Designation: E3063 – 24

Standard Test Method for
Antimony Content Using Neutron Activation Analysis (NAA)[1]

1. Scope*

1.1 This test method covers the measurement of antimony concentration in plastics or other hydrocarbon or organic matrix by using neutron activation analysis (NAA). The sample is activated by irradiation with neutrons from a research reactor and the subsequently emitted gamma-rays are detected with a germanium semiconductor detector. The same system may be used to determine antimony concentrations ranging from 1 ng/g to 10 000 µg/g with the lower end of the range limited by numerous interferences and the upper limit established by the demonstrated practical application of NAA.

1.2 This test method may be used on either solid or liquid samples, provided that they can be made to conform in size and shape during irradiation and counting to a standard sample of known antimony content using very simple sample preparation. 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 neutron activation analysis using reactor neutrons (**1**).[2]

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific precautions are given in Section* 9.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

E170 Terminology Relating to Radiation Measurements and Dosimetry

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *U.S. Government Document:*[4]

Code of Federal Regulations, Title 10, Part 20

2.3 *Joint Committee for Guides in Metrology (JCGM) Reports:*[5]

JCGM 100:2008, GUM 1995, with minor corrections Evaluation of measurement data—Guide to the expression of uncertainty in measurement

3. Terminology

3.1 *Definitions:* See also Terminology E170.

3.1.1 *comparator standard*—a reference standard of known antimony content whose specific activation and counting sensitivity (counts (mg of antimony)$^{-1}$) may be used to quantify the antimony 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. Differences in size, density, shape, and matrix composition between sample and standard may be corrected for using physical or empirical models.

3.1.2 *gamma-ray spectrometer*—a system comprising a detector which detects individual gamma-rays and converts their energy into an electronic pulse whose voltage is proportional to the energy deposited in the detector, and a multichannel

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A Summary of Changes section appears at the end of this standard

pulse-height analyzer which measures the pulse heights, assigns a digital value, and stores the individual counts in the channels of a gamma-ray spectrum according to the digital values assigned.

3.1.3 *intensity*—the probability of emission of a gamma-ray of a given energy per decay. Another commonly used term is gamma abundance.

3.1.4 *monitor*—any type of detector or comparison reference material that can be used to produce a response proportional to the neutron fluence rate in the irradiation position, or to the radionuclide decay events recorded by the sample detector.

3.1.4.1 *Discussion*—An aluminum wire with 1 mg/g Au content is often used as a fluence rate monitor. Iron wires are used as well. It is important to distinguish that the monitor is not a standard used to scale the antimony content of the samples to be measured, but rather is used to normalize the analysis system among samples irradiated simultaneously at different positions in the polyethylene irradiation sample container or among successive analytical passes within the procedure. When using reactors with highly reproducible fluence rate, such as those with 1 % variation over long periods of time, monitors may not be necessary for every irradiation.

3.1.5 *neutron fluence rate*—the fluence rate (see definition in Terminology E170) of neutrons. In this test method it refers to the value at the site in the reactor where sample and comparator standard are irradiated.

3.1.6 *pneumatic transfer system*—a system used to transport the sample to the irradiation site in the reactor and then to a sample receiver.

3.1.6.1 *Discussion*—It may also be used to transport the sample directly to the counting station where the activity of the sample is measured. For the measurement of antimony, where a long decay time between irradiation and counting is usually required, the samples are manually transferred from the receiver to the germanium semiconductor detector or to a mechanical sample changer which transports them one by one at the appropriate time to the counting position at the detector.

3.1.7 *research nuclear reactor, n*—a nuclear reactor that uses the fission of uranium to operate at a well-controlled power level and produces neutrons that can be used for experiments and for neutron activation analysis. The operational characteristics of reactor types believed to be applicable to this test method are given in Refs (2-6).

3.1.7.1 *Discussion*—Another term in common usage is research reactor. Reactor conditions which may make the reactor unsuitable for this test method (for example, very low neutron fluence rates or high operating temperature) are sample and reactor dependent. Such conditions should be considered prior to use of this test method.

3.1.8 *standard uncertainty*—measurement uncertainty of the results of a measurement expressed as a standard deviation (GUM, see 2.3).

4. Summary of Test Method

4.1 The test method can be applied directly to solid samples such as plastic pellets or cylindrical pieces of cable insulation.

The weighed sample to be analyzed is placed in a polyethylene container for transfer from the sample loading port to the irradiation site in the reactor. Several samples, standards, and monitors may be irradiated simultaneously provided that the self-shielding effects of multiple samples on each other are well understood (7). After irradiation for a pre-selected time, the samples are returned to the sample receiver. After an appropriate decay period to allow the decay of short-lived radio-isotopes, typically 24 h, the samples are manually unpacked and transferred from the receiver to the germanium semiconductor detector or to a mechanical sample changer which transports them one by one at the appropriate time to the counting position at the detector. The signals from the detector are sent to a multichannel pulse-height analyzer which measures the energies of the individual gamma-rays and places them in a gamma-ray spectrum. The spectrum has peaks at the characteristic energies of the elements present in the sample. The spectrum for each sample is stored for subsequent analysis.

4.2 The amount of total antimony (all chemical forms) in the sample is proportional to the corrected and normalized peak area and is quantified by use of the corrected and normalized peak area of the comparator standard(s).

4.3 When antimony is irradiated with neutrons, the atoms of the isotope ^{121}Sb capture neutrons and are converted to ^{122}Sb which is radioactive with a half-life of 2.72 days. ^{122}Sb decays by emitting a beta-ray and gamma-rays of several possible energies. From Ref (8), the main gamma-ray, at 564.2 keV, is emitted in 70.67 % of decays. The amount of total antimony (all chemical forms) in the sample is proportional to the corrected number of counts in the peak at 564.2 keV. The area of the peak at 564.2 keV is corrected for counts beneath the peak due to Compton scattered gamma-rays and for pulse losses (dead-time) in the combined detector-multichannel pulse-height analyzer system. All modern multichannel pulse-height analyzers accurately correct for pulse losses up to their maximum useable count-rates.

4.3.1 The detector must have good energy resolution because the peak at 564.2 keV must be well separated from nearby peaks such as those from ^{82}Br at 554.3 keV and ^{76}As at 559.1 keV.

4.4 In addition to ^{121}Sb capturing neutrons to produce ^{122}Sb, the ^{123}Sb isotope captures neutrons to produce ^{124}Sb, with a 60-day half-life. This isotope has strong gamma lines at 603 keV and 1691 keV. Measurement of both ^{122}Sb and ^{124}Sb provides an additional verification of the method's accuracy. This standard employs the most sensitive ^{122}Sb gamma-ray, but the same methods and equations apply equally to all gamma-rays of both isotopes.

5. Significance and Use

5.1 High levels of antimony are commonly used in flame retardant formulations for various materials. NAA is a test method that can be useful for verifying these levels and, for other materials, NAA can also be useful in establishing the amount of low level contamination, if any, with high sensitivity and high precision.

5.2 Neutron activation analysis provides a rapid, highly sensitive, nondestructive procedure for antimony determination in a wide range of matrices. This test method is independent of the chemical form of the antimony.

5.3 This test method can be used for quality and process control in the petrochemical and other manufacturing industries, and for research purposes in a broad spectrum of applications.

6. Detection Limit and Range of Application

6.1 Using a research nuclear reactor and germanium semiconductor detector, the estimated detection limit for antimony in plastics is 1 ng/g (**9**). This detection limit may be reduced by using a larger sample, a reactor with higher neutron fluence rates, higher counting efficiency detectors, and longer irradiation and counting times. However, under the conditions of this test method, the main factor determining the detection limit is the amount of interfering elements in the sample.

6.1.1 The detection limit of 1 ng/g provided in this test method presumes clean materials. In materials containing high amounts of interfering elements, the detection limit may be higher. This detection limit of 1 ng/g implies that, for samples actually containing 1 ng/g (not known by the analyst), there is a 50 % chance that the analysis will result in a peak area corresponding to greater than 1 ng/g and it will be judged that antimony was detected and a quantitative result will be given.

6.1.2 For this same sample, there is also a 50 % chance that the analysis will result in a peak area corresponding to less than 1 ng/g and it will be judged that antimony was not detected and a result of "not detected" will be given. For samples containing no antimony (or less than 0.1 ng/g) there is a 2.5 % probability that the result of the analysis will be greater than 1 ng/g and a quantitative result will be given (false positive).

6.2 Near the detection limit, the uncertainty in the measured antimony mass fraction is 0.5 ng/g. This standard uncertainty is caused mainly by statistical fluctuations in the Compton background under the small antimony peak at 564.2 keV.

6.3 With a detection limit of 1 ng/g, the limit of quantitation (for 10 % uncertainty) is 5 ng/g. This means that, for samples containing 5 ng/g antimony or more, it is possible to produce an analysis result with 10 % standard uncertainty or less.

6.4 At levels above 10 mg/g (1 %), nonlinear effects in the relation between observed peak area and antimony concentration shall be considered and the application of corrections for saturation effects such as neutron self-shielding shall be permitted.

6.4.1 For samples with high antimony content, neutron self-shielding correction may use a procedure such as that of Ref (**10**) which takes into account sample size, observed antimony content, and the ratio of thermal to epithermal fluence rates of the reactor irradiation site used.

7. Interferences and Necessary Corrections

7.1 All radionuclides which emit high-energy gamma-rays may potentially interfere with the detection of the 564.2 keV gamma-ray of ^{122}Sb. When these gamma-rays are detected in large numbers, the high count rate may saturate the detector and force the analyst to count the sample farther from the detector or to wait until the amount of radioactivity decreases. This reduces the sensitivity for the detection of antimony. Also, high-energy gamma-rays which scatter in the detector by the Compton process and deposit only part of their energy in the detector may produce counts in the gamma-ray spectrum near 564.2 keV. These counts under the ^{122}Sb 564.2 keV gamma-ray peak make it more difficult to determine the peak area and increase the uncertainty of the peak area due to counting statistics.

7.2 A specific potentially interfering radionuclide is ^{76}As which emits a weak gamma-ray at 563.2 keV, almost the same energy as the gamma-ray of ^{122}Sb. However, this interference only becomes significant when there is as much arsenic as antimony in the sample and it can easily be corrected. Knowing that the ratio of the areas of the ^{76}As peaks at 563.2 keV and 559.3 keV is a constant for a given germanium detector and a given counting geometry, approximately 0.025, one can correct the interference for each sample using the observed area of the ^{76}As peak at 559.3 keV.

7.3 There are a number of other potentially interfering radionuclides which emit gamma-rays near the ^{122}Sb energy of 564.2 keV. They are listed in Table 1. In most cases the elements producing these nuclides will be present in the sample in low quantities and the interfering gamma-rays will have a negligible effect on the 564.2 keV peak area.

7.3.1 However, for materials with expected low antimony content and which may contain these interfering elements in higher quantities, it is prudent to verify the spectrum for the presence of the associated gamma-ray. If the associated gamma-ray peak is detected, then the interference should be corrected using the area of the associated gamma-ray peak. The quantity to subtract from the area of the ^{122}Sb peak at 564.2 keV is the area of the associated peak multiplied by the intensity ratio and multiplied by the ratio of detection efficiencies at the interfering gamma-ray energy and the associated gamma-ray energy.

7.3.2 ^{228}Ac is a naturally occurring radionuclide in the ^{232}Th decay series. It is found in the materials of the floor and walls surrounding the detector and will give a peak in the spectrum at 562.9 keV if the detector is not sufficiently shielded from background radiation.

7.4 An important aspect of this analysis method that must be controlled is the geometry during both irradiation and counting. Fluence rates will vary between standard and samples

TABLE 1 Potentially Interfering Radionuclides

Element	Nuclide Produced	Half-life	Interfering gamma-ray		Associated gamma-ray		Intensity Ratio
			Energy		Intensity		
As	^{76}As	26.3 h	563.2	1.20	559.3	45.0	0.0267
Cd	^{117m}Cd	3.4 h	564.4	14.7	1066.0	23.1	0.6364
Cs	^{134}Cs	2.06 years	563.2	8.38	604.7	97.6	0.0859
Nd	^{151}Pm	28.4 h	564.9	0.35	340.1	22.0	0.0159
Eu	^{152}Eu	13.4 years	564.0	0.467	1408.0	20.8	0.0225
Eu	^{152m}Eu	9.34 h	562.9	0.226	841.6	14.6	0.0155
Th	^{228}Ac	background	562.9	1.01	911.2	29.0	0.0348

which are at different positions in the irradiation container. These variations are easily corrected using flux monitors to measure the fluence rate gradients or from the knowledge of variations that are reproducible.

7.4.1 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 germanium detector, a 1 mm change in position of the sample along the detector axis was found to result in a 5 % change in detector efficiency.

7.4.2 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 antimony concentration. Such very close sample-detector geometries are only used for samples with very low antimony content and the effect of sample-detector distance variations is greatly reduced when samples are counted farther from the detector.

7.5 Since ^{122}Sb emits high-energy gamma rays, determinations are usually not significantly affected by variations in gamma-ray self-absorption in the sample. Corrections for gamma-ray attenuation during counting are usually negligible, except for very large samples and those of very high density such as heavy metal matrices.

7.6 The effect of neutron self-shielding may be significant at high antimony concentrations. Antimony is activated by two types of neutrons: thermal (energies below 0.5 eV), and epithermal (energies above 0.5 eV). As thermal and epithermal neutrons penetrate into the sample, some are absorbed and the center of the sample receives a lower fluence rate than the outside of the sample, and possibly significantly lower than the flux monitor or the standard.

7.6.1 As an example of the importance of addressing self-shielding, for a cylindrical sample with a diameter of 3 mm and length of 10 mm and 10 mg/g or 1 % antimony, the average reduction in fluence rate over the volume of the sample is 0.007 % for thermal neutrons and 2.1 % for epithermal neutrons (**10**). Each facility should characterize their own self-shielding conditions considering the neutron spectrum at the specific research nuclear reactor and the size and antimony content of the sample.

7.6.2 If neutron self-shielding correction is required in order to achieve an acceptable accuracy and detection limit, neutron self-shielding correction may use a procedure such as that of Ref (**9**) which takes into account sample size, observed antimony content, and the ratio of thermal to epithermal fluence rates of the reactor irradiation site used.

7.7 Thermal neutron self-shielding may be significant in samples of PVC because PVC contains 56.7 % chlorine by weight and chlorine is a strong absorber of thermal neutrons. For a cylindrical sample of polyvinyl chloride (PVC) with a diameter of 3 mm and a length of 10 mm analyzed in a Slowpoke reactor, the average reduction in thermal neutron fluence rate over the volume of the sample is approximately 9 % (**10**). For PVC samples, thermal neutron self-shielding should be corrected. A procedure such as that described in Ref (**10**) can be used to perform this correction.

7.8 The antimony content of the high-purity polyethylene sample vials or bags used for irradiation is usually very low and it is usually not necessary to transfer the sample to a fresh container between irradiation and counting, except when the antimony content is expected to be in the nanogram per gram range.

8. Apparatus

8.1 *Research Nuclear Reactor*—The operational characteristics of common research reactor types are given in (**2-6**). These and larger research nuclear reactors are all suitable for the measurement of antimony by neutron activation analysis. Larger reactors produce higher neutron fluence rates.

8.1.1 However, since even the smaller reactors can produce adequate sample activities, the use of larger reactors does not result in better sensitivity for the detection of antimony. With smaller reactors, the tendency is to use larger samples. The larger samples are more representative of the material to be analyzed but they may lead to higher neutron self-shielding corrections. Larger reactors may have a very well thermalized irradiation site which essentially eliminates the need for an epithermal neutron self-shielding correction.

8.1.2 Smaller reactors, developed mainly for neutron activation analysis, tend to be more flexible for neutron activation analysis and more readily available. Larger reactors may be unavailable for long periods of time for refueling or for higher priority experiments and their neutron spectra and power levels are not under the control of the neutron activation analysis personnel.

8.1.3 Some smaller reactors have stable and highly reproducible neutron fluence rates at the irradiation sites, which may eliminate the need for the repeated use of fluence rate monitors. If a laboratory chooses not to use fluence rate monitors and to rely on the reproducibility of the neutron fluence rate, it should have in place a quality assurance program that ensures this reproducibility.

8.2 *Pneumatic Sample Transfer System*—Samples are usually transferred to and from the reactor irradiation position with a pneumatic system operating with compressed air. However, with the fairly long half-life of ^{122}Sb, 2.72 days, even slower manual insertion and removal of the samples from the reactor is acceptable.

8.3 *Counting Equipment:*

8.3.1 *Sample Changer*—For the measurement of antimony in batches of samples, a mechanical sample changer is desirable. It may be a robotic arm or a turntable. It places the samples one by one at the counting position on the germanium detector.

8.3.2 *Gamma Detector*—A high-resolution germanium semiconductor detector is used. The resolution is usually specified as full-width-half-maximum at 1332 keV; 1.6 keV to 2.0 keV is typical. The resolution should be approximately 1.5 keV at the antimony energy of 564.2 keV. The largest volume high-efficiency detector (200 cm^3) does not offer much advantage over a smaller volume detector (50 cm^3). All high-purity germanium (HPGe) detectors are very stable over long periods of time and the counting conditions are highly reproducible. The standards and samples are usually held at the same