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THE DETERMINATION OF OXYGEN BY FAST NEUTRON ACTIVATION ANALYSIS

by

Hugh P. Dibbs*

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SYNOPSIS

An account is given of the quantitative determination of oxygen by fast neutron activation. The method, which is both rapid and non-destructive, covers a very wide range of oxygen concentrations and is almost free from matrix effects. A description is presented of the shielding requirements and of the automatic system for sample transfer. Interference effects that may arise from the presence of certain elements are also discussed.

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DÉTERMINATION DE L'OXYGÈNE PAR L'ANALYSE D'ACTIVATION AU MOYEN DE NEUTRONS RAPIDES

par

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RÉSUMÉ

L'auteur donne ici un compte rendu de la détermination quantitative d'oxygène par activation au moyen de neutrons rapides. Le procédé, qui est à la fois rapide et non destructif, permet d'étudier une grande étendue de concentrations d'oxygène et il est presque libre d'effets de matrice. Il donne une description des écrans requis et du système automatique de manipulation des échantillons. Il traite aussi des effets qui peuvent se produire à la suite de la présence de certains éléments.

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INTRODUCTION

The determination of oxygen, in either combined or elemental form, is possible by a number of conventional techniques. However, these methods are often time-consuming, lead to the destruction of the sample, and are usually limited to one type of sample matrix, e.g. oxygen in metals (1) or oxygen in hydrocarbons (2). In recent years, a number of nuclear techniques have been developed for oxygen determination, based upon charged particle, photon or neutron reactions (3). One such technique, that has gained wide acceptance (4, 5, 6, 7), is based upon the fast neutron reaction

$$O\text{-}16 + n = N\text{-}16 + p.$$

The half-life of nitrogen-16 formed in the (n, p) reaction is only 7.31 seconds (8), so that the method is inherently rapid and non-destructive. The method also possesses the advantages of being almost free from interference or matrix effects and of covering a very wide range of oxygen concentrations. Since this technique depends upon a nuclear interaction, the total oxygen content of a sample is obtained, independent of its state of chemical bonding.

The determination of oxygen by fast neutron activation is performed by a comparison of the nitrogen-16 activity produced in an unknown sample with the nitrogen-16 activity produced in a standard sample of known oxygen content. The weight of oxygen in the unknown sample is then given by:

$$\text{Wt. of } O_2 \text{ in unknown} = \frac{\text{N-16 counts in unknown}}{\text{N-16 counts in standard}} \times \text{Wt. of } O_2 \text{ in standard}$$

The threshold value of the O-16 (n, p) N-16 reaction is 9.6 MeV; hence, neutrons of energy greater than this value are required for the reaction to take place. Although reactors produce high-intensity fluxes of neutrons, very few of the neutrons resulting from the fission of uranium have energies in excess of 10 MeV (9). A more convenient and economical source of high-energy neutrons is available in the form of a positive-ion accelerator (or neutron generator). A number of these relatively low-cost machines ($20,000) are now commercially available. They produce essentially mono-energetic, 14 MeV neutrons, in 4π yields of up to 2×10^{11} n/sec, and hence are ideally suited for use in oxygen determinations. The neutron generator may be operated by a small staff and is under direct control of the individual laboratory. Because of the different neutron energy distribution in a reactor, a neutron generator produces a usable high-energy neutron flux, comparable to a reactor of a much greater total neutron output (10).

EXPERIMENTAL TECHNIQUE

(a) Neutron Source

The accelerator used was a Texas Nuclear Model 150-1HV neutron generator. Neutrons are produced according to the reaction

$$H\text{-}2 + H\text{-}3 = He\text{-}4 + n + 17.6 \text{ MeV}$$

by the bombardment of a tritium-loaded target with deuterium ions that have been accelerated through a potential of 150 kV. The output of the generator is a function of the positive-ion beam current and also of the tritium concentration of the target. The latter decreases as a result of loss of tritium by thermal effects, as well as by charged particle bombardment. A half-life for the target may be defined as the time in which the neutron output decreases to half its value for a given beam current. For targets containing 3-5 curies/sq.in. of tritium, the half-life is about 240 minutes at 1 milliampere of beam current. The half-life of the target increases with decrease in beam current.

Shielding of the high-energy neutrons from an accelerator poses problems not dissimilar to those resulting from the shielding of a small reactor. The maximum permissible exposure for 14 MeV neutrons, for a 40-hour-week exposure, is $10 n/cm^2/sec$. (11). About four feet of concrete, or comparable shielding material, is required to reduce the neutron field to this level. The weight of the material required for effective shielding makes it necessary to use a basement room for housing the generator. A schematic diagram of the shielding arrangement is shown in Figure 1. The three-feet-cube water tank is used both for neutron shielding and as a thermalising medium in cases where a thermal neutron flux is required. For oxygen determination the irradiation position was such that there was a negligible amount of water between the sample and the tritium target.

(b) Counting Technique

The decay scheme of nitrogen-16 is shown in Figure 2, and is characterized by the emission of very-high-energy beta and gamma radiation. By counting either the beta or gamma radiation arising from nitrogen-16 in an unknown sample, and by comparing the count (under conditions of the same neutron flux) with the count obtained from the same radiation in a sample of known oxygen content, a quantitative measure may be made of the oxygen content of the unknown. A number of authors (4, 12) have successfully determined oxygen concentration by measuring the beta emission from nitrogen-16. However, this method is of limited scope, because the standard and the unknown have to be of the same material. In addition, allowance has to be made, by half-life determinations, for the presence of other beta emitters in the sample.

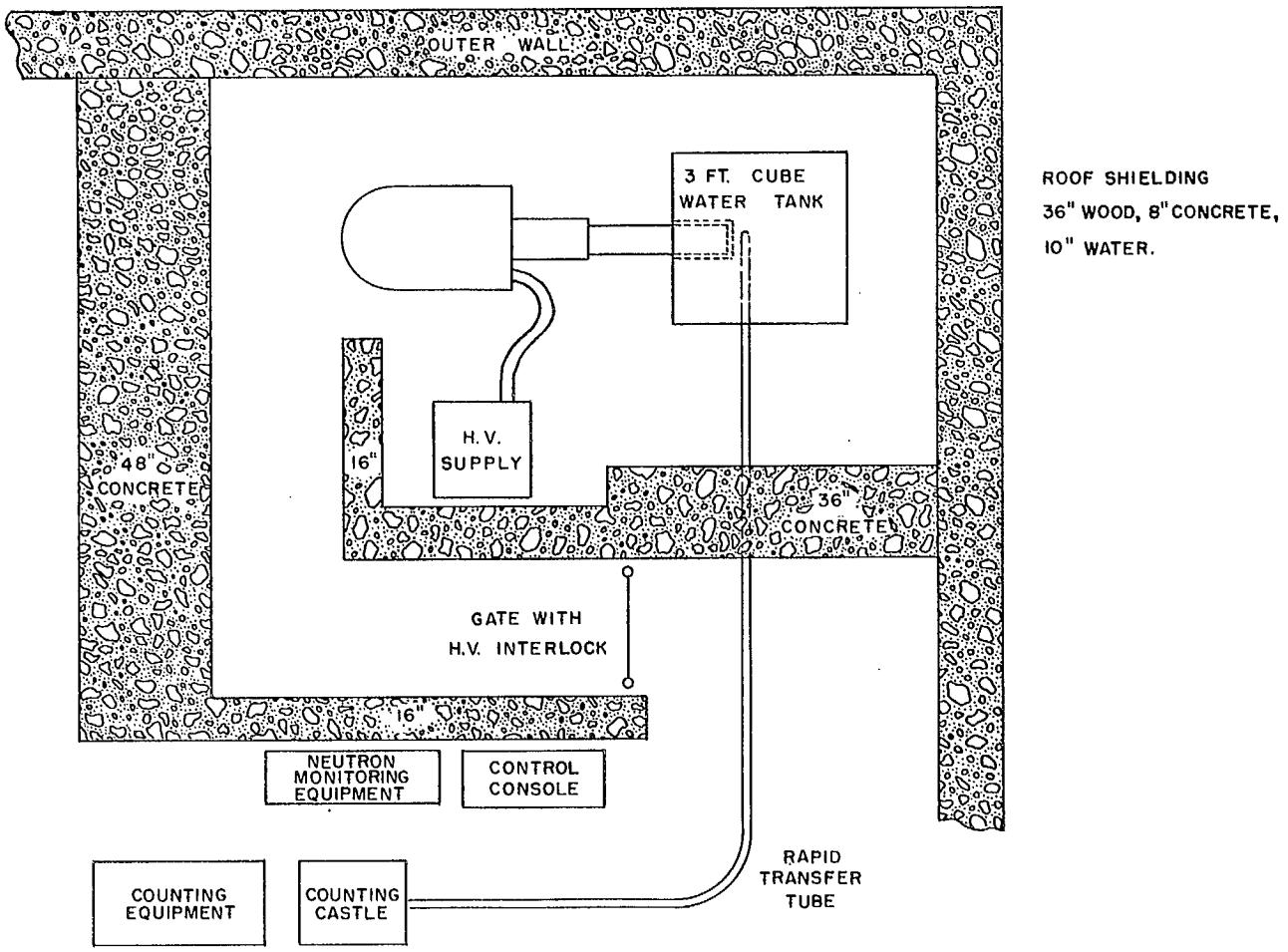


FIGURE I. SHIELDING FOR THE NEUTRON GENERATOR.

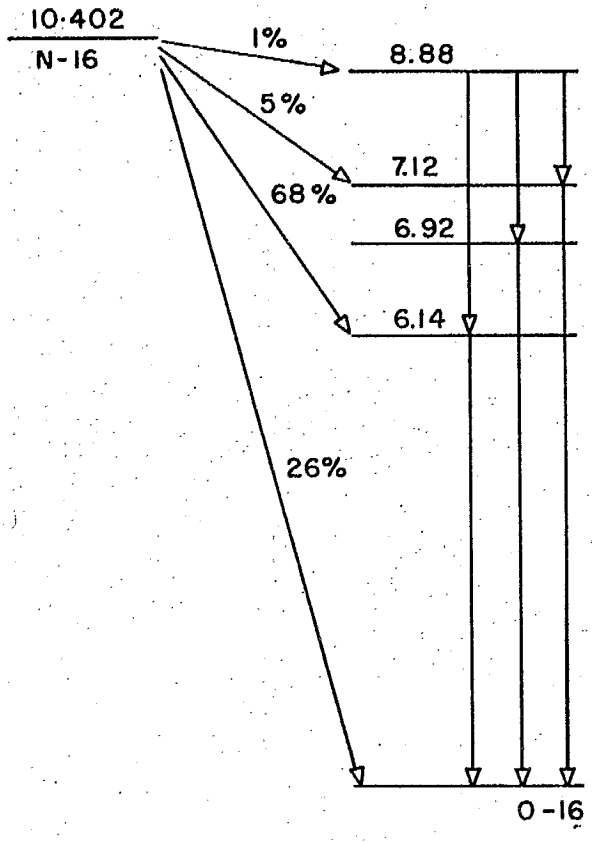


FIGURE 2. ENERGY LEVEL DIAGRAM OF N-16—O-16.

(Energy levels in MeV)

A simpler and more specific counting method is to count the high-energy gamma radiation from nitrogen-16 with a scintillation counter. The gamma radiation effectively ranges in energy from 4.5 MeV to 6.5 MeV (Figure 3), and is almost unique, in that, with the exception of short-lived uranium fission products and bremsstrahlung arising from some high-energy beta emitters, no other isotopes decay by photon emission in this energy region of the spectrum. Thus, in most cases, a single-channel gamma spectrometer, with a window setting of 4.5 MeV to 6.5 MeV, may be used for counting. A 2" x 3" NaI (Tl) scintillation detector, coupled to a Nuclear Chicago single-channel analyser (Model 1820) was used in the present work. For samples where interference was possible, the nitrogen-16 was counted simultaneously on a 100-channel gamma spectrometer. A block diagram of the system is shown in Figure 4.

The time of neutron irradiation for the determination of oxygen is established by the relationship governing the build-up of induced activity with time, under conditions of constant neutron flux (13). This relationship is shown graphically in Figure 5. Irradiation times of greater than five to six half-lives lead only to a negligible increase in induced activity and hence in analytical sensitivity. The rate of decay of nitrogen-16, after irradiation, follows a complementary curve to that of the build-up of nitrogen-16 during irradiation; i.e., after a decay of six half-lives, less than 2% of the initial activity remains. For these reasons the times of irradiation and measurement were chosen as 40 seconds.

(c) Transfer System

The short half-life of nitrogen-16 (half-life 7.31 seconds) necessitates a system to transfer the sample rapidly for counting after irradiation. This was accomplished with a pneumatic facility, shown in Figure 6. It is made of 3/4" I.D., rigid polyvinyl chloride tubing. This tubing may be bent by heating to 80°-90°C. Dry air, at a pressure of about 60 p.s.i., is used to blow the sample into the generator room for irradiation, and after irradiation, to return it for counting. The air pressure, in each case, is admitted to the transfer tube through a solenoid valve (Versa Products Company, Inc. Model VSG-4322). The time during which each solenoid valve is open is controlled by a timer (six seconds full-scale) that may be set to 0.1 second. Transit times for the 35 feet of travel between the counter and the irradiation position depend on the sample weight and are of the order of one second. For very heavy samples, the air pressure in increased to maintain transit times at about this value.

To perform oxygen analysis on a routine basis, it is necessary to have a supply of sample containers that ideally should be cheap, contain no oxygen, and be of uniform construction. The containers used in this work were polythene vials, polythene having been shown to have the smallest

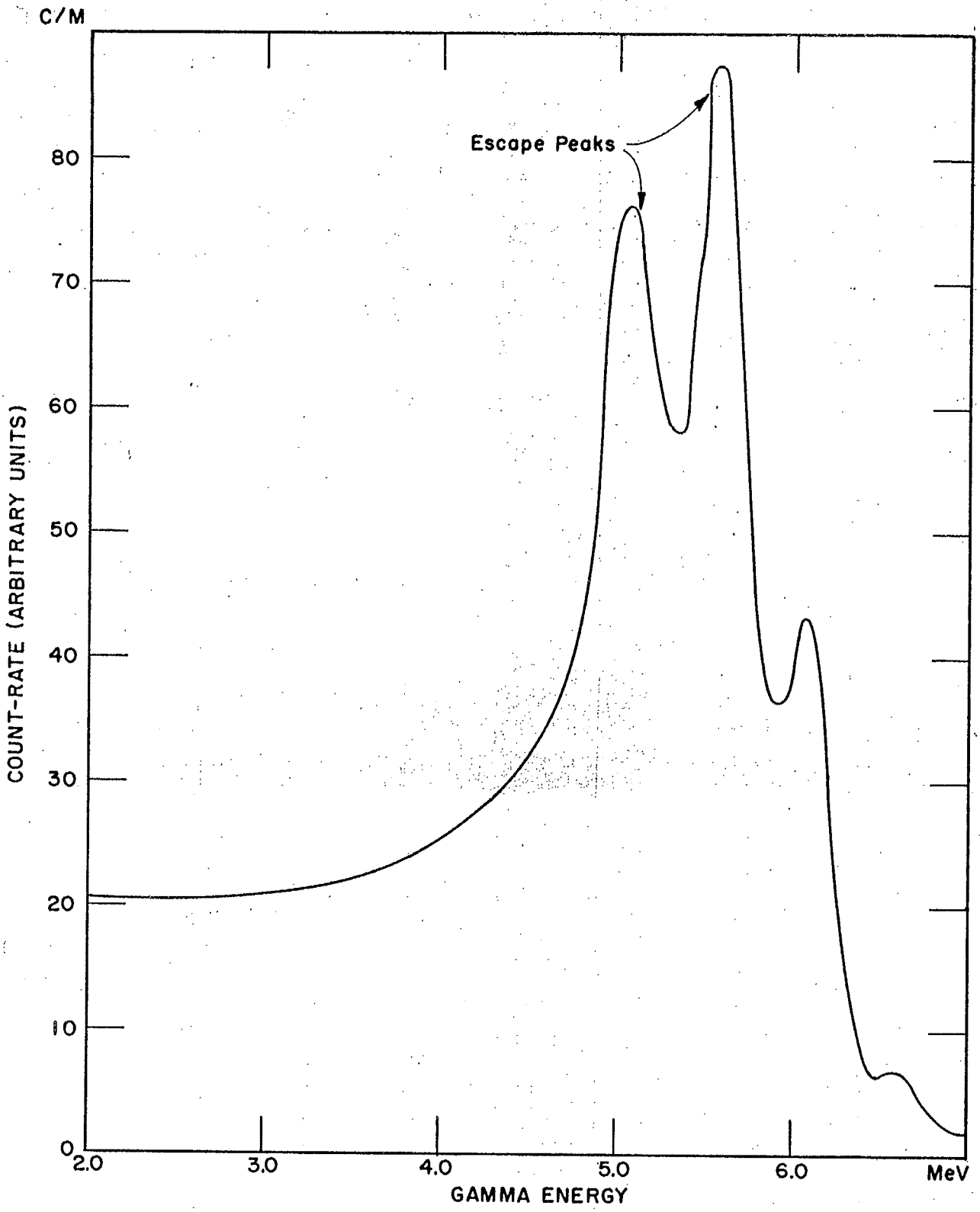


FIGURE 3. GAMMA SPECTRUM OF NITROGEN-16.

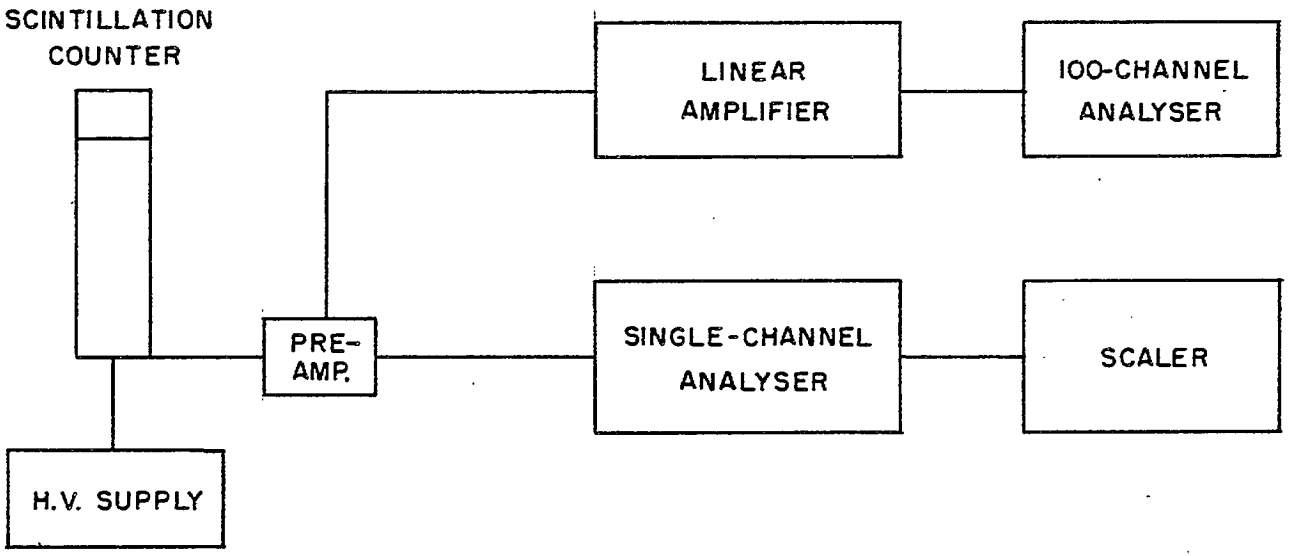


FIGURE 4. BLOCK DIAGRAM OF NITROGEN-16 MEASUREMENT SYSTEM.

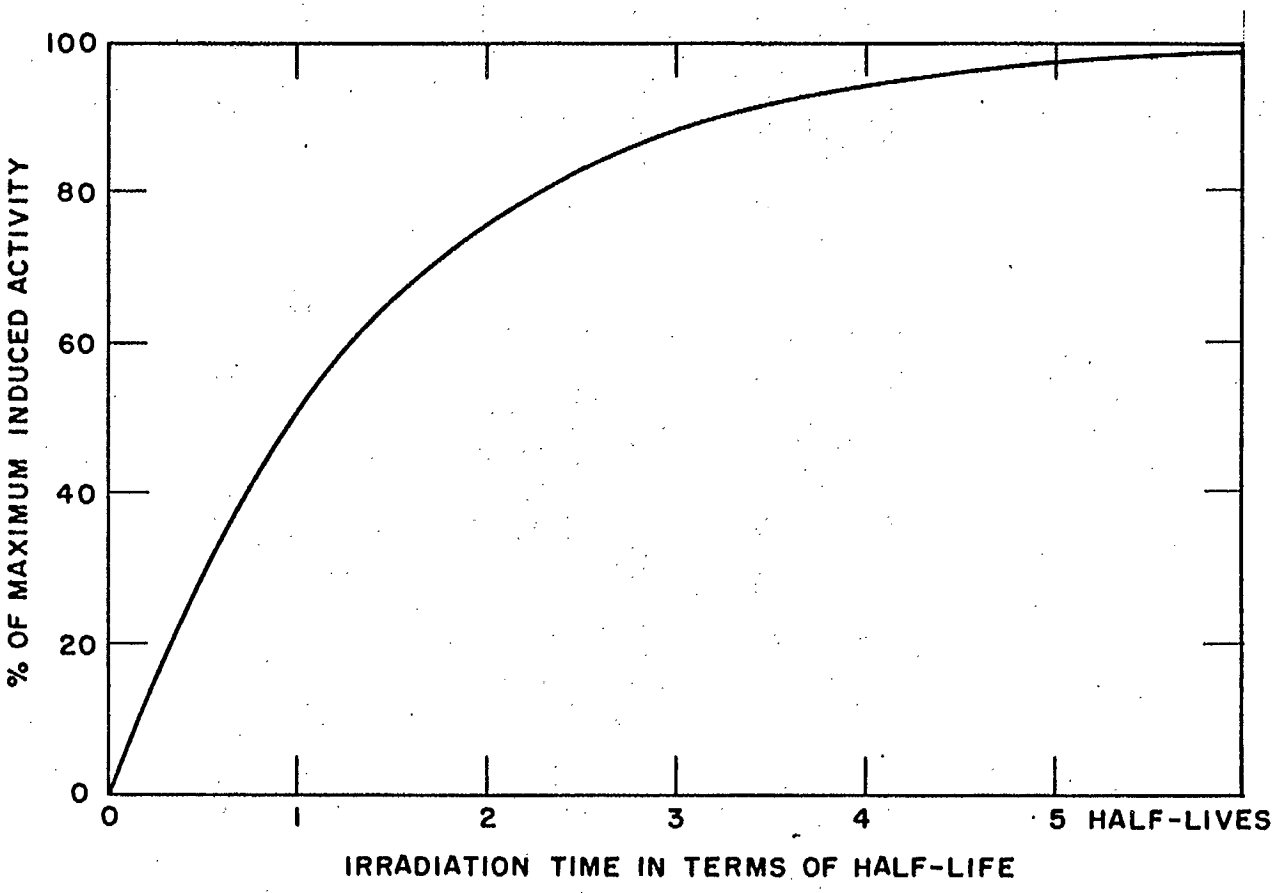


FIGURE 5. BUILD-UP OF INDUCED ACTIVITY AS A FUNCTION OF IRRADIATION TIME FOR CONSTANT NEUTRON FLUX.

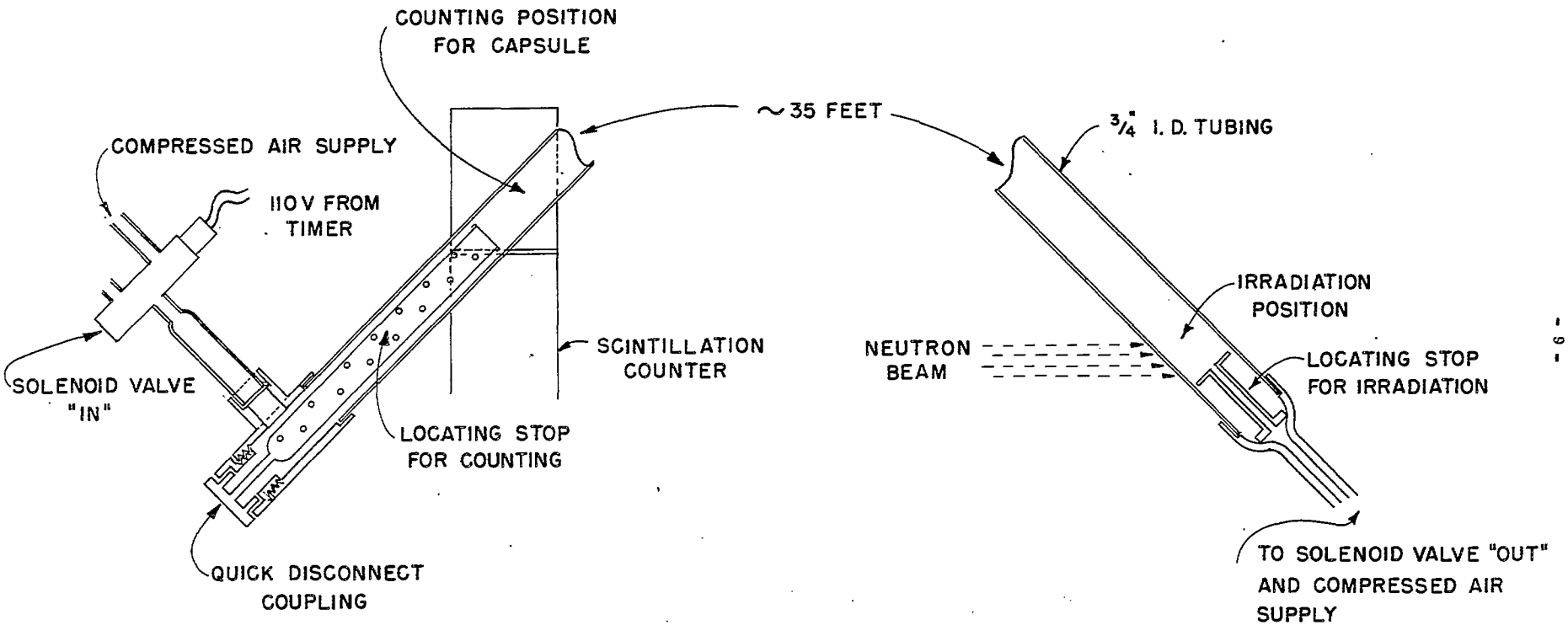


FIGURE 6. RAPID TRANSFER IRRADIATION AND COUNTING SYSTEM.

oxygen content of the readily available hydrocarbon plastics (14). Similar-capacity vials from two different suppliers have been used (A.D. Wood, Ltd., London, England, 5-ml capacity; Olympic Plastics Co., Inc., Los Angeles, U.S.A., 2-dram capacity). Although the Olympic vials were of more uniform construction and slightly lighter than those from A.D. Wood, Ltd., (~3 grams as compared to~4 grams), their oxygen content was significantly higher (500 ppm as compared to 220 ppm), which precluded their use for low oxygen concentration measurements. To ensure reproducible positioning of the vials, in the neutron beam and beside the counter, the transfer tubing in these positions was inclined at an angle of about 35 degrees.

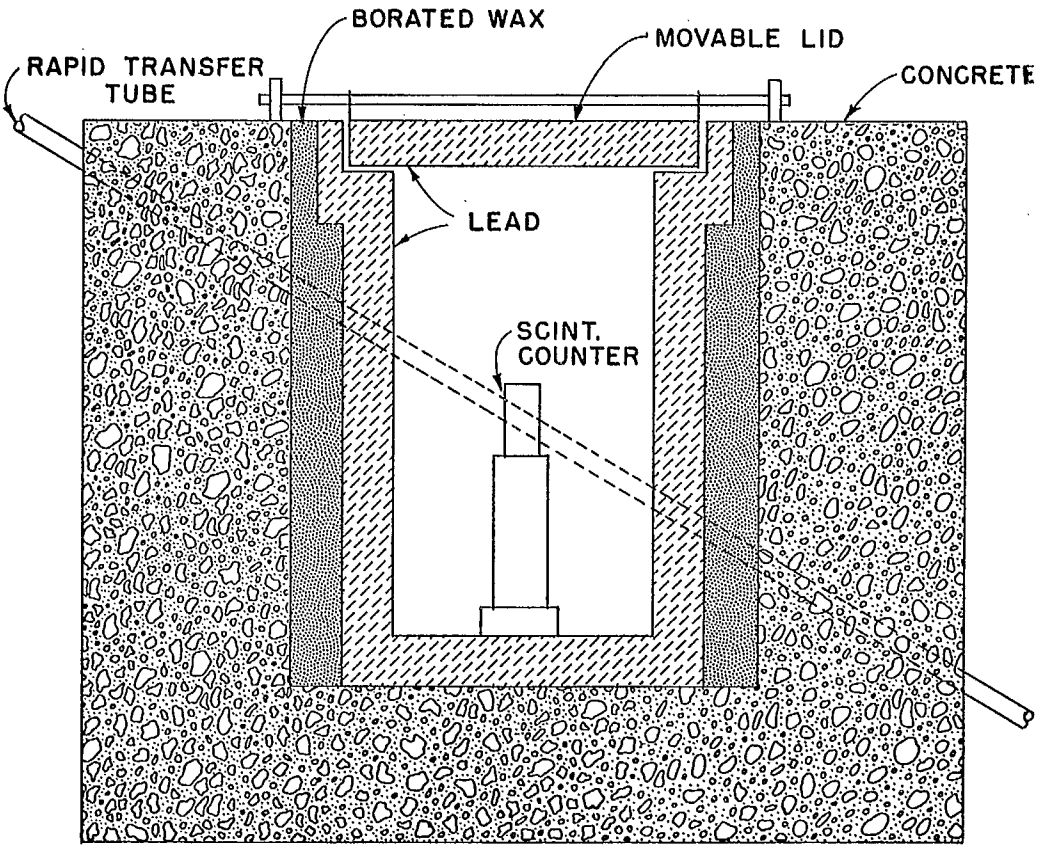
When the generator is operating, a neutron-induced background is found on the scintillation counter. This was minimized by the construction of the shielded enclosure shown in Figure 7. The scintillation crystal, in addition to two inches of lead shielding, is also shielded by two inches of boron-loaded paraffin wax and eight inches of concrete. The background reading in this shielded enclosure, during generator operation, was normally a negligible proportion of the total number of counts measured. However, when the oxygen content being measured was very low, it was necessary to switch off the generator during the counting period. This was achieved in the present system by arranging the beam switch on the generator to be tripped automatically at the end of the irradiation portion of the cycle.

The natural, cosmic ray background count on the scintillation counter, over a 4.5 MeV-6.5 MeV energy interval, was slightly less than 2 counts per minute.

(d) Automatic Transfer Control System

In order to perform the irradiation, monitoring and counting sequence accurately and reproducibly, an automatic control system was constructed for oxygen determination. The operation of this system is controlled by an Industrial Timer Corporation multi-cam timer (Model RC3 with an A-18 gear train). This unit consists of a 2 R.P.M. synchronous motor and gear train assembly, that drives a shaft through one revolution in 90 seconds. Seven adjustable cams are mounted on the shaft, each of which opens or closes a Micro Switch for any selected portion of the operating cycle between about one second and eighty-nine seconds. The motor is started by a momentary pulse of current, which energizes a starting magnet, and stops after one revolution. For continuous re-cycling, the starting magnet is maintained energized for as many cycles as required.

In the present application, it was necessary to perform the following sequence of operations, each operation being controlled by one cam/Micro Switch combination:



SCALE 1:5

FIGURE 7. SHIELDED ENCLOSURE FOR SCINTILLATION COUNTING.

(1) Start the IN timer, to activate the IN solenoid valve, to send the capsule into the irradiation position.

(2) Monitor the neutron flux as soon as the capsule is in the irradiation position.

(3) Irradiate the sample for 40 seconds.

(4) Start the OUT timer, to activate the OUT solenoid valve, and stop the neutron monitor at the end of the 40-second irradiation period.

(5) When the capsule is in front of the scintillation counter, start the counting circuit to the single-channel analyser and/or the multi-channel analyser. (With the multi-channel analyser, it was also necessary to measure the dead time associated with the analyser.)

(6) Stop the counting after 40 seconds.

In those cases where it was necessary to switch off the generator during the counting period, a double-coil latching relay was used. One coil was activated by a cam/Micro Switch combination at the end of the irradiation period, to switch off the generator beam switch. At the end of the counting period, the other coil of the relay was automatically activated to switch on the beam switch again, so that the generator would be ready for a further run.

For samples of low oxygen content it is necessary to re-cycle the sample a number of times to accumulate a statistically significant number of counts. This was done by energizing the start switch on the multi-cam timer for as long as necessary, the number of cycles run being recorded on a mechanical register.

The reproducibility of the control system was checked by the use of two 60 c/s sources to simulate the output of the neutron monitor and of the single-channel analyser detector. The reproducibility of the irradiation and counting periods was better than 0.1%.

This automatic cycle was designed specifically for the determination of oxygen via 7.31 second nitrogen-16. However, there are a number of other short-lived isotopes, of half-lives somewhat longer than nitrogen-16, that require a rapid transfer system to obtain the maximum counting efficiency. For this reason, the utility of the system was increased by arranging all the operations described earlier to be controlled manually. As the irradiation and counting times are increased, small timing errors that may arise with manual control become less significant and manual operation is satisfactory. The manual system of control was found useful in

setting the IN and OUT timers to obtain the correct transit times for capsules of different weights in the automatic cycle.

A complete circuit diagram for the automatic and manual control system is given in Figure 8.

(e) Neutron Monitor

In order to normalize the neutron flux received by a sample to that received by a standard during separate neutron irradiations, it is necessary to have an accurate measurement of the neutron output of the generator during both of the irradiations. A number of methods have been used to monitor the neutron flux during irradiation, including associated alpha measurements (15) and the measurement of the output of various types of counters close to the generator (4, 5, 16). The method adopted in this work was to measure the output of a large boron trifluoride neutron counter (Chalk River Type BP 11 B) situated in the shielding wall around the generator. The output of the counter is fed to a scaler and, also, through a ratemeter to a chart recorder situated by the operating console. The trace on the chart recorder serves to guide the operator as to the approximate neutron output of the generator, and the scaler gives an accurate integral measurement of the relative neutron flux during an irradiation.

In the case of oxygen determination (or for other short-lived isotopes), however, a problem arises in flux monitoring because of variations in the neutron flux during irradiation. Slight fluctuations in beam intensity, and some movement of the beam over areas of the target of different tritium concentrations, can cause the neutron flux to vary by several per cent during an irradiation. The varying neutron flux results in a varying rate of formation of nitrogen-16, so that the rate of decay of nitrogen-16 at the end of the irradiation is no longer proportional to the integral flux during irradiation. This effect is found to be more significant with a used target than with a new target. The simultaneous irradiation and counting of the sample and standard is one means of avoiding this difficulty, but would involve the use of two transfer and counting systems. Another approach that has been successfully used (17) is to irradiate an oxygen-containing plastic close to the target and then count the beta particles emitted by it at the same time as the sample is counted. A further approach that has the merit of being simple and requiring less equipment (7) depends on the fact that the charging of a condenser through a resistance is analogous to the rate of formation of an isotope in a neutron flux. The time constant of the R-C network is equivalent to the mean life of the radioisotope formed; in the case of nitrogen-16 this is 10.6 seconds.

This technique was used and the resultant data compared with that obtained with a simultaneous integral neutron measurement of the flux during repeated irradiations of a vial of pure oxalic acid. For the data

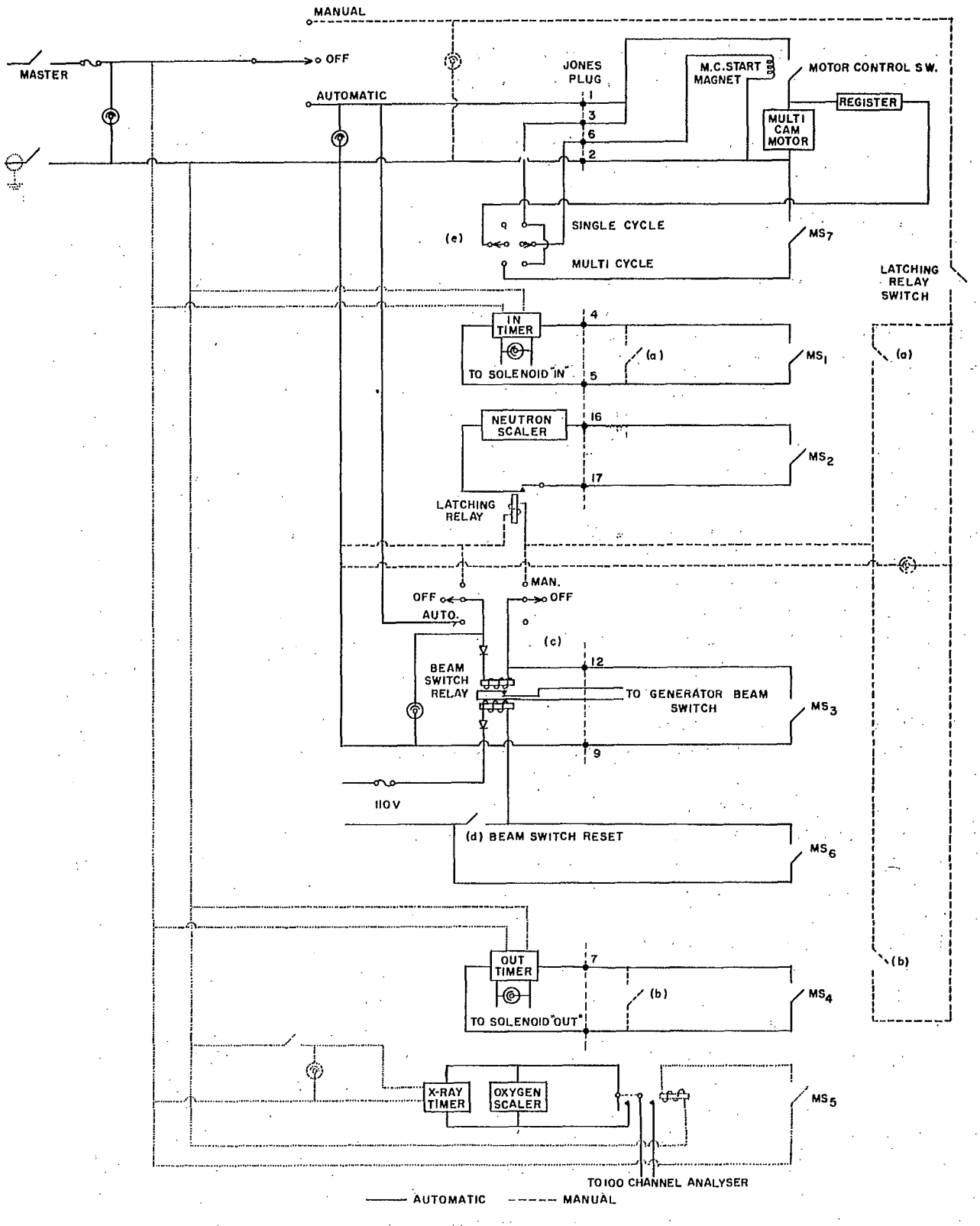


FIGURE 8. CIRCUIT DIAGRAM FOR AUTOMATIC AND MANUAL CONTROL AND COUNTING SYSTEM.

shown in Table 1 (a), the flux was kept approximately constant during the irradiation, while, for the data in Table 1 (b), the beam current (and hence the flux) was deliberately varied by up to a factor of three during the irradiation. The two ratios of oxygen count to integral neutron count and oxygen count to R-C reading shown in Table 1 (a) have a standard deviation of about 2%. In Table 1 (b), however, the ratio of oxygen count to integral neutron count varies by a factor of almost four, while the maximum difference with the R-C method of monitoring is only 15%. The standard deviation expected, as a result of statistical errors in counting, is 1.6% for these counting rates.

A block diagram of the equipment used for flux monitoring in oxygen determination is given in Figure 9.

TABLE 1

Comparison of Integral Neutron Count and R-C Measurement of Neutron Flux

a) Neutron flux approximately constant:

Integral Neutron Count (I.N.C.)	Resistance-capacitance Reading (R-C)	Oxygen Count	Oxygen Count / I.N.C.	Oxygen Count / R-C ($\times 10^{-2}$)
4,751	62.2	15,666	3.30	2.52
4,861	60.3	16,030	3.30	2.66
4,956	62.2	16,008	3.23	2.57
5,330	65.6	17,443	3.27	2.66
5,281	68.8	17,960	3.40	2.61
5,279	67.0	17,961	3.40	2.68

b) Neutron flux deliberately varied:

Integral Neutron Count (I.N.C.)	Resistance-capacitance Reading (R-C)	Oxygen Count	Oxygen Count / I.N.C.	Oxygen Count / R-C ($\times 10^{-2}$)
3,914	72.0	19,559	5.13	2.72
5,238	35.0	8,455	1.61	2.42
2,752	62.0	17,436	6.34	2.81
4,414	37.8	10,078	2.28	2.67

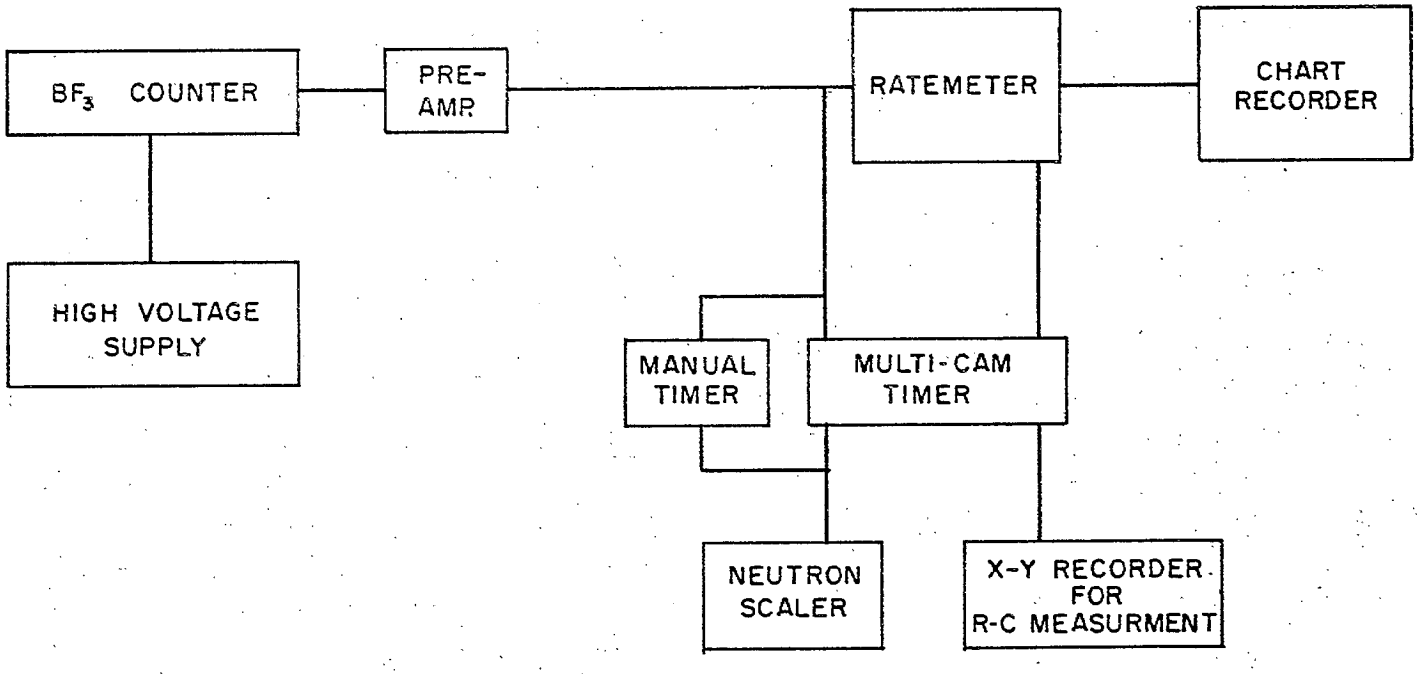


FIGURE 9. BLOCK DIAGRAM OF NEUTRON MONITORING SYSTEM.

INTERFERENCE

Interference in the determination of oxygen via nitrogen-16 will arise from any other neutron-induced reactions that yield either nitrogen-16 or gamma emitters of similar energies. Fortunately, there is only one other neutron reaction that gives nitrogen-16. This is an (n,α) reaction on fluorine-19. The cross section for this reaction has been measured as being about 0.7 of the cross section of O-16 (n, p) N-16 (18). This means that 170 milligrams of fluorine will be equivalent to 100 milligrams of oxygen in terms of nitrogen-16 counts. In many cases, the presence of fluorine, in an oxygen-fluorine mixture, may be assessed by a simultaneous (n, p) reaction that takes place on fluorine-19. This reaction yields oxygen-19 which decays with a half-life of 29 seconds and gamma emission of 0.19 MeV. Thus, the irradiation of an oxygen-free fluorine compound, followed by the simultaneous measurement of the ratio of the oxygen-19 and nitrogen-16 count-rate, allows a calibration factor to be established for the presence of fluorine. Any oxygen in a fluorine sample will increase the nitrogen-16 count-rate relative to that of oxygen-19, and allow the oxygen concentration to be measured. The accuracy of the determination of oxygen in the presence of fluorine decreases as the fluorine-to-oxygen ratio increases, because the oxygen measurement involves taking the difference between two numbers of similar magnitude.

The neutron irradiation of uranium gives rise to a large number of fission products that decay by high-energy emission, comparable to the energy of nitrogen-16, and prevents the determination of oxygen in the presence of this element. The only other interference arises from bremsstrahlung radiation that is produced in the slowing-down of high-energy beta particles. Although a variety of isotopes decay by relatively high-energy beta emission, only beryllium-11 (formed by B-11 (n, p) Be-11) has a half-life (13.6 seconds) that is comparable to nitrogen-16 and thus is likely to cause interference. Figure 10 shows the spectrum obtained following the irradiation, for 40 seconds, of a sample of commercially pure boron. Also shown in Figure 10, for reference purposes, is a nitrogen-16 spectrum obtained from the irradiation of a sample of pure oxalic acid. Although the presence of oxygen is apparent in the boron, the shape of the spectrum below 5 MeV is quite different from that of nitrogen-16 and counting with a single-channel analyser could lead to serious errors. It is estimated that a sample of oxygen-free boron would give an apparent oxygen content of about 1.5% on a single-channel analyser.

A summary of the interfering reactions is given in Table 2.

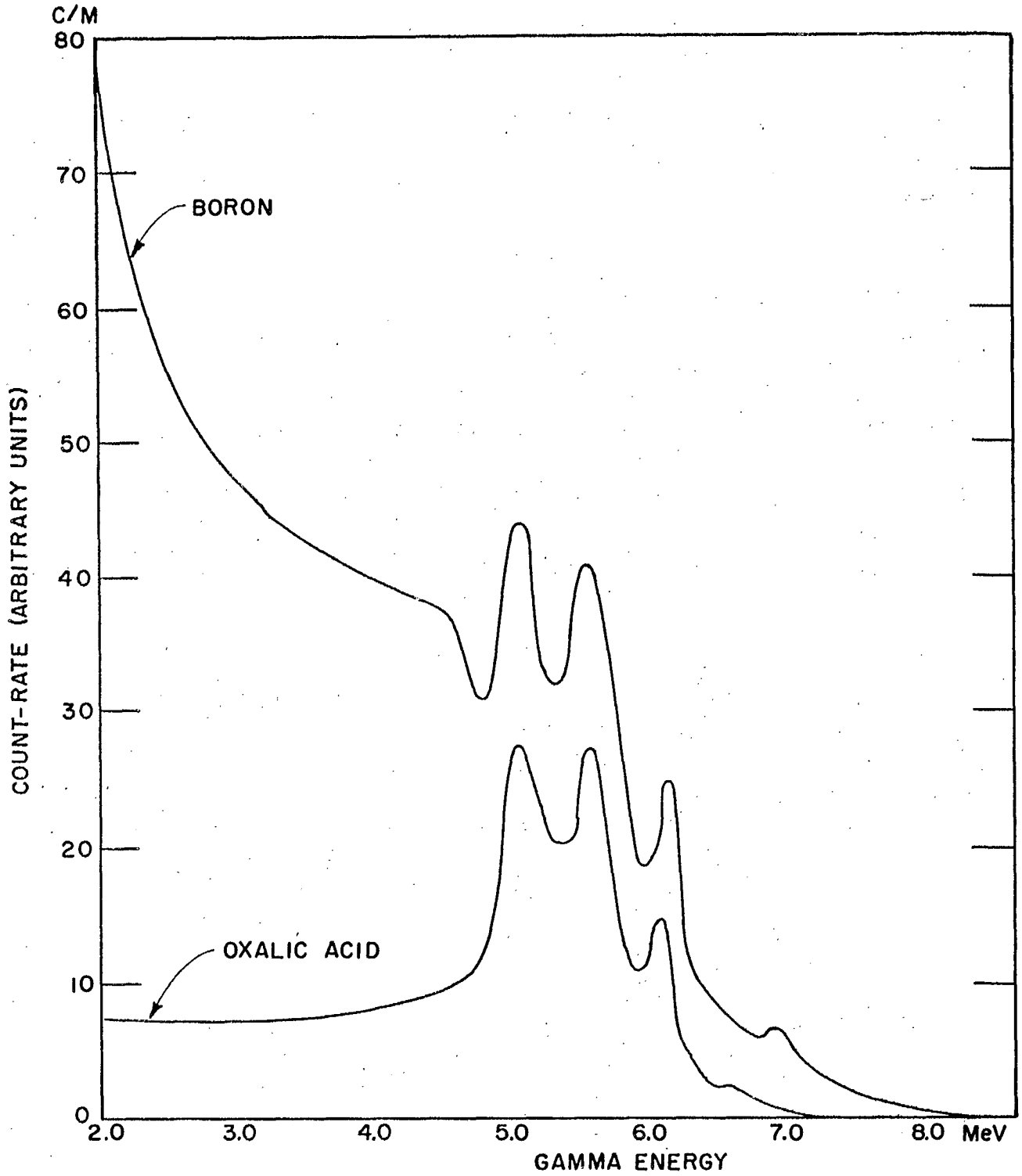


FIGURE 10. GAMMA SPECTRA FROM FAST NEUTRON IRRADIATION OF BORON AND OXALIC ACID.

TABLE 2

Principal Interfering Reactions in the Determination of Oxygen by Fast Neutron Activation

Element	Reaction	Half-life of Product	Principal Radn., MeV		Apparent Oxygen Content of Oxygen-free Material
			$\beta_{max.}$	γ	
F	F-19(n,α)N-16	7.31 sec	10.4, 4.4	7.1, 6.1	60%
B	B-11(n,p)Be-11	13.6 sec	11.5, 9.4, 4.7	6.8, 2.1	1.5%
U	U(n, fission)	Many	Wide range of beta and gamma energies		-

CONCLUSIONS

The method of oxygen determination by fast neutron activation is both rapid and non-destructive, and has been applied to oxygen determinations in a variety of matrices, ranging from high-purity metals of very low oxygen content to mineral samples containing up to 50% oxygen. The time required for a determination is dependent on the oxygen content of a sample, but is rarely more than ten minutes. The equipment described in this report was designed as a multi-purpose unit for the study of neutron activation as applied to a number of elements, and has not been optimised specifically for oxygen determinations. However, in cases where oxygen determinations would be of primary interest, the equipment could be readily modified to give a completely automatic analysis of a large group of samples.

The analytical sensitivity may also be increased by decreasing the target-to-sample distance, which is about 1.5 cm in the present system. As the fast flux decreases with distance from the tritium target, according to the inverse square law, a gain in sensitivity of two to three fold may be obtained by placing the sample closer to the target. An increase in counting efficiency would also result from the use of two larger NaI (Tl) crystals to count the gamma radiation from nitrogen-16.

A small error in the determination of oxygen by gamma counting can arise from the use of a standard of density different from the unknown. Although the high-energy gamma radiation from nitrogen-16 is very penetrating, gamma attenuation does occur in high Z materials. An empirical correction factor may be obtained for this attenuation by the use of standards with a range of densities. A second error will also arise because the fast neutron flux through the sample is not constant but decreases with distance from the tritium target. With a single-crystal counting system, the side of the capsule of higher activity may not always be in the same position with respect to the crystal. Performing the analysis a number of times will average this effect. The ultimate accuracy obtained in a determination, however, is controlled by the statistics of radioactive counting. As the oxygen content of a sample (and the counts obtained) decreases, so the method becomes less accurate. In the present work, oxygen values as low as 100 ppm, in a 30 g sample, have been measured with a statistical standard deviation of $\pm$ 10%.

The lowest oxygen contents that may be measured are limited by the oxygen content of the containers (~1 mg). For a count-rate equal to that obtained from the container, a sensitivity of 35 ppm may be obtained from a 30 g sample.

ACKNOWLEDGEMENT

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