THE DETERMINATION OF THE TOTAL OXYGEN CONTENT OF ORGANIC MATERIALS BY NEUTRON ACTIVATION

By

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INTRODUCTION

Although oxygen in elementary or combined form is one of the most commonly occurring constituents of organic materials and its direct determination has been the subject of extensive investigation, the development and application of rapid instrumental methods have not kept pace with existing requirements.

Prior to 1939, methods for direct determination of oxygen in organic compounds were based on either complete oxidation of the compound with measurement of the oxygen consumed or catalytic hydrogenation (1) to form water. Both of these techniques were cumbersome, required complex apparatus, and were excessively tedious and time consuming. Neither could be considered amenable to routine application.

In 1939, Schutze (2) proposed a semi-micromethod in which the sample is thermally decomposed in a stream of nitrogen and the cracked products are passed over carbon at about 1000°C. The resulting carbon monoxide is then oxidized at room temperature with iodine pentoxide yielding carbon dioxide and iodine, either of which may be determined and used as a measure of oxygen content. Unterzaucher (3) adapted the method to the microchemical scale by making various improvements in the apparatus. Modifications permitting the use of larger sample sizes were made by Dinerstein and Klipp (4) in an effort to minimize errors in the analysis of low oxygen content petroleum products. Oita (5) made further modifications in applying the technique to light hydrocarbons. The problems of sensitivity and volatility were overcome by using a magnetically controlled section of spiral quartz tubing as the sample container permitting the use of as much as 5 grams of sample. Although methods based on thermal decomposition require somewhat simpler apparatus and are less subject to interference than the complete oxidation and catalytic hydrogenation methods, time requirements of the order of 60 to 70 minutes per analysis make them equally unattractive for routine use.

The answer to the oxygen analysis problem now appears to be fast neutron activation analysis (6-8). The purpose of this paper is to describe the techniques employed at this laboratory for determining oxygen in petroleum products and related materials by the activation method.

In the determination of oxygen by fast neutron activation, the sample to be analyzed is irradiated with neutrons of sufficient energy to initiate the $O^{16}(n,p)N^{16}$ reaction (Q = -9.62 Mev). The 7.4-second N^{16} activity induced in the sample is then measured and the oxygen content computed from the slope of a calibration curve prepared from a series of standards containing known amounts of oxygen. Samples and standards are prepared, irradiated, and counted in exactly the same way; all activities are normalized to a fixed neutron flux and weight.

Fast neutrons for this work are most conveniently produced by bombarding a tritiated target (e.g. tritiated titanium) with deuterons in a relatively low voltage accelerator, the yield of the $H^3(d,n)He^4$ reaction being such that an adequate output ($\sim 10^{10}$ neutrons/sec) of 14-Mev neutrons is obtained at accelerating voltages as low as 125 kilovolts.

Either beta-ray or gamma-ray counting techniques can be employed to measure the N^{16} activity (see Fig. 1). Because of the short half-life of N^{16}, the irradiation time and the time at which the irradiation stops, as well as the counting time and the time at which the counting starts, need to be very carefully controlled. An automatic timing and sample transfer system is therefore necessary if accurate, reproducible results are to be obtained.

INSTRUMENTATION

A diagram of the sample transfer system used for the oxygen analyses with detail sketches of a sample bottle in the irradiation and counting positions is shown in Fig. 2. The system is operated with air at 65 psi and is equipped with three timers and four solenoid valves that automatically time and control the irradiation, transfer, and counting sequence. Samples are transferred through the 32-foot long polyethylene tube, which makes a 200° bend over the top of the shielding wall, in less than 1-1/4 seconds. A photoelectric device is employed at the target end of the transfer tube to assure reproducible positioning of the sample bottles in front of the water-cooled tritiated titanium target (on a 2-mil thick stainless steel backing) of the 130 kilovolt accelerator. The 14-Mev neutron flux on the deuteron beam axis 3/4-inch from the target (center of sample bottle) is approximately 2×10^8 neutron/cm^2-sec with a 250 μamp magnetically analyzed (20° deflection) beam of deuterons (D_1^+).

Two 3-inch diameter x 3-inch thick NaI(Tl) scintillation counters are used to detect the 6.1 and 7.1 Mev gamma rays from N^{16}. The outputs of the two counters are fed in parallel through an amplifier to either a discriminator-scaler or a multichannel analyzer, the latter being needed only to determine the optimum discriminator setting for a given matrix material. (For most petroleum products the discriminator can be set to accept gamma rays with energies greater than about 0.5 Mev without introducing any appreciable error in the oxygen determination.) The neutron output of the accelerator is monitored with a BF_3 counter located in a position in the shielding wall where preliminary tests showed that the total count during an irradiation period would be proportional to the fast flux through the sample. The monitor is used to normalize sample data to a fixed neutron flux thereby compensating for fluctuations due to changing beam and target conditions.

EXPERIMENTAL

Sample Preparation - The samples, which to date have been predominantly rather volatile liquid petroleum products, are poured into 1/4-ounce polyethylene bottles (weighing about 1.5 grams) fitted with extended dropper tips* for sealing and machined polyethylene driving caps. Sample bottles are weighed before and after filling and the weight of the sample (~6 grams) determined to 0.01 grams. The filling and sealing operations are carried out in an atmosphere of nitrogen or helium.

Irradiation and Counting - Samples are put in the irradiation position by inserting in a sample loader located near the counter end of the transfer tube and pressing a button which momentarily opens solenoid valves No. 1 and No. 2 (Fig. 2). The irradiation, delay and counting sequence are initiated by a manual switch which simultaneously starts the irradiation timer and the neutron monitor and directs the deuteron beam onto the tritium target by energizing a beam deflector located in the drift tube of the accelerator. After the preset irradiation time (20 seconds), the beam is automatically deflected onto a water-cooled slit stopping the generation of neutrons, valves No. 3 and No. 4 are opened, and the delay timer is started. The delay timer then turns on the counting equipment for a preset counting time (usually 20 seconds) 1-1/4 seconds after being actuated. Experience has shown that the heaviest samples, and consequently the slowest to transfer, reach the counting position within this period. After the counting data are recorded, the cycle is repeated until the desired total count is accumulated.

DISCUSSION

One of the most important problems to be solved before oxygen analysis by neutron activation can be put on a routine basis is that of obtaining a moderately sized (~5-15 ml), cheap, disposable, sample container. Ideally, the container material should be relatively free of oxygen, fluorine† and other elements that give rise to reaction products with short half lives. Short of this, the concentration of contaminants in the material should not vary significantly from container to container.

Following a rough survey by the fast activation method of the oxygen and fluorine contents of a number of possible container materials, polyethylene was selected for further study. Samples were either machined in the form of solid cylinders (weighing about 6 grams) or cut into small pieces and sealed in a bottle in an atmosphere of helium. They were irradiated and counted as described above. Relative gamma-ray activities per gram measured above a discriminator level corresponding to 0.5 Mev for several types of polyethylene are given in Table I; a polypropylene value is included for comparison purposes.

These results led us to the use of the commercially available 1/4-ounce polyethylene bottle (costing $37 per thousand) for our standard sample container. Subsequent activation measurements have

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* Tips (No. D13-370) are purchased with the bottles (No. 5-6045) from Erno Products Company, Philadelphia, Pennsylvania.

† N^{16} is also produced from fluorine by the $F^{19}(n,\alpha)N^{16}$ reaction.

shown that the polyethylene in these bottles contains approximately 320 ppm of oxygen; changes in oxygen content from bottle to bottle are too small to be detected by present procedures.

TABLE I

Comparison of Activities Induced in Polyethylene and Polypropylene by Fast Neutrons

		Relative Activity Per Gram*
Conventional Polyethylene	Allied Resinous Products, Inc.	2.7 ± 0.4
Linear Polyethylene	Allied Resinous Products, Inc.	1.9 ± 0.2
Marlex 5003	Westlake Plastics Company	1.9 ± 0.2
Polyethylene from Commercial 1/4-Ounce Bottle	Plax Corporation (Erno Products Co.)	1.0 ± 0.2
Polypropylene	Allied Resinous Products, Inc.	5.5 ± 0.6

* Errors are standard deviations due to counting statistics.

The polyethylene bottle will lose product by diffusion through the wall and become distorted when left filled at room temperature for more than a few minutes with some hydrocarbons, particularly the aromatics. Best results are obtained, therefore, when samples are irradiated and counted immediately after preparation.

Smooth transit of the bottles through the transfer tube is made possible by the lip on the top of the bottle cap (see Fig. 2). Before this feature was added transit times would vary considerably, and occasionally a bottle would be suspended in a vertical section of the tube by the air streaming through the annulus between the bottle and the tube.

RESULTS

A typical calibration curve for oxygen is shown in Fig. 3 for counts taken above an energy level of 0.5 Mev; the errors are standard deviations from counting statistics. The standards were prepared by mixing known amounts of dibutyl carbitol $[(C_4H_9OCH_2CH_2)_2O]$ in white mineral oil. After appropriate corrections had been made for variations in neutron flux and bottle weight, the count from a blank run (bottle filled with mineral oil) was used to correct the standard sample counts for the oxygen in the polyethylene and the oil.

Neutron activation results are given in Table II for a group of synthetic samples containing known amounts of added oxygen and a group of typical petroleum product samples. The poor agreement with chemical analysis loses most of its significance when the unreliableness of the chemical method in the range below 1% total oxygen, as exemplified by the data in the the third and fourth columns of Table II, is taken into consideration. The two activation analysis values given for the last seven samples are from runs made several days apart using different sample bottles. In all runs, the samples were cycled twice; blank runs were made with helium.

CONCLUSIONS

The fast neutron activation method for determining oxygen in petroleum products and related materials is accurate and is relatively free of trace element interference in the range above 0.01 per cent. It allows oxygen to be measured faster and with a higher precision than any other method yet developed. With additional developmental work it should be possible to analyze for as little as 10 ppm of oxygen with an error of about ± 20 per cent.

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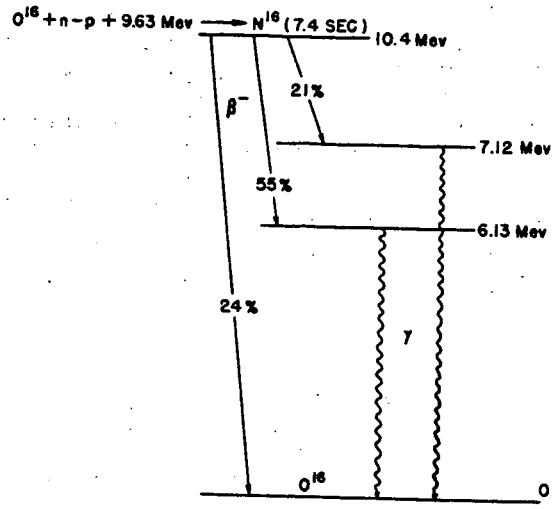

FIGURE 1
DECAY SCHEME FOR N^{16}

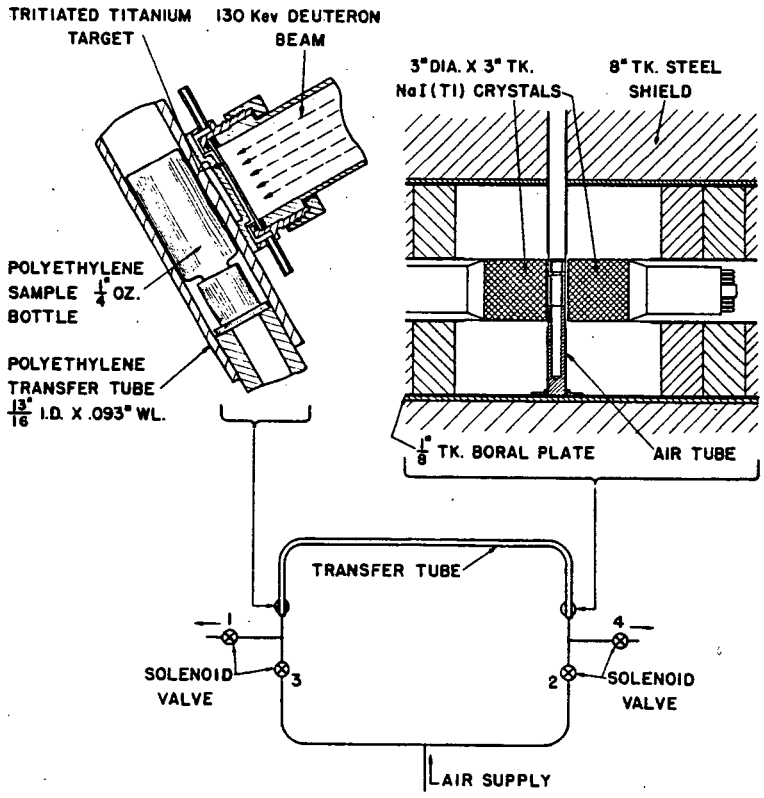

FIGURE 2
IRRADIATION, TRANSFER AND COUNTING SYSTEM FOR OXYGEN ANALYSIS

TABLE II

Analysis For Oxygen By Fast Neutron Activation

Sample	Oxygen Content (%)			
	Calculated	Chemical Analysis GR&DC	Chemical Analysis Commercial Lab	Neutron Activation*
Mineral Oil	0	---	0.03, 0.12, 0.06	0±0.02
Mineral Oil + Diethyl Carbonate	0.252	---	0.10, 0.11, 0.47	0.24±0.01
Mineral Oil + Diethyl Carbonate	0.556	---	0.31, 0.37, 0.51	0.53±0.01
Mineral Oil + Diethyl Carbonate	1.094	---	0.34, 0.43, 1.08	1.1 ±0.03
GR39362 - Heavy Gas Oil	---	0.30, 0.33	0.20, 0.20	0.22±0.01, 0.21±0.01
GR48962 - Fuel Oil Distillate	---	0.22, 0.24	0.25, 0.20	0.15±0.01, 0.14±0.01
GR53049 - Furnace Oil Distillate	---	0.26, 0.23	0.14, 0.18	0.07±0.01, 0.07±0.01
GR56085 - Light Furnace Oil	---	0.14, 0.12	0.17, 0.22	0.10±0.01, 0.09±0.01
GR58790 - Furnace Oil	---	0.20, 0.19	0.14, 0.18	0.10±0.01, 0.10±0.01
Mineral Oil + Dibutyl Carbitol	0.28	---	0.35, 0.37	0.27±0.01, 0.29±0.01
Mineral Oil + Dibutyl Carbitol	0.73	---	0.67, 0.80	0.73±0.02, 0.72±0.01

* Errors are standard deviations due to counting statistics.

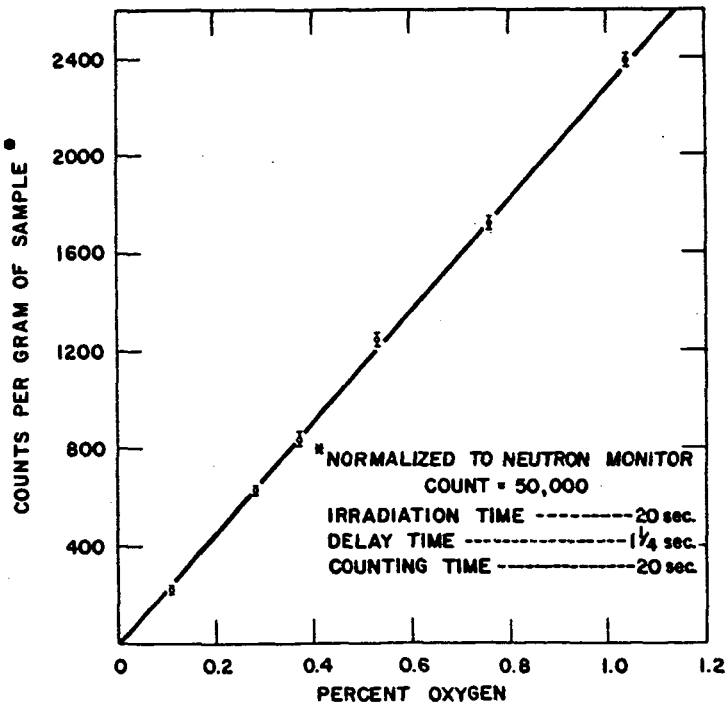

FIGURE 3
CALIBRATION CURVE FOR OXYGEN