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For publication in Analytical Chemistry

UCRL-10324

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

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ABSTRACT

He³-activation analysis, by use of the Hilac at the Lawrence Radiation Laboratory in Berkeley, has been found ideal for oxygen determination. Oxygen can be determined in as low a concentration as 0.001% in a few hundred μg of matrix material.

Interference by activation of other elements can be restricted by control of the bombarding energy of the He³ particles. This makes the method applicable to the analysis of fissionable actinides (because only small amounts of material are available).

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THEORETICAL CONSIDERATIONS

INTRODUCTION. The direct determination of microamounts of oxygen remains a difficult analytical problem. Different methods were elaborated upon with more or less success and under different experimental conditions: vacuum-fusion methods (1-4), isotopic methods (5-9), carrier-gas techniques (10), and others (11-12).

Since activation analysis offers a sensitive and nondestructive method for many elements, as shown in several review articles (13-16), a number of activation methods have been proposed for oxygen. Those methods employing neutrons (17-26) are impractical in our case, because of fission which complicates in many senses the detection and counting problems.

Charged-particle reactions induced by protons (27), deuterons (28-29), α particles (30), or γ activation (31-35) are either inapplicable or of low sensitivity.

ACTIVATION BY He^3 . A suitable activation analysis was proposed by S. S. Markowitz and J. D. Mahony (36). They used He^3 bombardments for the determination of oxygen in Al or Be. Mylar sheets were used as monitoring foils. The nuclear reactions involved are either exothermic or slightly endothermic, and have a rather large cross section. The following are reactions of practical use:

and

A count of the ^{18}F can be made either by β^+ counting or by γ detection of the annihilation radiation.

The approximate cross section of both reactions together is about 400 mb at an energy of 7.5 MeV, as determined by Markowitz and Mahony. They determined the σ over a wide range of energy, which gave the excitation function.

Oxygen analyses performed by these authors and further analyses of Th foils by Mahony and S. B. Hingorani (37) were done on large samples of previously prepared foils, with Mylar sheets used as beam monitors. Furthermore, the metallic foils were thin enough to be used in thin-target irradiation.

For more general application to the actinide metals, the experimental setup had to be changed extensively, since metallic foils of the heavier transuranides are not available and samples of 1 mg represent an upper limit. To maintain adequate sensitivity, beam intensities must be increased and Mylar eliminated because of its poor thermal stability.

Moreover, the heavier metals were prepared essentially as "thick target" samples, requiring an increase in beam energy to obtain adequate sub-surface activation; this had the disadvantage of increasing the activation of nonoxygen impurities. A beam energy up to 12 MeV can activate nuclides with A up to 75 ($Z = 36$), (38).

EXPERIMENTAL

PRELIMINARY EXPERIMENTS. Americium metal pellets were flattened by pressing them between pieces of tool steel and their surface area was measured under a microscope.

As Mylar could not be used, quartz discs of known oxygen content were employed as beam monitors. By placing several monitors in the immediate neighborhood of the sample, it was shown that enormous beam inhomogeneities could appear. Flux differences up to ratios of 1/100 were noted within 2.25 cm² of beam cross section in a beam of 7/8 in. diam. This showed the necessity of beam monitoring near the sample.

Encapsulation of the very alpha-active samples also proved difficult. In the previous work (36-37), the Th foils were irradiated in plastic bags but, when using the smaller samples and higher beam intensities, it was necessary to change to Pt capsules. This encapsulating technique was worked out by Billy Abram of our Health Chemistry Department.

After irradiation, the sample was counted in a γ spectrometer; to avoid alpha contamination, the Pt seal was not opened. The γ spectra were very complicated owing to many impurities which had been activated in the Pt. The estimated oxygen content was also too high, because of oxygen in the Pt.

For accurate work, the Pt seal must be removed in a gloved box after irradiation. Then, to avoid contamination, the active sample is sealed in a plastic sheet before it is counted.

Another difficulty may arise because of overloading the γ spectrometer with the low-energy γ rays from Am²⁴¹, which may overload the electronic equipment. Overloading can be avoided by use of thick Sn absorbers (1/8 mil or 3.56 g/cm² ± 0.3%). The intensity of the annihilation radiation is reduced by only a factor of 1.36.

FINAL EXPERIMENTAL SETUP. Beam Monitoring and Sample Sealing. Since the beam must be monitored in the sample area for accurate analyses, thin sheets of material of known oxygen content were required. Anodized Al of 1-mil thickness ($6.74 \text{ mg/cm}^2 \pm 1\%$) proved suitable. Anodized foil was supplied by H. P. Robinson (Chemistry Department, Lawrence Radiation Laboratory), but its oxygen content was not known. The oxygen content was determined by activation analysis against quartz-foil monitors. These were of a few mg/cm^2 thickness (determined by weight and surface-area measurement in each case) and 1/8-in. diam. They were made in the glass shop of the Radiation Laboratory. However, they were brittle and difficult to handle and were of no direct use for further activation analysis.

The calibration of the anodized Al gave an oxygen content of 0.49 mg/cm^2 within 10%. This figure agrees fairly closely with that calculated for Al_2O_3 from microscopic measurement of the thickness of the oxide layer.

Circular flakes of 62.5 mil ($1.59 \text{ mm} \pm 1\%$) diam. were cut from this material and put on top of the sample to be analyzed. A thin Al absorber of the same diameter was placed between the sample and the monitoring foil to avoid radioactive contamination. The three pieces were sealed together in a Pt seal (Fig. 1). The assembly is about 1/8-in. diam.

Target Assembling and Beam Reading. Since a well-focused beam was required, a special target holder was designed by A. Ghiorso's group to follow the focusing quadrupole magnets of the Hilac (heavy-ion linear accelerator). The target holder is designed for both water and He-gas cooling of the sample and degrader foils to avoid melting or sublimation of the target materials. (Beam intensities up to 1 or 2 μA may be reached.) The target chamber wherein the target-holder is mounted and flushed with He gas, is separated from the

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Fig. 1. Platinum Seal:

- (1) Anodized Al beam monitor of $1.59 \text{ mm} = 0.0625$ in. diameter.
- (2) Plain Al absorber (same size as monitor).
- (3) Thick-target sample (different configuration and smaller than monitor).
- (4) Platinum seal.

accelerator vacuum tank by a Be window of 6-mil thickness. The beam is collimated to 1/8-in, thick by an Al collimator, and a relative beam reading can be obtained from an Ni foil. Absolute determination of beam intensities is done by calibration of the Ni-foil reading against the Faraday cup reading in a dummy run, without target. Direct Faraday cup readings cannot be made as the target intercepts the beam completely.

To be sure that the beam strikes the target fairly homogeneously, the beam is wobbled within the 1/8-in. collimator.

CALCULATIONS. Range-Energy Relations. The excitation function of the activation reaction has been studied extensively by Markowitz and Mahony who degraded the He^3 beam with Al foils. They computed the range-energy relation for He^3 in Al from the Al-proton range.

Since no He^3 range-energy curves were found in the literature for quartz, Be, Ni, Pt, Th, U or the transuranides, all these had to be calculated from the proton ranges or from α ranges in the different materials.

The formulas used for these calculations were of the form

$$R_{\text{He}^3}(E) = \frac{3}{4} R_n\left(\frac{E}{3}\right) + 0.25 \text{ mg/cm}^2 \quad (1)$$

and
$$R_{\text{He}^3}(E) = \frac{3}{4} R_\alpha\left(4 \frac{E}{3}\right). \quad (2)$$

For most cases, agreement within 5% was found; a few were only within 10%. Better curves could be computed from the direct theoretical formulas.

Derivation of Activation Formulas. The classical activation formula, used by Markowitz and Mahony, is applicable only when the foils have a surface area larger than the beam cross section.

Under the conditions of our experiments, the target cross-sectional areas are much smaller than the homogeneous-beam cross sections. In these cases, the activities are dependent upon the sample surface. The total activity $(-\frac{dN}{dt})_0$ of the irradiated sample now is

- (a) A function of the target surface area (the number of target nuclei is directly proportional to the surface area), and
- (b) A function of sample thickness (the number of target nuclei is directly proportional to the thickness, and the thickness, which degrades the beam energy, affects the mean cross section).

The activation formula now takes the form

$$(-\frac{dN}{dt})_0 = SN\Phi \bar{\sigma} \left[1 - \exp\left(-\frac{0.693\tau}{T_{1/2}}\right) \right], \quad (3)$$

where $(-\frac{dN}{dt})_0$ is the total activity at the end of the bombardment,

S is surface in cm^2 ,

N is number of particular target nuclei per cm^2 contained in the sample,

Φ is average flux or beam intensity per cm^2 , expressed in incident particles per sec and per cm^2 ,

and $\bar{\sigma}$ is the mean cross section, which is dependent on the energy.

As N is proportional to the number of mg/cm^2 of target atoms ($N = \alpha a$), where a is the quantity of the isotope in mg/cm^2 , and α a constant specific for O^{16} , Equation (3) becomes

$$\left(-\frac{dN}{dt}\right)_{\text{O}} = S \alpha a \Phi \bar{\sigma} \left[1 - \exp\left(-\frac{0.693\tau}{T_{1/2}}\right)\right] \quad (4)$$

The same equation can be written for the beam monitor. Hence,

$$\frac{\left(-\frac{dN}{dt}\right)_{\text{O}_m}}{\left(-\frac{dN}{dt}\right)_{\text{O}_s}} = \frac{S_m \cdot \alpha_m \cdot a_m}{S_s \cdot \alpha_s \cdot a_s} \cdot \frac{\Phi}{\Phi} \cdot \frac{\bar{\sigma}_m}{\bar{\sigma}_s} \cdot \frac{\left[1 - \exp\left(-\frac{0.693\tau}{T_{1/2}}\right)\right]}{\left[1 - \exp\left(-\frac{0.693\tau}{T_{1/2}}\right)\right]},$$

$$\text{or } \frac{\left(-\frac{dN}{dt}\right)_{\text{O}_m}}{\left(-\frac{dN}{dt}\right)_{\text{O}_s}} = \frac{S_m \cdot a_m}{S_s \cdot a_s} \cdot \frac{\bar{\sigma}_m}{\bar{\sigma}_s} \quad (5)$$

where the index m means monitor and the index s means sample.

In this Equation 5, $\bar{\sigma}_m$ and $\bar{\sigma}_s$ are functions of the energy intervals of the He^3 particles and can be computed by graphical integration of the excitation function. The surfaces S_m and S_s are measured and a_m , the oxygen content of the beam monitor is known.

Thus, the amount of oxygen (in mg/cm^2) in the irradiated region of the samples (thick target) can be computed from

$$a_s = \frac{S_m}{S_s} \cdot a_m \cdot \frac{\bar{\sigma}_m}{\bar{\sigma}_s} \cdot \frac{\left(-\frac{dN}{dt}\right)_{\text{O}_s}}{\left(-\frac{dN}{dt}\right)_{\text{O}_m}} \quad (6)$$

The percentage is given by

$$\% = \frac{a_s \times 100}{b_s},$$

where b_s is the irradiated sample thickness in mg/cm^2 .

RESULTS AND CONCLUSIONS

Preliminary experiments with Th foils of 62.5-mil diam. and known oxygen content (0.6% by vacuum fusion analysis) showed that 0.5% oxygen could be easily detected in 1.07 mg of Th. In later experiments, 0.8% and 0.6% oxygen were determined in 150 μg and 450 μg of Am^{241} , respectively. An estimation of the sensitivity of the method shows that at least 0.001% oxygen in 200 μg of Am can be detected.

However, the accuracy of the method is only about 20%, since it is affected by the range calculations and the relative mean cross-section ratio. Furthermore, the oxygen content of the beam monitor is somewhat uncertain and may be inhomogeneous.

By this method, however, the oxygen is determined independent of absolute beam-intensity measurements and absolute cross-section values.

ACKNOWLEDGMENTS

The author thanks Professor B. B. Cunningham and his co-workers for their hospitality and helpful discussions about the work.

Acknowledgments are also due Mr. Albert Ghiorso and his group for providing their accelerating facilities, and their complete willingness in adapting and redesigning their equipment for this work.

Special thanks are due the Health Chemistry people for the help they supplied, especially to Billy Abram for designing and mounting the target capsules.

This work is financially supported by the "Interuniversitair Instituut voor Kernwetenschappen" of Belgium.

Work also supported in part by the U. S. Atomic Energy Commission.

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