchange, have been utilized in these determinations. A discussion of the applications of these methods and some of the results obtained follows.

I. Sodium

A. By "Direct-Reading":

1. One of the earliest applications of this technique was employed in the analysis of mixtures of lithium and sodium sulfates. Portions of the unknown sample together with known amounts of standard samples (as Na_2CO_3) were irradiated under the same pile conditions for one hour. The bulk constituent, lithium, gave no appreciable activity. However, sufficient Na^{24} was produced to permit a rapid analysis. After discharge from the pile, the samples and aliquots of the comparative samples (after solution) were placed in individual radioactivity-free glass tubes and the gamma radiation was measured directly in a high pressure ionization chamber(2). A simple ratio of the values of the ionization current per weight of the unknown to that per weight of the comparative sample gave the results shown in Table II. These results are compared with spectrochemical data on the same sample.

TABLE II

Comparison of Activation and Spectrochemical Methods for Determining Sodium in Mixed Sulfates

Sample	Sodium in Sample, Per Cent	
	Activation Analysis	Spectrochemical Analysis
1	12.6	13.7
2-a*	9.8	10.3
2-b*	9.9	11.1
3-a*	16.2	15.0
3-b*	16.3	16.1

*Duplicate analysis of each sample; probable error ±5%.

2. Table III furnishes additional data on the use of the direct-reading method for the determination of sodium in an organic compound.

TABLE III

Determination of Sodium in Sodium Oxalate Using Activation Analysis

Theoretical	Observed*
34.3%	34.0% 35.0

The above results were obtained after the irradiation of 10 - 30 mg of material in the graphite reactor. By making a longer exposure, smaller samples could have been used. Also, by the use of other counting techniques, a large increase in sensitivity could be obtained with slightly less accuracy.

B. By Precipitation:

The method ultimately decided upon for the determination of trace amounts of Na by radioactivation analysis, in which the radioisotope, Na^{24}, is carried by an isotopic carrier, was an adaptation of the zinc uranyl acetate method(1). However, the uranium upon separation as sodium zinc uranyl acetate, gives rise to UX beta radiations (following U^{238} alpha decay). If the sample is counted several hours after the initial separation of Na, this growth of beta activity will result in an erroneous count. For example, counting data obtained as the UX activity grew indicated that in 3 hours after separation the activity will have grown sufficiently (about 10%) to seriously affect any analysis for sodium in the range of 0.01% or less. In order to avoid these effects, it was proposed to precipitate Na as NaCl by the method of Willard and Smith(15) in which NaCl is precipitated from a solution of hydrogen chloride in n-butanol.

*Reading of duplicate samples made in high pressure gamma ionization chamber.

In a typical analysis, the samples after irradiation were dissolved in a small quantity of a mineral acid. To this solution a known amount of inactive sodium was added as an isotopic carrier. Small amounts of compounds of Cu, Fe, Sr, Co, phosphate and K were also added as 'holdback' carriers. The heavy elements were separated by successive precipitations with H_2S and ammonia. After boiling the solution to remove the sulfide ions, sulfate was added and precipitated with $BaCl_2$. Excess ammonia and ammonium carbonate were added to separate Sr.

After evaporation and ignition to remove the ammonium salts, the residue was dissolved in a few milliliters of water, excess zinc uranyl acetate reagent* added, and the resulting mixture allowed to digest 30-45 minutes. After centrifugation, the precipitate was washed several times with dilute zinc uranyl acetate reagent, 95% alcohol, and ether. It was then treated with 12% n-butanol-HCl reagent** and digested for 10 minutes in an ice bath. The precipitate was washed with a mixture of 10 ml ethyl ether and 10 ml n-butanol reagent and transferred to a tared filter paper, washed with ethyl ether and dried at 110°C for 10 minutes. After cooling, it was weighed as NaCl, mounted and counted. Aliquots from solutions of the irradiated comparative samples (Na_2CO_3) were treated in a similar manner.

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*Zinc uranyl acetate reagent: 77 grams of crystallized uranyl acetate is dissolved in 13.5 of glacial acetic acid and 410 ml of distilled H_2, and added to a solution of 231 grams of crystallized zinc acetate in 6.6 ml of glacial acetic acid and 262 ml of distilled water. The solutions are mixed at about 70° C, cooled to approximately 20° C, and allowed to stand overnight. The reagent is then filtered into a clean, dry glass bottle.

**n-butanol-HCl reagent: Prepared by generation of HCl when conc. H_2SO_4 is added dropwise to NaCl. The gas is passed into C.P. butanol until the density is 0.86-0.87 (12% HCl).

1. Some results on the determination of Na in metal foils by precipitation are given in Table IV.

TABLE IV

Comparison of Activation Analysis and Spectrochemical Methods for Determining Sodium in Metal Foils

Sample	Sodium in Sample, Per Cent	
	Activation Analysis	Spectrochemical Analysis
1	0.0008	0.0007
2	0.0006	0.0006
3	0.0008	0.0009
4	0.0015	0.0013
5	0.0010	0.0009

2. Sodium was determined in aluminum by a procedure similar to the one given above. The results are shown in Table V and are compared with results by spectrochemical and colorimetric analyses of the same material.

TABLE V

Comparison of Activation Analysis and Conventional Methods for Determining Sodium in Aluminum

Sample	Sodium in Sample, Per Cent		
	Spectroscopic	Colorimetric*	Activation
Foil	<0.003	<0.0045	0.001
Ingot	<0.003	<0.003	0.001

3. Sodium has been determined in reagent K_2CO_3 by precipitation methods at a concentration of about 0.01%. These results are given in Table VI.

*Colorimetric analysis involved precipitation of sodium magnesium uranyl acetate, with dissolution and colorimetric determination of uranium.

TABLE VI

Determination of Na in Reagent K_2CO_3 by Activation Analysis

Sample	Sodium in Sample, Per Cent	
	Activation	Supplier's Analysis
1	0.0092	0.01
2	0.0093	0.01
3	0.0097	0.01
4	0.0098	0.01
5*	0.0099	0.01

C. By Ion-Exchange

Sodium (as well as K, Rb, and Cs) has been separated by a cation-exchange process. Brooksbank(4) in independent work, found conditions almost identical to those of Kayas(9) for the separation of the alkali metals. Using these techniques, Na was determined in K_2CO_3 and Rb_2CO_3 and results of these separations are reported in Tables VI and VIII respectively.

II. Potassium

Precipitation and Ion-Exchange methods have been employed in the determination of trace amounts of potassium. A discussion of these applications and some of the results obtained are given below.

A. By Precipitation

Potassium has been determined in magnesium and lithium salts in which the potassium, as K^{42} ($t_{1/2}$ = 12.4 hour), is carried by an isotopic carrier and precipitated as chloroplatinate, K_2PtCl_6, after being separated in the manner of Hicks(7) and O'Leary and Papish(12).

In these analyses, a numerous amount of inactive potassium was added as an isotopic carrier to the solution of an irradiated sample. Also, small amounts of compounds of each of the following elements were added: Cu, Fe, Co,

*Separation by ion-exchange.

Ba, Sr, and Na. After a separation of the heavy metals by H_2S and NH_4OH precipitations, and a precipitation of the alkaline earths with ammonium carbonate, the filtrate was evaporated to a volume of approximately 1 ml. The solution was then made acid with a minimum quantity of HCl (or HNO_3) and sufficient chloroplatinic acid (containing 1 gm of Pt in each 10 ml of solution) was added to convert all the chlorides (or nitrates) present to corresponding chloroplatinates. Absolute ethanol was added until the solution contained 60 to 70% of alcohol by volume. A few ml of ethyl ether was then added to the solution, and the precipitate allowed to settle while cooling in an ice bath. The K_2PtCl_6 was then transferred to a tared filter paper using small portions of ethanol and washed several times with ethanol until the liquid became colorless. The precipitate was dried at 110°C. for 10 minutes, cooled, weighed, mounted and counted.

The results obtained for the determination of potassium in magnesium, using such a procedure as given above, are tabulated in Table VII.

TABLE VII

Determination of Potassium in Magnesium by Activation Analysis

Sample	Potassium in Sample, Per Cent	
	Activation*	Spectrochemical
1	0.0014	0.001
2	0.0018	0.001
3	0.0013	No data reported.
4	0.0020	-.-.-
5	0.0016	-.-.-
6	0.0014	-.-.-

*Results on duplicate analyses, probable error ±10%.

B. By Ion-Exchange

Using the same ion-exchange separation techniques mentioned in Section C on sodium, activation analysis has been applied to the determination of potassium in Rb_2CO_3. These results are given in Table VIII.

TABLE VIII

Determination of Sodium, Potassium and Cesium by Ion-Exchange After Neutron Irradiation

Sample	Element in Sample, Per Cent		
	Na	K	Cs
1	Present	0.055	0.10
2	0.007	0.050	0.40
3	-----	0.060*	0.02

III. Rubidium and Cesium

Although precipitation methods can be applied to the determination of both Rb and Cs, ion-exchange methods have been found to be more convenient. Briefly, using techniques similar to those described above under Sodium, Rb has been sought, but not found in samples of Na_2CO_3. The aforementioned sample (#3 in Table VIII) of Rb_2CO_3 was analyzed for Cs by ion exchange. Spectrochemical methods gave checking results at 0.02%.

SUMMARY

In general, activation analysis is especially useful in the analysis for certain elements difficult to determine by other means. Most elements when irradiated by the neutrons of a chain-reacting pile (or by the charged particles from an accelerator) give rise to artificially radioactive species that have their own characteristic modes of decay. The rate of decay and the radiation emitted are characteristic of the nuclide produced and will not be exactly duplicated by any other radionuclide. Thus, this specificity makes radioactivation

*Spectrochemical analysis indicated 0.08%.

analysis an unusual technique in that it is essentially free from interference by other elements. Also, once the irradiation has been completed, there is no danger of contamination as experienced in conventional analyses.

Neutron activation analysis furnishes a reasonably easy, sensitive, and accurate means for determination of the alkali metals. Coupled with precipitation methods and ion-exchange techniques, it constitutes probably the best method for determining small quantities of one or more of the alkalies in a variety of materials.

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