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Standard Test Method for Oxygen Content Using a 14-MeV Neutron Activation and Direct-Counting Technique[1]

This standard is issued under the fixed designation E 385; 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 (ε) 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 over 50 % to about 10 μg/g, or less, 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**).[2]

1.3 The values stated in either SI or inch-pound units are to be regarded separately as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety problems 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:*

E 170 Terminology Relating to Radiation Measurements and Dosimetry[3]

E 181 Method for Detector Calibration and Analysis of Radionuclides[3]

E 496 Method for Measuring Neutron Flux Density and Average Energy from $^3H(d,n)^4He$ Neutron Generators by Radioactivation Techniques[3]

2.2 *U.S. Government Document:*

Code of Federal Regulations, Title 10, Part 20[4]

3. Terminology

3.1 *Definitions (see also Terminology E 170):*

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 Cockroft-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. A review of operational characteristics, descriptions of accessory instrumentation, and applications of accelerators used as fast neutron generators is given in Ref (**2**).

3.1.2 *comparator standard*—a reference standard of known oxygen content whose specific counting rate (counts min^{-1} [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. Comparative standards prepared in this way may be used directly as "monitors" (see 3.1.4) in order to avoid the need for monitor-sample calibration plots, in those cases where the usual monitor reference standard is physically or chemically dissimilar to the samples 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 cm^{-2} 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 is also commonly referred to as "flux density." The total neutron fluence is the fluence rate integrated over time.

3.1.3.1 *Discussion*—The $^3H(d,n)^4He$ reaction is used to 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 known oxygen content is often used as a monitor reference standard in dual sample transfer systems. It is never removed from the system regardless of the characteristics of the

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[2] The boldface numbers in parentheses refer to a list of references at the end of the text.

[3] *Annual Book of ASTM Standards*, Vol 12.02.

[4] Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

sample to be analyzed. In this case monitor-sample calibration plots are required.

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 INAA determination of oxygen, the multichannel analyzer may also be used to receive and record both the BF_3 neutron detector monitor counts and the sample gamma-ray detector counts as a function of stepped time increments (**3, 4**). 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 assure 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}N produced by the (n,p) nuclear reaction on ^{16}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 monitor reference standard sample are not irradiated simultaneously, the neutron dose received during each irradiation must be recorded, typically by use of a BF_3 neutron proportional counter. The amount of total oxygen (all chemical forms) in the sample is proportional to the corrected sample count and is quantified by use of the corrected specific activity of the monitor, or comparator standard(s).

4.1.1 ^{16}N decays with a half-life of 7.13 s by β-emission, thus returning to ^{16}O. About 69 % of the decays are accompanied by 6.13-MeV gamma rays, 5 % by 7.12-MeV gamma rays, and 1 % by 2.74-MeV gamma rays. Other lower intensity gamma rays are also observed. About 26 % of the beta transitions are directly to the ground state of ^{16}O. (All half-lives and gamma-ray energies are taken from Ref (**5**) and decay schemes are given in Ref (**6**). A useful elemental data base and calculated sensitivities for 14-MeV instrumental neutron activation analysis (14-MeV INAA) are provided in Ref (**7**). See also Method E 181.)

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}N, there are very few elements that will produce interfering radiations; nevertheless, caution should be exercised. ^{19}F, for example, will undergo an (n,α) reaction to produce ^{16}N, the same indicator radionuclide produced from oxygen. Because the cross section for the $^{19}F(n,\alpha)^{16}N$ reaction is approximately one-half that of the $^{16}O(n,p)^{16}N$ 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}B will undergo an (n,p) reaction to produce ^{11}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}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}N.

NOTE 2—Argon produces an interferent, ^{40}Cl, by the $^{40}Ar(n,p)^{40}Cl$ reaction. Therefore, argon should not be used for the inert atmosphere during sample preparation for oxygen analysis. ^{40}Cl ($t_{1/2}$ = 1.35 m) has several high-energy gamma rays, including one at 5.88 MeV.

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 will result in a 3.5 to 5 % change in detector efficiency (**8**). 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. Positioning errors are normally minimized by rotating the sample around a single axis, or biaxially, during both irradiation and counting. Alternately, dual detectors at 180° can be used to minimize positioning errors at the counting station.

6.4 Since ^{16}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 in the highest sensitivity determinations where sample sizes may be large.

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 μg/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 (**9**). 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. This "containerless" approach provides optimum sensitivity for low-level determinations, but care must be taken to avoid contamination of the transfer system.

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 $^{3}H(d,n)^{4}He$ 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, 2**).

7.1.1 Other nuclear reactions may be used, but the neutron energy must exceed 10.22 MeV (**10**) for the $^{16}O(n,p)^{16}N$ reaction to take place. The 14-MeV neutron output of the generator should be 10^{9} to 10^{12} neutrons s^{-1}, with a usable fluence rate at the sample of 10^{7} to 10^{9} neutrons cm^{-2} s^{-1}. The 14-MeV fluence rate may be measured as described in Method E 496.

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}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}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}N atoms produced in the air onto the sample surface. The transfer system and data processing may be controlled by PC-type microcomputers using programs written in BASIC (**11**), or by a minicomputer using programs written in FORTRAN (**4**). 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 monitor reference standard, or 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}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 standard is used with each sample, and is never removed from the system. Since the sample and monitor reference standard are irradiated and counted simultaneously, and ^{16}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 dependance 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 standard 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 standard.

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 monitor reference standard (or 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 cm^{-2} s^{-1} passing through the sample. A wide variety of ingenious systems have been devised and used for this purpose (**12**). Probably the most commonly used and simplest system is a boron trifluoride (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 BF_3 monitor does not directly measure neutrons of the