



# Standard Test Method for Oxygen Content Using a 14-MeV Neutron Activation and Direct-Counting Technique<sup>1</sup>

This standard is issued under the fixed designation E385; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the measurement of oxygen concentration in almost any matrix by using a 14-MeV neutron activation and direct-counting technique. Essentially, the same system may be used to determine oxygen concentrations ranging from under 10  $\mu\text{g/g}$  to over 500  $\text{mg/g}$ , depending on the sample size and available 14-MeV neutron fluence rates.

NOTE 1—The range of analysis may be extended by using higher neutron fluence rates, larger samples, and higher counting efficiency detectors.

1.2 This test method may be used on either solid or liquid samples, provided that they can be made to conform in size, shape, and macroscopic density during irradiation and counting to a standard sample of known oxygen content. Several variants of this method have been described in the technical literature. A monograph is available which provides a comprehensive description of the principles of activation analysis using a neutron generator (1).<sup>2</sup>

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautions are given in Section 8.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E10 on Nuclear Technology and Applications and is the direct responsibility of Subcommittee E10.05 on Nuclear Radiation Metrology.

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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of the text.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E170 Terminology Relating to Radiation Measurements and Dosimetry

E181 Test Methods for Detector Calibration and Analysis of Radionuclides

E496 Test Method for Measuring Neutron Fluence and Average Energy from  $^3\text{H}(d,n)^4\text{He}$  Neutron Generators by Radioactivation Techniques

2.2 U.S. Government Document:

Code of Federal Regulations, Title 10, Part 20<sup>4</sup>

## 3. Terminology

3.1 *Definitions* (see also Terminology E170):

3.1.1 *accelerator*—a machine that ionizes a gas and electrically accelerates the ions onto a target. The accelerator may be based on the Cockcroft-Walton, Van de Graaff, or other design types (1). Compact sealed-tube, mixed deuterium and tritium gas, Cockcroft-Walton neutron generators are most commonly used for 14-MeV neutron activation analysis. However, “pumped” drift-tube accelerators that use replaceable tritium-containing targets are also still in use. Reviews of operational characteristics, descriptions of accessory instrumentation, and applications of accelerators used as fast neutron generators for activation analysis are available (2,3).

3.1.2 *comparator standard*—a reference standard of known oxygen content whose specific counting rate ( $\text{counts min}^{-1} [\text{mg of oxygen}]^{-1}$ ) may be used to quantify the oxygen content of a sample irradiated and counted under the same conditions. Often, a comparator standard is selected to have a matrix composition, physical size, density and shape very similar to the corresponding parameters of the sample to be analyzed.

3.1.3 *14-MeV neutron fluence rate*—the areal density of neutrons passing through a sample, measured in terms of neutrons  $\text{cm}^{-2} \text{s}^{-1}$ , that is produced by the fusion reaction of deuterium and tritium ions accelerated to energies of typically 150 to 200 keV in a small accelerator. Fluence rate has been commonly referred to as “flux density.” The total neutron fluence is the fluence rate integrated over time.

3.1.3.1 *Discussion*—The  $^3\text{H}(d,n)^4\text{He}$  reaction is used to

<sup>4</sup> Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

produce approximately 14.7-MeV neutrons. This reaction has a  $Q$ -value of + 17.586 MeV.

3.1.4 *monitor*—any type of detector or comparison reference material that can be used to produce a response proportional to the 14-MeV neutron fluence rate in the irradiation position, or to the radionuclide decay events recorded by the sample detector. A plastic pellet with a relatively high oxygen content is often used as a monitor reference in dual sample transfer systems. It is never removed from the system regardless of the characteristics of the sample to be analyzed. It is important to distinguish that the monitor, whether an independent detector or an activated reference material, is not a standard used to scale the oxygen content of the samples to be measured, but rather is used to normalize the analysis system among successive analytical passes within the procedure.

3.1.5 *multichannel pulse-height analyzer*—an instrument that receives, counts, separates, and stores, as a function of their energy, pulses from a scintillation or semi-conductor gamma-ray detector and amplifier. In the 14-MeV instrumental neutron activation analysis (INAA) determination of oxygen, the multichannel analyzer may also be used to receive and record both the  $\text{BF}_3$  neutron detector monitor counts and the sample gamma-ray detector counts as a function of stepped time increments (4-6). In the latter case, operation of the analyzer in the multichannel scaler (MCS) mode, an electronic gating circuit is used to select only gamma rays within the energy range of interest.

3.1.6 *transfer system*—a system, normally pneumatic, used to transport the sample from an injection port (sometimes connected to an automatic sample changer) to the irradiation station, and then to the counting station where the activity of the sample is measured. The system may include components to ensure uniform positioning of the sample at the irradiation and counting stations.

#### 4. Summary of Test Method

4.1 The weighed sample to be analyzed is placed in a container for automatic transfer from a sample-loading port to the 14-MeV neutron irradiation position of a particle accelerator. After irradiation for a pre-selected time, the sample is automatically returned to the counting area. A gamma-ray detector measures the high-energy gamma radiation from the radioactive decay of the  $^{16}\text{N}$  produced by the  $(n,p)$  nuclear reaction on  $^{16}\text{O}$ . The number of counts in a pre-selected counting interval is recorded by a gated scaler, or by a multichannel analyzer operating in either the pulse-height, or gated multiscaler modes. The number of events recorded for samples and monitor reference standard are corrected for background and normalized to identical irradiation and counting conditions. If the sample and a monitor reference sample are not irradiated simultaneously, the neutron dose received during each irradiation must be recorded, typically by use of a  $\text{BF}_3$  neutron proportional counter. The amount of total oxygen (all chemical forms) in the sample is proportional to the corrected and normalized sample count and is quantified by use of the corrected and normalized specific activity of the comparator standard(s).

4.1.1  $^{16}\text{N}$  decays with a half-life of 7.13 s by  $\beta$ -emission (7), thus returning to  $^{16}\text{O}$ . From Ref (8), sixty seven percent of the decays are accompanied by 6.12863-MeV gamma rays, 4.9 % by 7.11515-MeV gamma rays, and 0.82 % by 2.7415-MeV gamma rays. Other lower intensity gamma rays are also observed. About 28 % of the beta transitions are directly to the ground state of  $^{16}\text{O}$ . Useful elemental data including calculated sensitivities and reaction cross-sections for (14-MeV INAA) are provided in Refs (3) and (9). (See also Test Methods E181.)

#### 5. Significance and Use

5.1 The conventional determination of oxygen content in liquid or solid samples is a relatively difficult chemical procedure. It is slow and usually of limited sensitivity. The 14-MeV neutron activation and direct counting technique provides a rapid, highly sensitive, nondestructive procedure for oxygen determination in a wide range of matrices. This test method is independent of the chemical form of the oxygen.

5.2 This test method can be used for quality and process control in the metals, coal, and petroleum industries, and for research purposes in a broad spectrum of applications.

#### 6. Interferences

6.1 Because of the high energy of the gamma rays emitted in the decay of  $^{16}\text{N}$ , there are very few elements that will produce interfering radiations; nevertheless, caution should be exercised.  $^{19}\text{F}$ , for example, will undergo an  $(n,\alpha)$  reaction to produce  $^{16}\text{N}$ , the same indicator radionuclide produced from oxygen. Because the cross section for the  $^{19}\text{F}(n,\alpha)^{16}\text{N}$  reaction is approximately one-half that of the  $^{16}\text{O}(n,p)^{16}\text{N}$  reaction, a correction must be made if fluorine is present in an amount comparable to the statistical uncertainty in the oxygen determination. Another possible interfering reaction may arise from the presence of boron.  $^{11}\text{B}$  will undergo an  $(n,p)$  reaction to produce  $^{11}\text{Be}$ . This isotope decays with a half-life of 13.81 s, and emits several high-energy gamma rays with energies in the range of 4.67 to 7.98 MeV. In addition, there is Bremsstrahlung radiation produced by the high energy beta particles emitted by  $^{11}\text{Be}$ . These radiations can interfere with the oxygen determination if the oxygen content does not exceed 1 % of the boron present.

6.2 Another possible elemental interference can arise from the presence of fissionable materials such as thorium, uranium, and plutonium. Many short-lived fission products emit high-energy gamma rays capable of interfering with those from  $^{16}\text{N}$ .

NOTE 2—Argon produces an interferent,  $^{40}\text{Cl}$ , by the  $^{40}\text{Ar}(n,p)^{40}\text{Cl}$  reaction. Therefore, argon should not be used for the inert atmosphere during sample preparation for oxygen analysis.  $^{40}\text{Cl}$  ( $t_{1/2} = 1.35$  m) has several high-energy gamma rays, including one at 5.8796 MeV with a yield of 4.1 %.

6.3 An important aspect of this analysis that must be controlled is the geometry during both irradiation and counting. The neutron source is usually a disk source. Hence, the fluence rate decreases as the inverse square at points distant from the target, and less rapidly close to the target. Because of these fluence rate gradients, the irradiation geometry should be reproduced as accurately as possible. Similarly, the positioning of the sample at the detector is critical and must be accurately

reproducible. For example, if the sample is considered to be a point source located 6 mm from a cylindrical sodium iodide (NaI) detector, a 1-mm change in position of the sample along the detector axis was found to result in a 3.5 to 5 % change in detector efficiency (10). Since efficiency is defined as the fraction of gamma rays emitted from the source that interact with the detector, it is evident that a change in efficiency would result in an equal percentage change in measured activity and in apparent oxygen content. The sample and monitor (if present) may be rotated during exposure or counting, or both, to ensure exposure and counting uniformity. See, for example, Ref (11). For counting, dual detectors at 180° can be used as an alternative to rotation to minimize positioning errors at the counting station.

6.4 Since  $^{16}\text{N}$  emits high-energy gamma rays, determinations are less subject to effects of self-absorption than are determinations based on the use of indicator radionuclides emitting lower energy gamma rays. Corrections for gamma-ray attenuation during counting are usually negligible, except for large samples as may be needed in the highest sensitivity determinations.

6.5 The oxygen content of the transfer container (“rabbit”) must be kept as low as possible to avoid a large “blank” correction. Suggested materials that combine light weight and low oxygen content are polypropylene and high-density polyethylene (molded under a nitrogen atmosphere), high purity Cu, and high-purity nickel. A simple subtraction of the counts from the blank vial in the absence of the sample is not adequate for oxygen determinations below 200  $\mu\text{g/g}$ , since large sample sizes may be required for these high-sensitivity measurements and gamma-ray attenuation may be important when the sample is present (12). If the total oxygen content of the sample is as low as that of the container (typically about 0.5 mg of oxygen), the sample should be removed from the irradiation container prior to counting. Statistical errors increase rapidly as true sample activities decrease, while container contamination activities remain constant. For certain shapable solids, it may be possible to use no container at all (13). This “containerless” approach provides optimum sensitivity for low-level determinations, but care must be taken to avoid contamination of the transfer system.

6.6 Although the discriminator is used to eliminate the signal originating from gamma rays of energy less than 4.5 MeV, it is possible when analyzing certain materials that very high matrix activities can result in multiple gammas of lower energy being summed, thereby generating a signal in the energy window. This effect can be minimized by reducing the specific activity of the interfering radionuclide or by altering the counting geometry to reduce the solid angle. Since the decay of these “coincidence” events are subject to the half-life of the radionuclide from which they are emitted, it may be possible to differentiate the interfering signal from oxygen counts by decay rate if using an MCS-based system (14).

## 7. Apparatus

7.1 *14-MeV Neutron Generator*—Typically, this is a high-voltage sealed-tube machine to accelerate both deuterium and

tritium ions onto a target to produce 14-MeV neutrons by the  $^3\text{H}(d,n)^4\text{He}$  reaction. In the older “pumped” drift-tube accelerators, and also in some of the newer sealed-tube neutron generators, deuterium ions are accelerated into copper targets containing a deposit of titanium into which tritium is absorbed. Detailed descriptions of both sealed-tube and drift-tube machines have been published (1, 3).

7.1.1 Other nuclear reactions may be used, but the neutron energy must exceed 10.22 MeV (15) for the  $^{16}\text{O}(n,p)^{16}\text{N}$  reaction to take place. The 14-MeV neutron output of the generator should be  $10^9$  to  $10^{12}$  neutrons  $\text{s}^{-1}$ , with a usable fluence rate at the sample of  $10^7$  to  $10^9$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ . The 14-MeV fluence rate may be measured as described in Test Method E496.

7.1.2 The neutron output from targets in drift-tube machines decreases quite rapidly during use because of depletion of the tritium content of the target in the pumped system. Consequently, the target must be replaced frequently. The use of a sealed-tube-type neutron generator obviates the need to handle tritium targets and provides for longer stable operation.

7.2 *Sample Transfer System*—The short half-life (7.13 s) of the  $^{16}\text{N}$  requires that the sample be transferred rapidly between the irradiation position and the counting station by a pneumatic system to minimize decay of the  $^{16}\text{N}$ . If the oxygen content in the sample is low, it is desirable to use dry nitrogen, rather than air, in the pneumatic system to avoid an increase in radioactivity due to recoil of  $^{16}\text{N}$  atoms produced in the air onto the sample surface or other transfer of irradiated air back to the counting station. The transfer system and data processing may be controlled directly by laboratory computers (16), or by programmable logic controllers (5,6). Dual transfer systems transport the sample and a monitor reference standard simultaneously. In this case, two independent counting systems are often used. Single sample transfer systems based on sequential irradiations of a sample and a comparator standard, are also used.

NOTE 3—As mentioned previously in 6.2, argon should be avoided in the transfer gas, as well as in sample packaging, because of the interferent  $^{40}\text{Cl}$  produced.

7.3 *Monitor*—The number of counts obtained from any given irradiation is dependent upon the oxygen content of the sample, the length of irradiation, the neutron fluence rate, the neutron energy spectrum, the delay time between irradiation and counting, and the length of the count. It is desirable to make a measurement in which the result obtained is a function of only the oxygen content and independent of other variables. This can be achieved by standardizing the experimental conditions and use of a monitor.

7.3.1 In the dual sample transfer approach, the monitor is ordinarily a high-oxygen containing material that is irradiated with each sample in a position adjacent to the sample position, transferred to an independent detector, and counted simultaneously with the sample. The same monitor reference is used with each sample, and is never removed from the system. Since the sample and monitor reference are irradiated and counted simultaneously, and  $^{16}\text{N}$  is measured in both, most changes in the experimental parameters affecting the sample counts will affect the monitor counts equally. One possible exception is



that changes in the neutron energy spectrum due to incident accelerator particle energy changes may affect the sample and monitor in different ways due to angular dependence factors. However, a relatively constant particle energy can usually be achieved. Therefore, while the number of counts obtained from any given sample may vary greatly from one irradiation to another, the ratio of sample counts to monitor reference counts will be a constant. To determine the oxygen content of a sample, it is necessary to irradiate a comparator standard of known oxygen content with physical and chemical properties similar to those of the sample and determine the ratio of its counts to that of the monitor reference as well.

7.3.2 If a single sample transfer system is used, it is necessary to measure the neutron fluence rate during both the irradiation of the sample and the irradiation of the comparator standard. Variations in fluence rate from a neutron generator are to be expected, not only with time, but also with position. Compensation for these variations must be provided. It is not necessary to make an absolute measurement of the fluence rate at the irradiation position, but only to obtain a value that is proportional to the neutrons  $\text{cm}^{-2} \text{s}^{-1}$  passing through the sample. A wide variety of ingenious systems have been devised and used for this purpose (17). Probably the most commonly used and simplest system is a boron trifluoride ( $\text{BF}_3$ ) counter coupled to a rate meter, scaler, or multichannel analyzer operating in the multichannel scaler mode to detect thermalized neutrons. The greatest difficulty with this system is that it detects thermal neutrons, while the oxygen reaction proceeds only with fast neutrons. Therefore, the  $\text{BF}_3$  monitor, encased in a polyethylene cover to thermalize the fast neutrons from the generator, does not directly measure neutrons of the energy used for the analyses. Hence, the presumption of proportionality may not always be valid unless the neutron spectrum is constant. Fortunately, most newer sealed-tube generators provide consistent incident particle energies, reducing the likelihood of a variable energy spectrum during a single experiment. Another difficulty is that, if only a single scaler is used, total neutron fluence during the irradiation and not a representative fluence rate is measured. Since the length of irradiation is ordinarily at least as long as the half-life of the  $^{16}\text{N}$ , any changes in fluence rate during irradiation will introduce an error. This error can be overcome by using a pulse-height analyzer operating in the multichannel scaler mode and recording the  $\text{BF}_3$  monitor output and the induced  $^{16}\text{N}$  activity on the same multiscaler pass (4-6, 18). Changes in beam intensity can then be precisely compensated for by mathematically treating each channel recording the relative neutron fluence rate as an individual irradiation and decay correcting its relative contribution to the oxygen counts over the remainder of the irradiation period. This produces a beam normalization value that is tailored to correct for beam variations during the irradiation as well as beam intensity differences between irradiations.

7.3.3 Variations in the positions of the sample or monitor reference relative to the neutron generator will cause a variation in the ratio of sample counts to monitor counts. In order to avoid the effects of this nonuniformity, both the sample and the monitor reference standard can be rotated about an axis parallel

to the beam during irradiation. Selection of experimental irradiation and counting geometries normally can be done in such a way as to avoid significant errors (see 7.4.2).

7.3.4 The short half-life of  $^{16}\text{N}$  imposes some restrictions on the timing of the various steps of the analysis. For maximum accuracy in a single sample transfer system, the entire cycle of irradiation, transfer, and counting should be controlled automatically so that all times are reproduced within a few hundredths of a second. Alternately, the entire irradiation and counting process may be recorded by a multichannel analyzer operating in the multichannel scaler mode and the parameters later normalized by use of a computer program (4-6). Precise control or measurements of time and fluence rate are not usually necessary when a monitor reference is irradiated simultaneously with the sample in a dual sample transfer and counting system.

#### 7.4 Counting Equipment:

7.4.1 *Irradiation Container Receiver and Stopping Devices*—These are devices to accept the sample following irradiation, and to position it reproducibly for counting.

7.4.2 *Gamma Detector, or Detectors*—Detectors at least equal in sensitivity to a single 3 by 3-in. (76 by 76-mm) thallium-activated sodium iodide ( $\text{NaI(Tl)}$ ) scintillation counter should be used. Both the sensitivity and reproducibility of the measurement will be affected by the choice of radiation detectors. Where energy discrimination is required, the superior resolution of a semi-conductor high-purity Ge (HPGe) detector may be desirable. However, use of an affordable HPGe detector may also result in some loss of efficiency, as compared to use of a  $\text{NaI(Tl)}$  detector. Systems based on use of a large well-type  $\text{NaI(Tl)}$  detector, or two 5 by 5-in. (127 by 127-mm) solid  $\text{NaI(Tl)}$  detectors mounted at  $180^\circ\text{C}$  are commonly used for higher efficiency counting. Bismuth germanate (BGO) scintillation detectors have higher efficiencies than  $\text{NaI(Tl)}$  detectors for the high-energy gamma rays from  $^{16}\text{N}$ , but are also presently much more costly than equivalent-size  $\text{NaI(Tl)}$  crystals. BGO detectors also have poorer energy resolution than  $\text{NaI(Tl)}$  detectors and this could be a consideration in some types of analyses. In general, the sensitivity of oxygen analysis will be increased by increasing the volume of the detector, and analytical reproducibility will be increased by the use of multiple detectors. If a single detector is used, but not a well counter, the sample should be rotated during counting to minimize the effects of sample nonhomogeneity and positioning. An external radiation shield of heavy metal sufficient to reduce the detector background to an acceptable level should surround the detector assembly.

7.4.3 *Electronic Equipment*—Amplifiers, discriminators or multichannel analyzers, and data storage devices capable of taking the pulse from the detector, amplifying and shaping it, distinguishing it by its energy, and storing it are required.

7.4.4 *Scaler or Multichannel Pulse-Height Analyzer*—If a scaler is used for data collection, it should have a suitable speed to minimize dead-time losses and prevent pulse pileup. It should be preceded in the counting system by an energy analyzer. If a multichannel pulse-height analyzer is used, cognizance must be taken of the need for a dead-time correction. Very high counting rates with dead time may also result in

gain shift, and either automatic or manual gain shift control will be necessary, if surveillance of the multichannel spectrum shows any shift of peak positions. The multichannel analyzer may also be operated in the multichannel scaler (MCS) mode when using a single sample transfer system as described in 7.3.2. MCS capabilities are currently available as both printed circuit boards which reside in laboratory computers as well as in specialized MCA systems.

7.5 *Shielding*—Because the neutron generators used for this analysis are intense sources of radiation, shielding must be erected to prevent the exposure of personnel. The principal types of radiation of concern are fast and thermal neutrons and gamma rays. This leads to a complex shielding problem similar to that around a low power nuclear reactor. Typically, up to 2 m of ordinary concrete, or its equivalent in special materials, may be required. Sub-ground-level “down hole” installations can reduce shielding costs, but very narrow shielding cavities can also increase the fluence rate of thermal neutrons at the irradiation position. In some cases, the increased low-energy neutron fluence rate can result in interference problems.

## 8. Precautions

8.1 The operation of a high-energy neutron generator or accelerator poses a potential radiological safety hazard to operating personnel. Adequate biological shielding (see 7.5) and safety interlocks at these facilities, in addition to appropriate operator training, are essential to ensure that personnel hazards are minimized. A venting system for the return transfer-tube gas is desirable in order to keep radioactive gases or dust particles away from the operator. Radiation survey measurements must be made to ensure that the radiation levels in occupied areas are within the levels specified by Title 10, Part 20, of the Code of Federal Regulations, as well as any appropriate state and local radiation safety regulations.

8.2 For the “pumped” drift-tube neutron generators that have replaceable targets, there is an additional hazard from tritium release during target changes. Tritium is a radioactive gas with a relatively long half-life 12.312 years (19) that decays by emitting a low-energy beta particle (18.564 keV, maximum). Ingestion and work-area contamination are two potentially serious consequences that make safe handling of targets by trained and experienced operators mandatory. These hazards are greatly reduced by use of the newer sealed-tube neutron generators. The risk of tritium release through breakage of the sealed-tube during replacement does exist, but sealed-tube replacement intervals are many times longer than target replacement intervals on a “pumped” system.

## 9. Sampling

9.1 This test method of oxygen determination is independent of the method used for taking samples. However, for those applications where the analysis sample is intended to be representative of a larger body of material, appropriate sampling techniques must be used.

9.2 Once a sample has been taken, it should be handled in such a way as to minimize the possibility for contamination. Preferably, it should be encapsulated as soon as possible with an inert atmosphere such as dry nitrogen gas. Powdered

samples often pick up moisture from the air quickly and must be dried, weighed, and encapsulated quickly. Some organic liquids, especially some fossil fuel byproducts, may diffuse through the walls of polyethylene “rabbits,” resulting in sample weight loss if not analyzed promptly after packaging.

9.3 As stated in 6.3, the geometry of the sample/neutron generator and sample/counter must be identical to those of the calibration standard to avoid positioning errors. Therefore, the packaging of the sample is critical. Often, a completely filled container is used as a standard geometry for any specific analysis run. Care must be taken with powdered samples to ensure that sufficient packing has been accomplished during the loading of the sample vial to avoid further packing during the sample transfer process. Packing of the sample, resulting from the physical shock of pneumatic transfer and stopping, will result in a change to the sample package geometry, induce error, and add uncertainty to the measurement.

## 10. Calibration and Standardization

10.1 Prepare at least three weighed samples of material with oxygen contents known to three significant figures, bracketing the expected range in the samples. Many stoichiometric oxygen-bearing materials are available for use as comparator standards. The weighed samples may be either pure, or composite standards with an added diluent. In preparing comparator standards, it may be necessary to blend the oxygen-bearing material with a relatively oxygen-free “filler” material, such as graphite, or resublimed sulfur, which can be obtained in high purity and with low oxygen content, such that the geometry of the standards will conform to that of the samples. It is necessary to take into account the small oxygen content of the filler and the plastic irradiation container in assigning an oxygen content to the standard.

10.2 Put the  $\text{BF}_3$  neutron monitor (if used), scalars, recorders, amplifiers, and power supplies into operation in accordance with the manufacturer’s instructions. Adjust the voltages and gains of the individual detector systems so that they are operating properly and at the optimum voltages. Using a counting standard of known energy and activity, such as a calibrated pulse generator, adjust the multichannel pulse-height analyzer, or scaler-discriminator, so that only those gamma ray pulses above approximately 4.5 MeV are stored.

10.3 Turn on the neutron generator in accordance with the manufacturer’s instructions and adjust the neutron output to the desired level. Initiate the preselected irradiation, delay, and counting sequence, with one of the standards. If an automatic generator switching system is available, it may be desirable to discontinue the neutron production during the counting period to reduce the background of high-energy gamma-ray radiation at the counting station due to 14-MeV neutron capture and scatter. However, with the availability of a remote, well-shielded counting station, the neutron output will be found to be more stable if the generator is allowed to run continuously. In this latter case, it is necessary to establish that the transit times for the monitor and sample approaching and leaving the irradiation station are equivalent. With a dual sample transfer and counting system, record the total comparator standard

count and the total monitor reference standard count recorded by the scalers/analyzers during the counting interval. If the relative fluence rates are measured by a neutron monitor during irradiation, as when using a single sample transfer system, record these counts as the monitor counts. As noted in 7.3.2, a multichannel analyzer operating in the MCS mode may be used to record the entire irradiation sequence.

NOTE 4—In “pumped” drift-tube machines the deuteron beam should be defocused as much as possible to prolong target life consistent with desired neutron output.

10.4 Repeat the irradiation-delay-count sequence using the other comparator standard samples. Record as above the monitor count and the total comparator standard count recorded by the scalers during the counting interval.

10.5 Take the ratio of the activity of the comparator standards to that of the monitor for each standard. Plot these ratios versus milligrams of oxygen in each comparator standard. Such a plot results in a straight line intersecting the milligrams of oxygen axis at a point less than zero. The exact point depends on the oxygen content of the particular packaging material used in the preparation of the series of standards. This amount of oxygen can now be used to adjust the individual points so that the extended line goes through zero if no oxygen were present. This plot can then be used directly with experimental sample activities to compute oxygen contents.

10.5.1 Standards prepared by graphite dilution have a density of about  $1 \text{ g cm}^{-3}$ , and are used to determine oxygen in materials having a variety of densities. Gamma rays lose their energy by through interactions with matter that are dependent, in part, on density. In order to make the graphite standards applicable to samples of varying density, it is sometimes necessary to apply a correction factor to compensate for the attenuation of the gamma radiation by the sample itself. This correction can be determined by the use of a series of samples of increasing density, but of identical dimensions. For this purpose, samples are constructed with a hole drilled through the long axis so that a polymethylmethacrylate rod can be inserted to act as a reproducible source of oxygen. These samples can then be compared to a monitor in the same manner as the previous set of graphite standards. A plot is made of density versus the signal, where the sample of density equal to  $1.0 \text{ g cm}^{-3}$  is plotted as unity and signals for samples of higher density as fractions. This plot will provide an activity correction factor that may be divided into the observed sample activity, when dealing with samples of variable density, but similar matrix composition. Since gamma-ray sample self-absorption is also dependent on atomic number ( $Z$ ), it is desirable that the average  $Z$  of the standards be similar to that of the samples.

10.5.2 This test method of preparing and correcting oxygen comparator standards and monitor reference standards results in standards that can be referred to as “primary,” since they are independent of the methods used in conventional determinations of oxygen. The plastic monitor reference standards are stable with regard to changes in oxygen content, since there is little or no tendency for oxidation at the monitor surface. Secondary oxygen comparator standards consisting of previously analyzed materials may also be used as monitors. A set of

these secondary standards that have different matrix compositions and macroscopic densities is useful in matching standards to samples, hence minimizing potential matrix self-absorption problems (20).

## 11. Procedure

11.1 Place the weighed sample to be analyzed in an irradiation container identical to those used in the standardization procedure. Irradiate, delay, and count in the same sequence, at approximately the same neutron fluence rate ( $\pm 10\%$  would be satisfactory). Record the monitor count and the total sample count.

## 12. Calculation

12.1 Calculate the results in terms of weight percent of oxygen as follows. From the standards, it is possible to determine a sensitivity factor,  $K$ :

$$K = (A_{std}/A_m)/W_{std} \quad (1)$$

where:

- $A_{std}$  = total count from the comparator standard (corrected for natural background),
- $A_m$  = total monitor count (corrected for natural background, if required),
- $W_{std}$  = milligrams of oxygen in the comparator standard, and
- $K$  = sensitivity in counts per milligram of oxygen per unit monitor count.

12.1.1 The factor  $K$  is seen to be merely the slope of the calibration curve, and its value is not affected by the sample-container “blank” as long as the same “blank” is applicable for all experimental points of the calibration curve. Similarly, the natural detector background should be ordinarily negligible compared to the monitor count ( $A_m$ ), but may be significant compared to the standard count ( $A_{std}$ ), or the sample count ( $A$ ). This is especially true if oxygen concentrations in the sample are low. If this is the case, backgrounds should be subtracted from the counting rates before calculation.

12.2 Calculate the oxygen content of the sample in milligrams as follows:

$$\text{oxygen, mg} = (A/A_m)/K \quad (2)$$

where:

- $A$  = the total sample count recorded (corrected for natural background).

This oxygen content includes oxygen in the empty sample container. A “blank” value must be determined representing the milligrams of oxygen in the empty sample container without air, or the radioactivity due to air oxygen. The weight of oxygen in the blank is then subtracted from the gross oxygen content determined in Eq 2, or alternatively, the ratio ( $A_{blank}/A_m$ ) is subtracted from ( $A/A_m$ ) before calculating oxygen content in Eq 2. Either way, the net oxygen content in the sample alone is converted to oxygen concentration by Eq 3.

12.3 Calculate the percent of oxygen as follows:

$$\text{oxygen, \%} = (O/W) \times 100 \quad (3)$$



where:

$O$  = milligrams of oxygen in the sample, and

$W$  = milligrams of sample used.

12.4 The data that must be collected are the background corrected activities of the sample and the monitor ( $A$  and  $A_m$ , respectively), and the weight of the sample ( $W$ ).

12.5 The standard deviation of the factor  $K$ , due to counting statistics, may be calculated and minimized by replicate determinations on the standard samples. Similarly, if  $A_m$  is large enough that its contribution to the total error is negligible, the counting error of the sample may be calculated from  $A$  and combined with that of the standard by the usual methods of propagation of error (21).

### 13. Precision and Bias

NOTE 5—Measurement uncertainty is described by a precision and bias statement in this standard. Another acceptable approach is to use Type A and B uncertainty components (22, 23). This Type A/B uncertainty specification is now used in International Organization for Standardization (ISO) standards and this approach can be expected to play a more prominent role in future uncertainty analyses.

13.1 The precision of the oxygen determinations is dependent upon the counting statistics, the stability of the neutron generation rate (if not monitored), and the reproducibility of the irradiation, delay, and counting sequence including sample positioning. Errors due to counting statistics have been discussed previously. If the procedure using simultaneous irradiation of a monitor and sample is not used, time variations in the sample-monitor irradiation delay and counting sequence may be important causes of error, particularly the reproducibility of the delay time during which the sample leaves the irradiation position, comes to rest in the counting position, and the count is begun. This is particularly true when the generator is left running continuously. Normally, more than ample time is allowed to ensure that the sample and monitor can complete their transport and come to rest before the count is initiated, but samples of different masses may leave the irradiation position at different velocities and, hence, have slightly different irra-

diation times if the generator is running continuously. A high-speed timer may be used to record variable delay times, or the entire sequence may be continuously recorded as a function of time using a MCS analyzer technique. Another possible source of error, if a dual transfer system with a monitor reference standard is not used, can arise if the neutron fluence rate varies during the irradiation in such a way that the average fluence rate used for normalization is different from the average fluence rate for the last part of the irradiation period, and the irradiation lasts longer than the  $^{16}\text{N}$  half-life. This causes the fluence rate during the last few seconds of the irradiation to dominate the correction for the total neutron fluence. This problem may be avoided by use of a MCS analyzer to record all events in small time increments during the entire irradiation and counting sequence (4-6).

13.2 The overall precision of this test method is such that duplicate samples or replicate runs of the same sample should yield results that do not vary by more than three times the standard deviation determined from counting statistics alone, assuming other uncertainties such as improper sampling do not dominate.

13.3 For metal samples in the range from 100 to 200  $\mu\text{g/g}$  oxygen, the reproducibility has been found to be about  $\pm 3\%$ . However, the precision is highly dependent on the specific physical characteristics of the irradiation and counting facility and sample size. This value has been stated to range from about  $\pm 2\%$  at the level where counting statistics are not limiting, to as much as  $\pm 15\%$  when the oxygen concentration is comparable to that in the sample container “blank.”

13.4 In addition to the above precision factors, bias is affected by the dead time of the associated electronic counting circuits and the setting of the lower level of the pulses accepted by the scaler to eliminate spectral interferences. Changes in this latter factor can also affect precision and it should be checked periodically to be certain that no change from the desired setting has taken place.

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