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

2. Referenced Documents

2.1 *ASTM Standards:*[3]

E170 Terminology Relating to Radiation Measurements and Dosimetry

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 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 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.

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

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

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

[5] Document produced by Working Groups of the Joint Committee for Guides in Metrology (JCGM). Available free of charge at BIPM website (http://www.bipm.org).

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. Examples of reactor types believed to be applicable to this test method are TRIGA, SLOWPOKE and MNSR; their operational characteristics 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 %), non-linear 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 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

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

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 3-mm diameter, 10-mm long cylindrical sample with 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 3-mm diameter, 10-mm long cylindrical sample of polyvinyl chloride (PVC) 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 ng/g range.

8. Apparatus

8.1 *Research Nuclear Reactor*—Common research reactor types are TRIGA, SLOWPOKE and Miniature Neutron Source Reactor (MNSR); their operational characteristics 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 Reactors like SLOWPOKE and MNSR 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 turn-table. 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 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 distance from the detector using Plexiglas[6] supports. The laboratory should have in place a quality assurance program

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[6] Plexiglas is a trademark of ELF Atochem, now a subsidiary of Arkema in the United States.

that ensures the reproducibility of the detection efficiency for the counting geometry used.

8.3.3 *Gamma-ray Spectrometer*—A Gamma-ray Spectrometer is 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 pulse-height analyzer containing an analog to digital convertor (ADC) 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.

8.3.3.1 Modern spectrometers have typically 8192 channels, so that the details of the spectrum from a high-resolution detector are clearly visible. Older systems, comprising a pulse amplifier and an analog to digital converter (ADC) in a multichannel pulse-height analyzer, have now been largely replaced by a Digital Spectrometer, which digitizes the pulses coming directly from the detector preamplifier.

8.3.3.2 The digital spectrometer is usually more stable than the older systems with a pulse amplifier because the amplifier was often the cause of gain shifts and drift. The digital spectrometer uses a personal computer for the human interface. All spectrometers lose some counts when two gamma-rays arrive at the detector almost simultaneously. Losses increase with increasing sample activity and increasing count rate and they must be corrected. The digital spectrometers have excellent counting-loss correction systems and are faster than the older systems with amplifier and ADC: typically they have three times lower counting losses with the same sample activity.

8.3.4 *Gamma-ray Spectrometer Software*—The software controls the data acquisition parameters, displays the gamma-ray spectrum on the computer monitor and stores the spectra in files.

9. Hazards

9.1 *Precautions*—Staff handling radioactive material and working near a nuclear reactor need to be properly trained. Follow all radiation safety regulations and monitor radiation doses continuously.

10. Sampling

10.1 The sample should be representative of the material to be analyzed. If the material is not homogeneous, a larger sample is preferable. The analyst must judge the appropriate sample size, based on estimated homogeneity, amount of radioactivity which will be produced, and possible neutron self-shielding and gamma attenuation effects which increase with increasing sample size. Typical samples have masses from 0.1 to 1 g.

10.2 Samples should be handled in such a way as to minimize the possibility for contamination. Powdered samples sometimes pick up moisture from the air quickly and should be weighed and encapsulated quickly. Some organic liquids, especially some fossil fuel byproducts, may diffuse through the walls of polyethylene irradiation vials, resulting in sample weight loss if not analyzed promptly after packaging.

10.3 Ideally, the geometry of the sample and that of the comparator standard (see 3.1.1) should be similar in order to avoid positioning differences during counting. In practice, this is usually not possible. There are at least small differences in size, shape and density. A physical or empirical model is used to correct for these differences.

11. Calibration and Standardization

11.1 Ideally, the comparator standard would be a stable, homogeneous powder or solid material with density similar to the samples to be analyzed and with certified antimony mass fraction. Alternatively, if the ideal comparator standard is not available, comparator standards may be prepared from certified standard solutions of antimony, designed for inductively coupled plasma mass spectrometry or for atomic absorption spectrometry. Aliquots of solution of known mass or volume can be dried on strips of filter paper. These can be rolled into cylinders with shape, volume and density similar to the solid or powder samples to be analyzed.

11.2 The irradiation conditions used must be standardized for each research nuclear reactor, irradiation location, and sample configuration. The uncertainty under the standardized conditions shall be determined and documented.

12. Procedure for the Measurement of Comparator Standards and Samples to be Analyzed

12.1 Weigh all comparator standards, fluence rate monitors and samples with an accuracy of 1 % or better and place them in appropriately labelled high-purity polyethylene vials or bags. A black felt pen marker is good for labelling because black ink contains organic dye with no significant heavy metals.

12.2 Pack the comparator standards, fluence rate monitors and samples in the polyethylene irradiation container (rabbit). Include enough monitors to be able to interpolate the neutron fluence rate to the positions of the comparator standards and samples. One monitor may be sufficient if the neutron fluence rate gradient is known and is reproducible. A monitor may not be needed if the neutron fluence rate is known to be reproducible to 1 % or better.

12.3 After ensuring that the research nuclear reactor is operating at the desired power and neutron flux level, use the pneumatic transfer system to send the irradiation container (rabbit) to the irradiation site. Allow it to continue being irradiated for the appropriate irradiation time. An irradiation time of 1 h at a neutron fluence rate of 10^{12}cm^{-2}s^{-1}has been shown to be useful. Since the neutron fluence rate can vary, irradiation time can be adjusted accordingly.

12.4 Remove the irradiation container from the reactor and record the time and date and the irradiation time (duration). Allow the radioactivity to decrease, in the sample receiver or other shielded container, for at least 1 h to allow for short half-life nuclides to decay.

12.5 Remove the comparator standards, fluence rate monitors and samples from the irradiation container and prepare them for gamma-ray counting. The packaging of the samples may be changed to reduce contamination by stray ^{122}Sb if the antimony concentrations are expected to be very low. The monitors may be counted on a different detector from the comparator standards and samples and after any decay time because they are used for relative measurements only.

12.6 After an appropriate decay time, place the comparator standards and samples one by one at the desired position on the gamma-ray detector. This may be done either manually, by placing the standard or sample on a Plexiglas[6] support attached to the detector, or using an automated sample changer. Since the half-life of ^{122}Sb is 2.72 days, the decay time may be anything from 1 h to 10 days or more.

12.7 Count the comparator standards and samples for the chosen counting time and record the gamma-ray spectra using file names which allow the spectra to be associated unambiguously with the corresponding standard or sample. The counting time is limited by the time available and the number of samples to be counted, but it should be long enough to give good counting statistics in the ^{122}Sb peak at 564.2 keV, that is, a net peak area above baseline of 10 000 counts.

12.7.1 The time and date recorded with each spectrum file allow the determination of the decay time for each sample. The counting live-time and true-time are recorded along with the spectrum to allow correction of the counting losses. The losses are accurately corrected as long as the count-rate which causes excessive losses or peak broadening is not exceeded.

12.7.2 The analyst should verify each spectrum to ensure that the limit has not been exceeded. A typical count-rate limit is that which causes 20 % losses. If the limit has been exceeded, the samples should be recounted after a longer decay time or at a position farther from the detector.

12.8 Use appropriate software to calculate the net peak areas and the antimony mass fractions of the samples.

13. Calculation

13.1 If the comparator standard and unknown sample are irradiated together and then counted one after another for the same counting time and with the same counting geometry, then the analysis result (the mass fraction of antimony in the sample) may be calculated as follows:

$$C(\mu\ g/g) = C_{std}(\mu\ g/g)\frac{N_{p,sample}W_{std}e^{\lambda(t_{d,sample}-t_{d,std})}}{N_{p,std}W_{sample}(\varphi_{sample}/\varphi_{std})} \quad (1)$$

where:

C_{std} = the mass fraction of antimony in the comparator standard. The units µg/g are equivalent to mg/kg. These units are commonly referred to as parts per million by weight or ppm.

$N_{p,sample}$ = the corrected peak area for the sample, that is, the number of counts (corrected for counting losses and baseline counts under the peak) measured in the gamma-ray peak at 564.2 keV.

$N_{p,std}$ = the corrected peak area for the comparator standard.

W_{std} = the mass of the comparator standard, in grams.

W_{sample} = the sample mass, in grams.

$(\varphi_{sample}/\varphi_{std})$ = the ratio of neutron fluence rates for the sample and the comparator standard. This ratio can be measured with flux monitors.

13.1.1 The exponential corrects for the difference in decay times, $t_{d,sample}$ and $t_{d,std}$, between the sample and comparator standard. λ is the decay constant for ^{122}Sb, that is, ln(2)/$T_{1/2}$. The half-life of ^{122}Sb is 2.72 days. λ and t_d must be in consistent units so that when multiplied together the units cancel.

13.1.2 This formula is accurate only if neutron self-shielding is negligible. Also, in practice it is not usually convenient to co-irradiate a comparator standard with every sample to be analyzed and, furthermore, the size of the comparator standard is usually different from that of the sample, which implies that their counting geometries cannot be the same. Therefore, in practice the calculation should allow for different irradiation times for sample and comparator standard, as well as different counting geometries and counting times.

13.2 It is convenient to irradiate and count a comparator standard, determine a sensitivity factor, and use it for subsequent antimony analyses where only unknown samples and neutron fluence monitors are irradiated and counted. The sensitivity factor, *B*, is calculated as follows:

$$B(counts/\mu\ g) = \frac{N_{p,std}\ \lambda}{W_{std}C_{std}(\mu\ g/g)(1-e^{-\lambda t_i})e^{-\lambda t_d}(1-e^{-\lambda t_c})} \quad (2)$$

The factors in the denominator containing exponentials remove the dependence of the sensitivity factor on the irradiation time t_i, the decay time t_d and the counting time t_c. This sensitivity factor applies only to a comparator standard irradiated in a certain reactor neutron spectrum and at a specific neutron fluence rate, and counted in a specific counting geometry.

13.2.1 The sensitivity factor *B* can be thought of as the slope of the calibration curve. This curve is linear up to the antimony concentration where neutron self-shielding becomes significant. The intercept of the curve is zero because sample containers normally contain negligible amounts of antimony and contamination is easily avoidable. The detector background at 564.2 keV should be zero unless other activated samples with antimony are nearby and there is inadequate shielding. As a check, a background spectrum can be counted before or after the sample spectrum.

13.2.2 Using this sensitivity factor, *B*, one may calculate the antimony mass fraction (or concentration) in a sample to be analyzed:

$$C(\mu\ g/g) = \frac{N_{p,sample}\ \lambda}{B\ W_{sample}(1-e^{-\lambda t_d})e^{-\lambda t_d}(1-e^{-\lambda t_c})}\frac{\varphi_{std}}{\varphi_{sample}}\frac{G_{eff,std}}{G_{eff,sample}}\frac{EFF_{std}}{EFF_{sample}} \quad (3)$$

where:

$N_{p,sample}$ = the number of counts (corrected for counting losses, background counts under the peak, and interfereing gammas) measured in the gamma-ray peak at 564.2 keV for the sample.

W_{sample} = the sample mass, in grams.

t_i, t_d, and t_c = refer to the irradiation, decay and counting times for the sample. The decay time is the time between the end of irradiation and the beginning of counting.

$\varphi_{std}/\varphi_{sample}$ = the ratio of neutron fluence rates for the comparator standard and the sample. This ratio can be measured with flux monitors. It is assumed that the neutron spectrum, the ratio of thermal neutrons to epithermal neutrons, has not changed between the irradiation of the comparator standard and the sample.

$G_{eff,sample}$ = the neutron self-shielding factor for the sample, which can be calculated as described in 7.6 and 7.7.

$G_{eff,std}$ = the neutron self-shielding factor for the comparator standard.

$EFF_{std}EFF_{sample}$ = the counting geometry correction factor. It can be calculated using a physical or empirical model which calculates detection efficiencies $\mathrm{EFF_{std}}$ and $\mathrm{EFF_{sample}}$ for the counting geometries of the comparator standard and the sample. If a model to calculate detection efficiency is not available, the counting geometry correction factor can be made very close to unity by counting comparator standard and sample far from the detector, say at 10 cm, and ensuring that their centers are at the same distance from the detector. At a distance of 10 cm, a change in distance of 1 mm causes a change in detection efficiency of approximately 1.5 %.

13.3 Calculate the weight percent of antimony as follows:

$$C(\%) = C(\mu\ g\ /\ g) \div 10\ 000 \qquad (4)$$

14. Precision and Bias

14.1 *Precision*—It is not possible to specify the precision of the procedure in this Test Method for measuring Antimony Content using Neutron Activation Analysis because a repeatability study in strict accordance with the procedure has not been completed. Such a repeatability study is anticipated to be completed prior to 2017.

14.2 *Bias*—No information can be presented on the bias of the procedure in this Test Method for measuring Antimony Content using Neutron Activation Analysis because no study of the bias using material having an accepted reference value has been conducted.

15. Measurement Uncertainty

15.1 Measurement uncertainty can be broken down into type A and B uncertainty components (**11**,**12**). This type A/B uncertainty specification is used in International Organization for Standardization (ISO) standards

15.1.1 Type A components are those that can be estimated by statistical means, by repeating the measurements and observing the variation in the results. These type A uncertainty components include those arising from the inhomogeneity of the comparator standard or sample, the variation of the results of weighing, variations in determining the neutron fluence rate from the position of the sample and the flux gradient, variations in placing the sample at the correct position on the detector, counting statistics.

15.1.2 Type B components of uncertainty are those which are estimated using models or other known information. They cannot be estimated by repeating the measurements since they give the same error every time the measurement is repeated. Type B components include the uncertainty of the antimony mass fraction in the comparator standard, errors caused by a poorly calibrated balance, uncertainty of the counting loss correction method, systematic error in the peak area calculation method, uncertainty of the counting geometry correction method, uncertainty of the neutron self-shielding correction method. The type A uncertainty arising from the inhomogeneity of the comparator standard becomes a type B uncertainty when the same aliquot of the comparator standard is used for all the determinations; the resulting error is then the same for all determinations. In many cases the NAA method is known to have systematic errors. These errors are corrected as well as possible by prescribed procedures. However, these correction procedures have some uncertainty, leading to type B uncertainty in the corrected result.

15.1.3 For each measurement result, the type A components are estimated and combined to give the overall type A uncertainty. The type B components are combined to give the overall type B uncertainty. The type A and B uncertainty components should then be combined. If the type A and type B uncertainties are uncorrelated, they can be combined in quadrature that is:

$$u_c^2 = u_A^2 + u_B^2 \qquad (5)$$

15.1.4 The quantity u_c is a standard uncertainty, corresponding to one standard deviation

15.1.5 The analysis report could give $\mathrm{u_c}$ for each result. It is good practice to also indicate the separate $\mathrm{u_A}$ and $\mathrm{u_B}$ uncertainty components. The errors caused by type *B* uncertainties are usually the same for all samples of a series analyzed by the same method. Thus, if one is examining the variation among individual samples of a series, type *B* uncertainties have no influence on the differences and only the type *A* uncertainties should be used for the comparison. On the other hand, if one needs to judge whether the mass fractions in individual samples exceed a regulatory limit or are close to some other absolute value, then the combined uncertainty should be used for the comparison.

15.1.6 When the material to be analyzed is homogeneous and when the NAA method is done carefully and is working well, most of the components of the type *A* uncertainty are small and it may be dominated by the counting statistics. If the peak area is more than 40 000 counts and if the background counts under the peak are negligible, then the uncertainty due to counting statistics may be as low as 0.5 % (it can be estimated from the square-root of the number of counts in the peak). At lower concentrations the antimony peak area will be smaller and this component of uncertainty will be larger. It approaches 50 % uncertainty when the mass fraction is near the detection limit. Thus, the type *A* uncertainty depends on the antimony mass fraction; it is not known in advance and must be estimated for each sample.

15.1.7 In the ideal case where the NAA method is working perfectly, the type *B* uncertainty is equal to the uncertainty of the antimony mass fraction in the comparator standard, which can be as good as 1 % at the 95 % confidence level.

15.1.8 In favorable cases, the combined standard uncertainty of this NAA method for the determination of antimony can be of the order of 1%. It increases in more difficult cases where large corrections need to be applied and when the antimony mass fraction is near the detection limit.

16. Keywords

16.1 antimony concentration; comparator standard; gamma-ray spectrometer; neutron activation analysis; neutron fluence rate; research nuclear reactor

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