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Chemistry

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MASTER

DETERMINATION OF OXYGEN BY NEUTRON
ACTIVATION ANALYSIS

W. O. Tucker

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** Contract W-7405 eng 26



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Nuclear Division

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ABSTRACT

Activation analysis, using 14-mev neutrons, has been used to determine oxygen in a variety of materials at concentrations from less than 100 ppm to 30 percent. The system uses a sealed-tube neutron generator with a pneumatic transfer system and dual-axis rotation during the irradiation period.

The relative percent error for a single determination (95 percent confidence level) varies from ± 18 percent at the 70-ppm level to ± 3.4 percent at the 1-percent level and ± 2.6 percent at the 30-percent level.

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SUMMARY

In neutron activation analysis, the sample material is loaded into a container and exposed to a 14-mev flux of 3×10^8 neutrons/cm²-sec for 30 seconds. Characteristic beta and gamma radiation from the activated oxygen is counted by NaI (TI) scintillation detectors. Total time for a complete oxygen analysis is approximately 30 minutes.

The relative percent error (95 percent confidence level) ranges from ± 18 percent at the 70-ppm level to ± 3.4 percent at the 1-percent level and ± 2.6 percent at the 30-percent level. Significant interferences are limited to fluorine, boron, and the fissionable elements.

INTRODUCTION

The determination of oxygen in most materials is time consuming and often an inexact procedure. In addition, the sample is generally destroyed in the process. A method capable of overcoming these difficulties is found in the neutron activation analysis procedure.

Development of small, relatively low-cost accelerators capable of producing usable fast neutron fluxes of 10^8 n/cm²-sec has made the method practical for semiautomated oxygen analyses on a production basis.

Various systems have been described for the determination of oxygen by fast neutron activation analysis.⁽¹⁻³⁾ The present system utilizes a Kaman Model A-710 neutron generator with a flux of 3×10^8 neutrons/cm²-sec at the sample irradiation position. Sensitivity is approximately 340 counts per milligram of oxygen, with a counter background of 20 counts.

OXYGEN BY NEUTRON ACTIVATION ANALYSIS

THEORY OF ANALYSIS

Neutrons having energies of 14 mev are produced by accelerating deuterium ions through a potential of 140 kv into a tritium target. The reaction is:



Oxygen in an irradiated sample forms N-16 by means of the O-16 (n,p) N-16 reaction. The N-16, in turn, decays by beta emission (a half life of 7.35 seconds) to excited states of O-16 which immediately go to the groundstate with the emission of 6.1 and 7.1-mev gamma rays.

The amount of oxygen in the sample is determined by counting the 6.1 and 7.1-mev gamma rays along with part of the beta radiation, and comparing the count to that from a standard that is irradiated and counted in exactly the same manner. A lucite reference is irradiated along with each sample or standard. Since the same piece of lucite is irradiated each time, counts from oxygen in the reference provide a normalizing factor to correct for time variation of the flux.

INSTRUMENTATION

A diagram of the activation analysis system layout is presented in Figure 1. The neutron generator is located in a pit in the basement while the counting apparatus and control console are one floor above. The pit installation places the neutron generator at the bottom of a ten-foot-deep well with earth furnishing most of the neutron shielding. Shielding directly above the generator is provided by a four-foot thickness of polyethylene. Both the generator and shielding are suspended on a rigid frame connected to a hoist for removing the generator from the pit. Figure 2 shows the generator, shielding, and supporting frame suspended over the pit.

This type of layout requires a transfer system for moving the sample between the irradiation point and counting equipment. The 7.35-second half life of N-16 requires that the transfer time be short. This system utilizes two 1/2-inch-diameter transfer tubes that are 52 feet in length. One tube carries the polyethylene sample container while the other carries the lucite reference. Nitrogen gas at a pressure of 40 psi propels the containers through the transfer tubes in less than two seconds.

The neutron generator is a Kaman Nuclear Model A-710 with a sealed accelerating tube. The tube consists of a deuterium gas reservoir, an ion source, an accelerating and focusing section, and a titanium-tritium target. Deuterium gas is released from the reservoir and ionized by a Penning ion gage-type ion source. The ions are then accelerated by a 140-kv potential into the target. A beam current of 0.8 milliampere produces a usable flux of approximately 3×10^8 neutrons/cm²-sec.

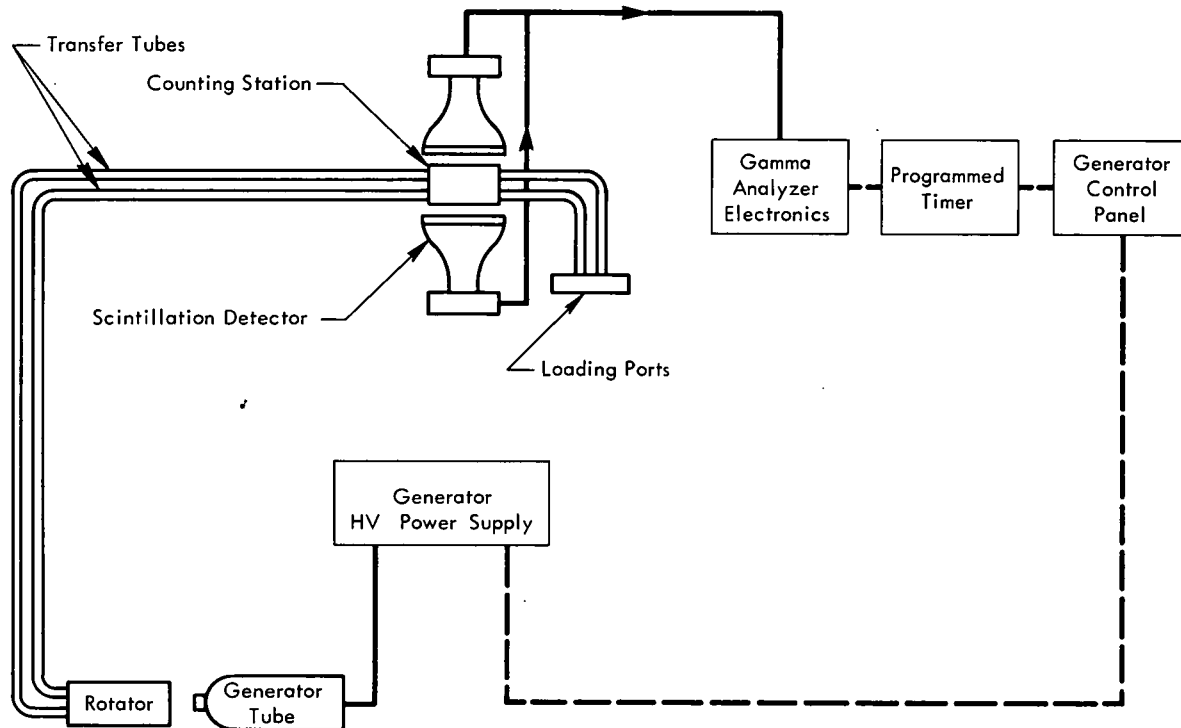


Figure 1. PRINCIPAL COMPONENTS OF THE NEUTRON GENERATOR AND ANALYZER.

A rotator which spins the sample and reference about both their axes improves the uniformity of irradiation. This type of rotator carries both containers through the same volume of space in the neutron beam so that both are exposed to essentially the same neutron flux.

The transfer tubes pass through an aluminum counting station containing pneumatically operated pins capable of blocking either transfer tube. The pins are raised to allow a container to pass on its way to be irradiated. Following irradiation, the appropriate pin stops the container and holds it in position during the counting period.

Two NaI (Tl) scintillation crystals (2" T x 4" D), mounted on RCA 8054 photomultiplier tubes, are positioned facing each other with the counting station between them. The photomultipliers are operated from a common high-voltage power supply. Both detectors and the counting station are enclosed in a shield built of lead bricks. This barrier provides four inches of shielding on the sides with two inches on the top and bottom. Figure 3 gives a detailed view of the detector and counting station arrangement.

Output pulses from the photomultipliers are fed in parallel into a Hamner Electronics Model NB-12 preamplifier. One of the photomultiplier tubes has a gain control so that the tube outputs may be matched. Amplification is provided by a Hamner Model NA-11 linear amplifier; energy discrimination is by means of a Hamner Model NC-11 single-channel analyzer operating in the differential mode. The window is set

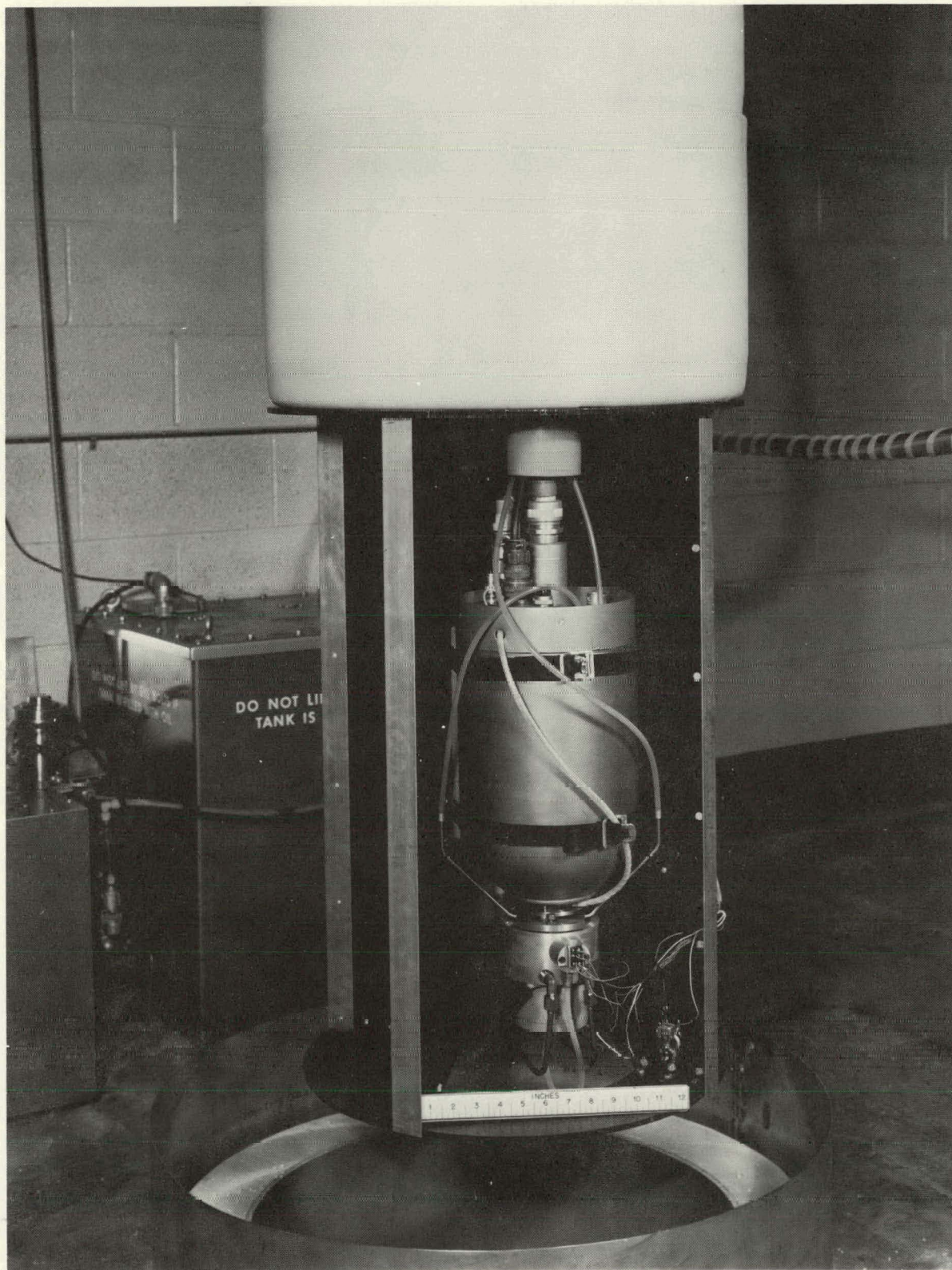
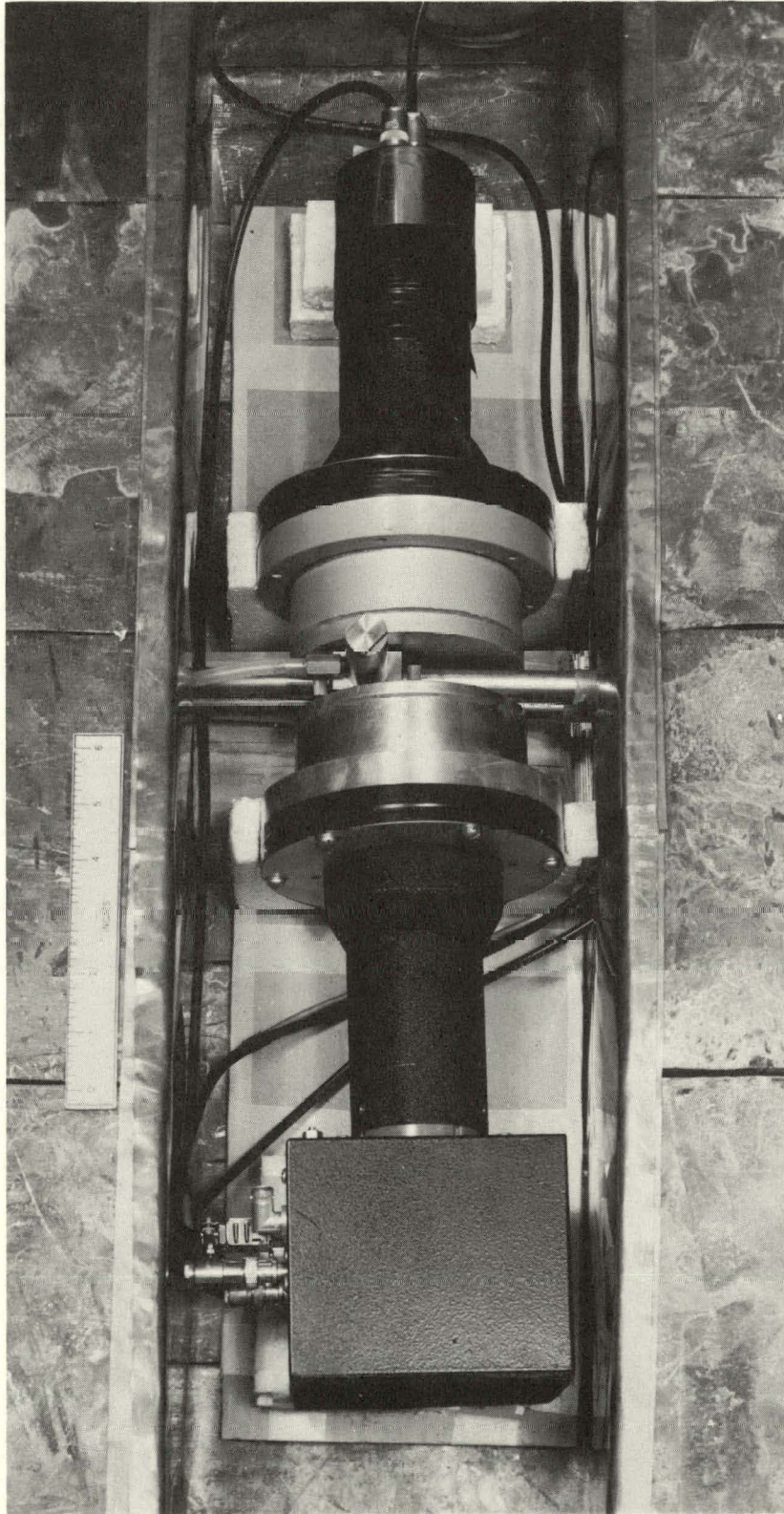


Figure 2. NEUTRON GENERATOR HEAD AND SUPPORT.

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Figure 3. DETECTORS AND COUNTING STATION.

to pass gamma energies from 3.5 to 10 mev, allowing some of the higher-energy beta radiation from the decay of N-16 to be counted in addition to the 6.1 and 7.1-mev gamma rays. The 10-mev upper limit discriminates against counts from high-energy cosmic rays.

Counts are recorded in one of two Hamner Model NS-11 scalers. The sample and reference are counted in sequence using the same detectors and single-channel analyzer. The analyzer output is automatically switched so that one scaler records counts from the sample and the other records counts from the lucite reference.

The sequence of events is controlled automatically by a Kaman Nuclear programmed timer which has adjustable timers for transfer time, irradiation time, delay between irradiation and count, and counting time.

Figure 4 presents a view of the control console for the neutron generator.

PROCEDURE

Samples considered in this study are primarily of two types: (1) powders (beryllium, organics, or hydrocarbons) or beryllium metal turnings, and (2) solid beryllium metal pieces. Samples in the form of powders or turnings are loaded into previously tared sample containers. A gross weight is obtained and the sample weight found by difference. The cylindrical sample containers, available from Kaman Nuclear, are made of low-oxygen polyethylene and hold about two cubic centimeters of sample. Oxygen content of the container is approximately 0.3 milligram.

Some metal samples, particularly those of low oxygen content, are run in the form of a solid piece (1 1/2" x 1/4" x 1/4"). This type of sample is fitted with a polyethylene cap on each end to guide it through the transfer tube. The caps, cut from the low-oxygen-content containers, reduce the blank by approximately one half. A sample container and a solid sample fitted with end caps are shown in Figure 5.

A prepared container is loaded into the transfer system at a loading port on the control console and the automatic irradiation-counting cycle initiated. Both the sample and reference are simultaneously propelled through the transfer system to the rotator and the neutron beam turned on. Following a 30-second irradiation, the rotator stops and the beam is turned off. The sample is transferred to the counting station and stopped in the counting position by an arrestor pin. After a 30-second count, the pin retracts and the sample returns to the loading port. At the same time that the sample moves to the loading port, the reference is transferred to the counting station. It also is counted for 30 seconds before being returned to the loading port. Total time required for the cycle is 104 seconds.

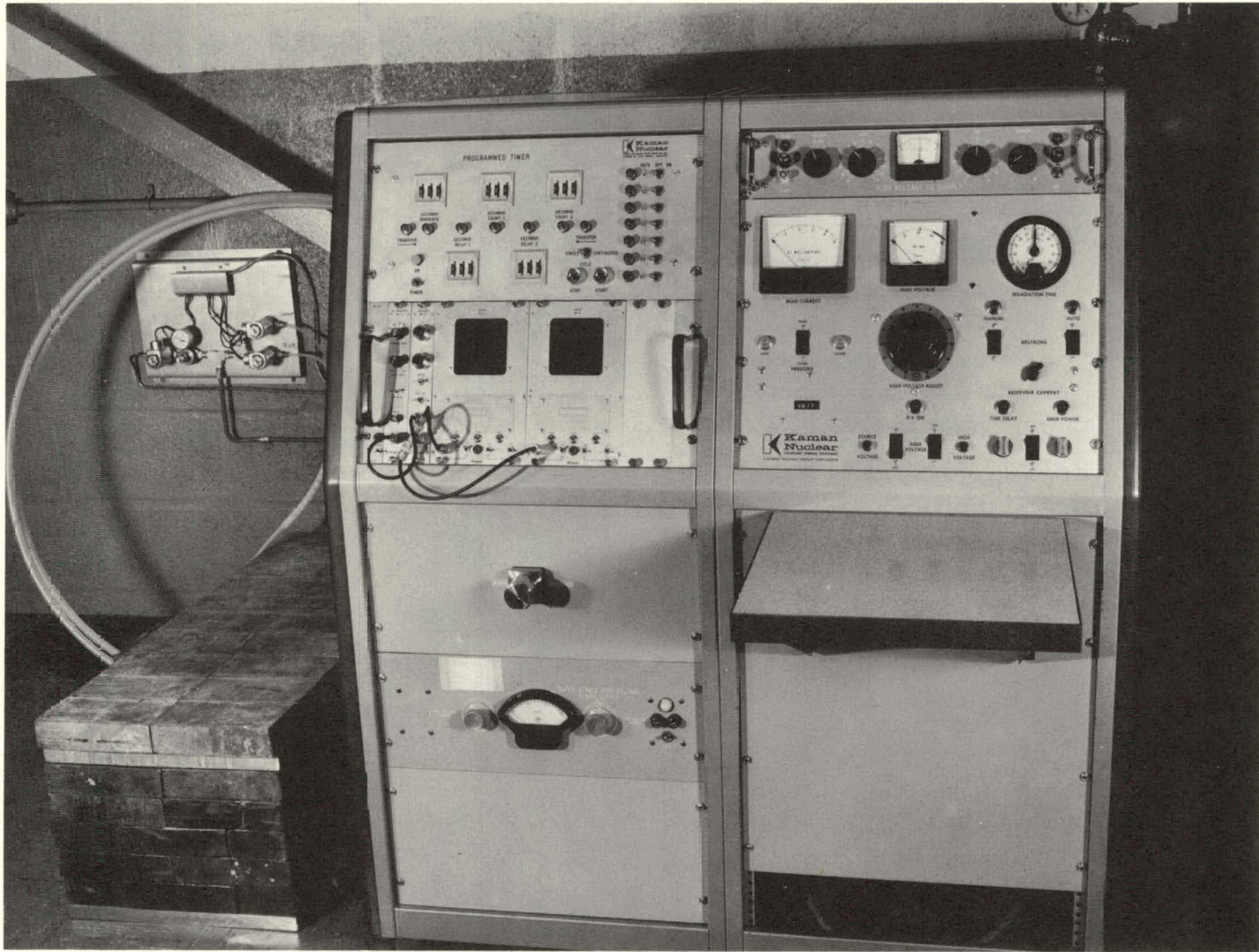
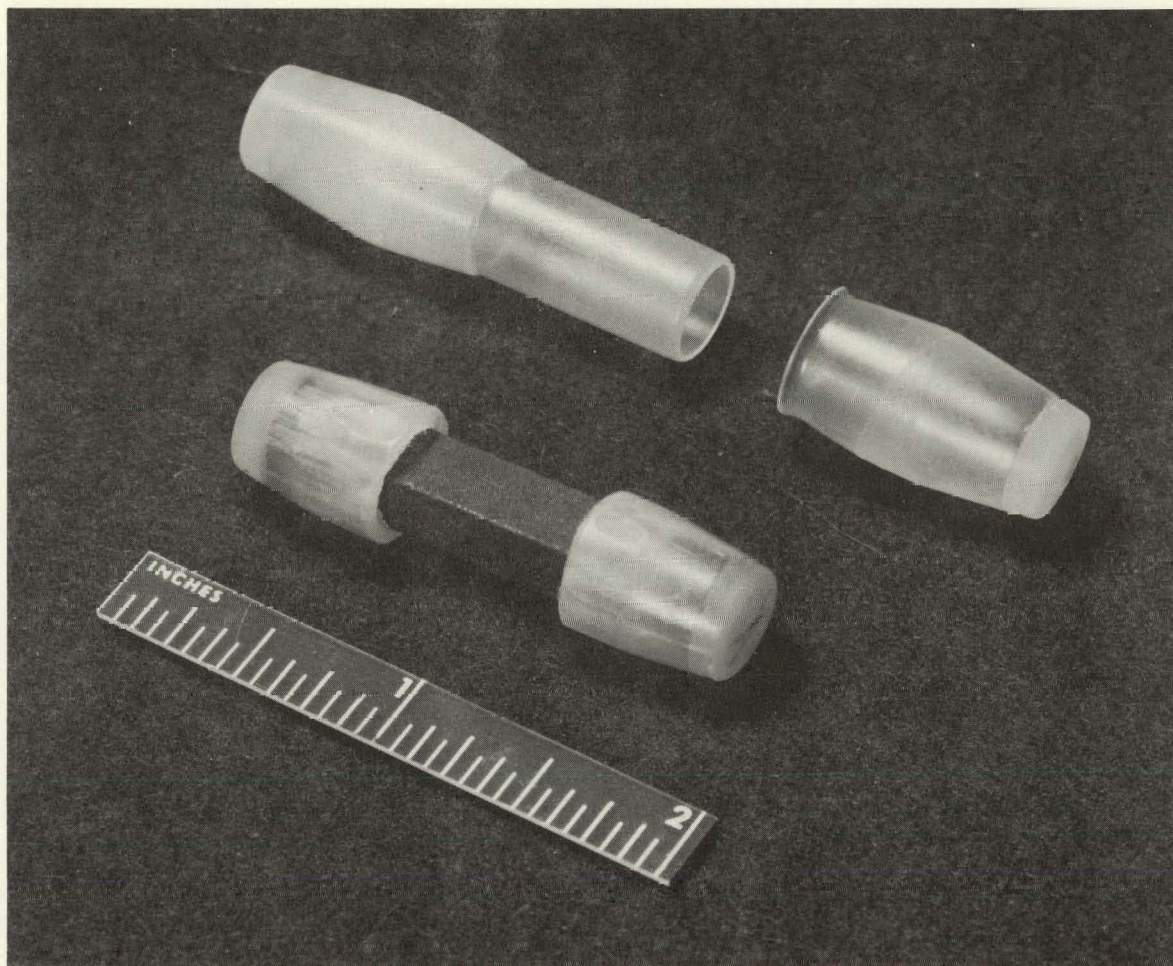


Figure 4. NEUTRON GENERATOR CONTROL CONSOLE.

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Figure 5. SAMPLE CONTAINERS FOR THE NEUTRON GENERATOR.

Samples are irradiated and counted twice with the exception of the low-level (< 250 ppm) ones which are cycled four times. The programmed timer can be operated in a "cycle" mode in which the sample and reference are repeatedly irradiated and counted. Counts from the repetitive irradiations are accumulated in the scalars. This type of operation is useful for low-level samples which produce few counts per irradiation. Results quoted in this report are derived from single irradiations for higher-level materials, and from cumulative counts of four cycles for low-level materials.

Since the polyethylene sample container constitutes approximately 0.3 milligram of oxygen, it is necessary to irradiate and count an empty container for a blank value. A 1/8-inch hole drilled in each end of the container allows the nitrogen transfer gas to displace the atmospheric oxygen that is trapped inside. For samples run in the end caps, a blank value is obtained using the ratio of the end cap weight to the empty container weight.

A sample container loaded with powdered beryllium metal (F-224 from New Brunswick Laboratories) is used as a standard. The full container holds 2.05 grams of standard containing 21 milligrams of oxygen.

For each sample, standard, or blank that is irradiated, the S/R ratio is determined. (S is the count from oxygen in the sample, standard, or blank; R is the corresponding count from the lucite reference.) Both S and R are corrected for counter background. Thus, S/R gives a normalized number that is independent of the neutron flux variation.

The weight of oxygen in a sample is then calculated from the following relationship:

$$\text{Oxygen Weight} = \frac{1}{C} (S/R - B),$$

where:

- S/R represents the normalized sample ratio, and
- B the S/R ratio for an empty sample container.
- C will be equal to $\frac{1}{W} (S/R - B)$ for a standard containing a known weight, W, of oxygen.

Both the empty sample container and standard are irradiated and counted at least five times to obtain average values of B and C.

RESULTS AND DISCUSSION

Seven standards containing from 1 to 30 milligrams of oxygen were made by filling sample containers with a mixture of dry reagent-grade benzoic acid and carbon from ground spectroscopic rods, or with New Brunswick Laboratories' beryllium standards F-224 or F-225. Each of these standards, an empty container blank, and a carbon blank were irradiated and counted. The S/R value was calculated for each standard and this number corrected for the appropriate carbon or empty sample container blank. A graph was then plotted of S/R - B vs milligrams of oxygen. The results, given in Figure 6, indicate that the system has a linear response and that the standards from the New Brunswick Laboratories check well with the benzoic acid standards. As a consequence of this study, the F-224 standard was chosen as a working standard for the system. It serves equally well for beryllium and for materials having densities close to that of beryllium.

It has been found that the precision of an analysis depends somewhat on the physical state of the sample. This problem was studied by Anders and Briden⁽¹⁾ and shown to be caused by a shifting of the sample material inside the container. To determine the extent to which this movement was occurring in the present system, a series of 15 irradiations was performed on each of two samples. One was a solid beryllium piece fitted with end caps; the other was a container filled with New Brunswick Laboratories' F-224 standard beryllium powder. Both samples contained approximately

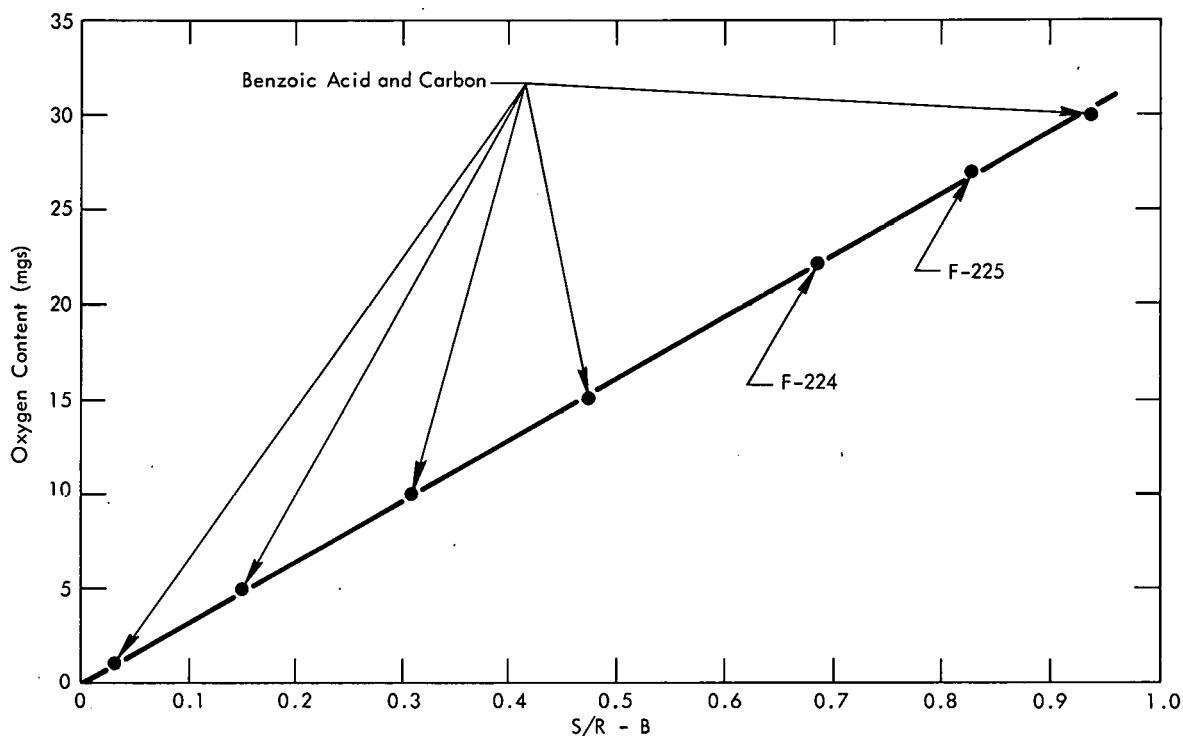


Figure 6. CALIBRATION CURVE FOR OXYGEN.

the same amount of oxygen at the one percent level so that count statistics would predict the same level of precision. The relative percent errors (95 percent confidence level) were ± 5.1 and ± 3.4 percent for the powder and solid, respectively.

These results indicate that there probably was some shifting of the powder sample. Thus, care must be taken to tightly pack and completely fill containers carrying material which might shift inside the container.

Relative percent errors (95 percent confidence level) for a single determination vary from ± 18 percent at the 70-ppm level to ± 3.4 percent at the 1-percent level and ± 2.6 percent at the 30-percent level.

Prior to the use of activation analysis, this laboratory determined oxygen in beryllium by the bromine-methanol process. Oxygen in hydrocarbons and organic materials was determined by difference; that is, all other constituents were determined by chemical methods and the remainder of the sample was assumed to be oxygen. These types of samples are now analyzed by activation analysis. Table 1 gives a comparison of the oxygen content of organics and hydrocarbons by activation analysis and by difference. Figure 7 compares the oxygen analyses by the bromine-methanol method with that by activation analysis.

Results of the analyses by neutron activation were found to be, on the average, seven relative percent lower than those by the bromine-methanol method. This difference

Table 1
 PERCENT OXYGEN IN HYDROCARBONS AND ORGANIC MATERIALS
 DETERMINED BY DIFFERENCE AND BY NEUTRON ACTIVATION

Sample Number	Oxygen Content (%)	
	By Difference (1)	By Activation Analysis
1	3.5	3.46
2	8.7	7.92
3	28.3	27.80
4	28.6	28.30
5	28.6	27.72
6	28.5	28.49
7	29.2	28.80
8	14.1	12.98
9	33.3	33.42
10	1.2	1.35

(1) This method consists of a chemical analysis for other elements in the sample and calculation of the percent oxygen by difference.

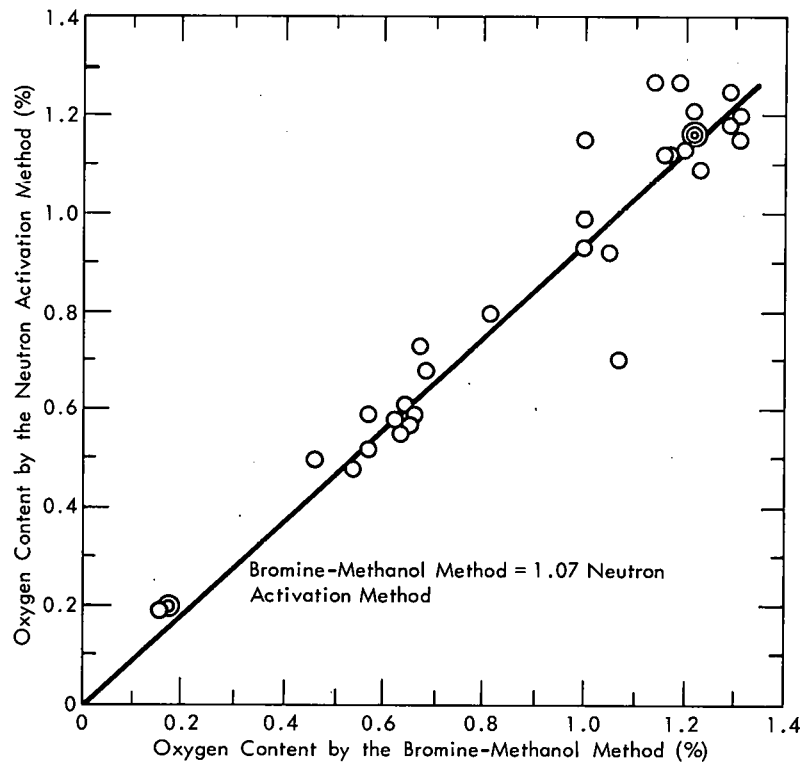


Figure 7. NEUTRON ACTIVATION VERSUS BROMINE-METHANOL METHODS OF OXYGEN ANALYSIS OF BERYLLIUM METAL SAMPLES.

was attributed to the fact that the bromine-methanol process determines oxygen as insoluble beryllium oxide. Thus, any other insolubles present would also appear to be beryllium oxide, causing a possible high bias.

With a lower-level-energy discriminator setting of 4.0 mev, almost all interfering radiation is eliminated except that from boron, fluorine, and any of the fissionable elements. Of these possible interfering elements, only boron and uranium have been encountered.

A study was made to determine to what extent boron and uranium would interfere. A sample container was filled with beryllium powder and the oxygen content determined. Normal uranium was added and the sample again analyzed for oxygen. It was found that one percent uranium in the sample caused an apparent 0.23 percent oxygen content. A similar experiment indicated that the presence of boron at the one-percent level would cause an apparent 0.15 percent oxygen content.

Many of the samples analyzed for oxygen are relatively pure beryllium or hydrocarbons which contain only traces of other elements. With this type sample, the single-channel analyzer discriminator can be set at 3.5 mev for better sensitivity without encountering any significant interferences.

The amount of oxygen from the air inside an empty sample container is approximately one milligram. This amount includes oxygen from the air occupying the volume of the closed container as well as from air trapped in the tight-fitting cap and compressed into the container volume when the cap is pressed onto the body of the container.

Since, most of the air is displaced when a container is filled with sample, generally no correction is made for the remaining air. When samples are analyzed which do not completely fill the container, the loading is done in an inert atmosphere. This method is also utilized for samples having an oxygen content less than 500 ppm.

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