An American National Standard

Standard Practice for
Alpha-Particle Spectrometry of Water[1]

This standard is issued under the fixed designation D 3084; 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 practice covers the process that is required to obtain well-resolved alpha-particle spectra from water samples and discusses associated problems. This practice is generally combined with specific chemical separations and mounting techniques, as referenced.

1.2 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*
C 859 Terminology Relating to Nuclear Materials[2]
C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride[2]
D 1129 Terminology Relating to Water[3]
D 3648 Practices for the Measurement of Radioactivity[4]
D 3865 Test Method for Plutonium in Water[4]
D 3972 Test Method for Isotopic Uranium in Water by Radiochemistry[4]

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminologies D 1129 and C 859. For terms not found in these terminologies, reference may be made to other published glossaries (1, 2).[5]

4. Summary of Practice

4.1 Alpha-particle spectrometry of radionuclides in water (also called alpha-particle pulse-height analysis) has been carried out by several methods involving magnetic spectrometers, gas counters, scintillation spectrometers, nuclear emul-sion plates, cloud chambers, absorption techniques, and solid-state counters. Gas counters, operating either as an ionization chamber or in the proportional region, have been widely used to identify and measure the relative amounts of differentα -emitters. However, more recently, the solid-state counter has become the predominant system because of its excellent resolution and compactness. Knoll (3) extensively discusses the characteristics of both detector types.

4.2 Of the two gas-counting techniques, the pulsed ionization chamber is more widely used as it gives much better resolution than does the other. This is because there is no spread arising from multiplication or from imperfection of the wire such as occurs with the proportional counter.

4.3 The semiconductor detectors used for alpha-particle spectrometry are similar in principle to ionization chambers. The ionization of the gas by α-particles gives rise to electron-ion pairs, while in a semiconductor detector, electron-hole pairs are produced. Subsequently, the liberated changes are collected by an electric field. In general, silicon detectors are used for alpha-particle spectrometry. These detectors are *n*-type base material upon which gold is evaporated or ions such as boron are implanted, making an electrical contact. A reversed bias is applied to the detector to reduce the leakage current and to create a depletion layer of free-charge carriers. This layer is thin and the leakage current is very low. Therefore, the slight interactions of photons with the detector produce no signal. The effect of any interactions of beta particles with the detector can be eliminated by appropriate electronic discrimination (gating) of signals entering the multichannel analyzer. A semiconductor detector detects all alpha particles emitted by radionuclides (approximately 2 to 10 MeV) with essentially equal efficiency, which simplifies its calibration.

4.4 Semiconductor detectors have better resolution than gas detectors because the average energy required to produce an electron-hole pair in silicon is 3.5 ± 0.1 eV (0.56 ± 0.02 aJ) compared with from 25 to 30 eV (4.0 to 4.8 aJ) to produce an ion pair in a gas ionization chamber. Detector resolution, defined as peak full-width at half-maximum height (FWHM), is customarily expressed in kiloelectron-volts. The FWHM increases with increasing detector area, but is typically between 15 and 60 keV. The background is normally lower for a semiconductor detector than for ionization chamber. Silicon detectors have four other advantages compared to ionization

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[2] *Annual Book of ASTM Standards*, Vol 12.01.
[3] *Annual Book of ASTM Standards*, Vol 11.01.
[4] *Annual Book of ASTM Standards*, Vol 11.02.
[5] The boldface numbers in parentheses refer to the list of references at the end of this document.

chambers: they are lower in cost, have superior stability, have higher permissible counting rates, and have better time resolution for coincidence measurements. However, the semiconductor detector requires sophisticated electronics because of the low charge that is generated by the incident α-particle in the detector. Low-noise and high-stability, charge-sensitive preamplifiers are used prior to the detection, analog-to-digital conversion, and storage of the voltage pulse by a multichannel analyzer. The counting is nearly always performed in a vacuum chamber so that the α-particles will not lose energy by collisions with air molecules between the source and the detector.

4.5 A gridded pulse-ionization chamber was developed by Frisch for high-resolution alpha spectrometry. The unit consists of a standard ionization chamber fitted with a collimator between the source and the collector plate and a wire grid to shield the collector from the effects of positive ions. The resolution of a gridded pulse ionization chamber is from 35 to 100 keV for routine work. The detector parameters that affect resolution are primarily the following: statistical variations in the number of ion pairs formed at a given alpha energy, the variation in rise time of pulses, and the effects of positive ions. An advantage of gridded ionization chambers is their ability to count large-area sources with good efficiency.

4.6 There are two reasons for collimating a sample in a gridded ionization chamber. When thick-sample sources are encountered, the alpha-particles emitted at a large solid angle would show an energy degradation upon ionization of the gas. The effect leads to tailing of the alpha-particle spectrum. This problem is reduced significantly by use of the collimator. Secondly, when the nucleus following an α-particle emission does not decay to a ground state, the γ-rays that may be produced are usually highly converted, and the conversion electrons ionize the gas. The special mesh-type collimators stop the conversion electrons and collimate the source simultaneously.

4.7 A more recently developed measurement method is photon-electron-rejecting alpha liquid-scintillation spectrometry. The sample is counted in a special liquid-scintillation spectrometer that discriminates electronically against non-alpha-particle pulses. The resolution that can be achieved by this method is 250 to 300-keV FWHM. This is superior to conventional liquid-scintillation counting, but inferior to silicon detectors and gridded pulse-ionization chambers. An application of this method is given in Ref **4**.

5. Significance and Use

5.1 Alpha-particle spectrometry can either be used as a quantitative counting technique or as a qualitative method for informing the analyst of the purity of a given sample.

5.2 The method may be used for evaporated alpha-particle sources, but the quality of the spectra obtained will be limited by the absorbing material on the planchet and the surface finish of the planchet.

6. Interferences

6.1 The resolution or ability to separate alpha-particle peaks will depend on the quality of the detector, the pressure inside the counting chamber, the source-to-detector distance, the instrumentation, and the quality of the source. If peaks overlap, a better spectrometer or additional chemical separations will be required.

7. Apparatus

7.1 *Alpha Particle Detector*, either a silicon semiconductor or a Frisch-grid pulse-ionization chamber.

7.2 *Counting Chamber*, to house the detector, hold the source, and allow the detector system to be evacuated.

7.3 *Counting Gas*, for ionization chamber, typically a 90 % argon–10 % methane mixture, and associated gas-handling equipment.

7.4 *Pulse Amplification System*, possibly including a preamplifier, amplifier, postamplifier, pulse stretcher, and a high-voltage power supply, as directed by the quality and type of detector employed.

7.5 *Multichannel Pulse-Height Analyzer*, including data readout equipment. This is now often computer based.

7.6 *Vacuum Pump*, with low vapor-pressure oil and preferably with a trap to protect the detector from oil vapors.

8. Source Preparation

8.1 The technique employed for preparing the source should produce a low-mass, uniformly distributed deposit that is on a very smooth surface. The three techniques that are generally employed are electrodeposition, microcoprecipitation, and evaporation. The first two usually are preferred. Fig. 1 compares the alpha-particle spectrum of an electrodeposited source with that of an evaporated source.

8.1.1 Electrodeposition of α-emitters can provide a sample with optimum resolution, but quantitative deposition is not necessarily achieved. Basically, the α-emitter is deposited from solution on a polished stainless steel or platinum disk, which is the cathode. The anode is normally made from platinum gauze or a spiralled platinum wire, which often is rotated at a constant rate. Variants of this technique may be found in Refs **5** and **6**. See also Test Method D 3865. Polonium can be made to deposit spontaneously from solution onto a copper or nickel disk **(7)**.

8.1.2 Micro-coprecipitation of actinide elements on a rare-earth fluoride, often neodymium fluoride, followed by filtration
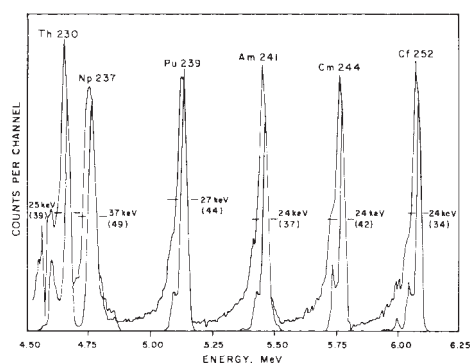
NOTE 1—Inner curve: nuclides separated on barium sulfate and then electrodeposited.
NOTE 2—Outer curve: carrier-free tracer solution evaporated directly.
FIG. 1 Resolution Obtained on Six-Component Mixture

$$N = G - B_C - I \tag{3}$$

$$\sigma_N = \left[G + I + B \times \left(\frac{t_S}{t_B} \right)^2 \right]^{1/2} \tag{4}$$

where:
N = net sample counts in the analyte's region of interest,
σ_N = one-sigma uncertainty of the net analyte counts,
G = gross sample counts in the analyte's region of interest, and
I = impurity (interference) counts in the analyte's region of interest.

11.2.1.3 *Combined Fractional Recovery and Counting Efficiency*:

$$RE = N_T / (A_T \times t_S \times D_T) \tag{5}$$

$$\sigma_{RE} = \frac{\left[\sigma^2_{GT} + \sigma^2_B \times (t_S/t_B)^2 + I + N^2_T \times \left[\left(\frac{\sigma_{A_T}}{A_T} \right)^2 + \left(\frac{\sigma_{t_S}}{t_S} \right)^2 + \left(\frac{\sigma_{D_T}}{D_T} \right)^2 \right] \right]^{1/2}}{A_T \times t_S \times D_T} \tag{6}$$

where:
RE = combined fractional recovery and efficiency term, c/d,
A_T = activity of tracer at reference date, Bq,
D_S = sample decay fraction from time of sample collection to midpoint of counting period,
σ_{DS} = uncertainty in the sample decay fraction,
σ_{DT} = uncertainty in the tracer's decay fraction,
D_T = tracer decay fraction from tracer's reference date to the midpoint of sample counting period,
σ_{RE} = uncertainty in the combined fractional recovery and efficiency term, c/d,
σ_{AT} = uncertainty in the activity of the tracer on tracer reference date, Bq,
σ^2_{GT} = G_T, and
σ^2_B = B.

11.2.1.4 *Analyte Concentration (Bq/L)*:

$$C = \frac{N}{RE \times t_S \times V \times D_S} \tag{7}$$

$$\sigma_C = \frac{\left[\sigma^2_N + N^2 \times \left[\left(\frac{\sigma_{t_S}}{t_S} \right)^2 + \left(\frac{\sigma_{RE}}{RE} \right)^2 + \left(\frac{\sigma_{D_S}}{D_S} \right)^2 + \left(\frac{\sigma_V}{V} \right)^2 \right] \right]^{1/2}}{RE \times t_S \times V \times D_S} \tag{8}$$

where:
C = nuclide concentration, Bq/L,
σ_C = total propagated uncertainty of the nuclide concentration, Bq/L,
V = sample volume, L, and
σ_V = uncertainty in the volume, L.

11.2.2 When there is no practical radiotracer available for the element of interest, an experimentally determined nominal chemical recovery factor can be applied to a series of sample sets. The nominal chemical recovery factor is determined by analyzing a group of samples to which a known quantity of the alpha-emitting nuclide of interest (or a radioisotope of the element of interest) is added in accordance with the procedure. The recovery should be greater than 50 % and the standard deviation of the measurements should not exceed 5 %. For this nominal recovery factor to be applicable, the recovery of matrix quality control samples processed within a given set of samples (<20) should be within ±10 % of the nominal recovery factor. When the recovery of the matrix quality control sample falls outside this range or when a different person performs the analysis, the nominal chemical recovery factor should be reestablished by processing another group of spiked standard samples.

11.2.3 When utilizing the nominal chemical recovery approach, the terms RE of Eq 5 and σ_{RE} of Eq 6 must be redefined as Eq 9 and Eq 10. In this case, RE is defined as the product of the nominal chemical recovery term and the absolute alpha detector efficiency and σ_{RE} is the propagated uncertainty of this product.

$$RE = NRF \times E_{FD} \tag{9}$$

$$\sigma_{RE} = RE \times \left[\left(\frac{\sigma_{NFR}}{NFR} \right)^2 + \left(\frac{\sigma_{EFD}}{E_{FD}} \right)^2 \right]^{1/2} \tag{10}$$

where:
NRF = fractional nominal chemical recovery factor,
E_{FD} = fractional detector efficiency,
σ_{NRF} = uncertainty in NRF, and
σ_{EFD} = uncertainty in E_{FD}.

11.3 If desired, calculate the net radioactivity concentration, C^1, of the analyte in becquerels per litre (Bq/L) by:

$$C^1 = C - R \tag{11}$$

and

$$\sigma_{C^1} = (\sigma_C{}^2 + \sigma_R{}^2)^{1/2} \tag{12}$$

where:
R = reagent blank correction, Bq/L, measured on one or more analyte-free samples of equivalent volume as the sample, and
σ_R = total propagated uncertainty of R.

11.4 Some alpha-particle-emitting nuclides, such as polonium-210, have half-lives sufficiently short that significant decay can occur between the sample collection time, or the time of chemical separation, and the measurement time. To calculate the activity at an earlier (reference) time, use the following equation:

$$A_o = A \times e^{0.69315\Delta t/T_{1/2}} \tag{13}$$

where:
A_o = disintegration rate at the reference time,
A = disintegration rate at the time of measurement,
0.69315 = approximate natural logarithm of 2,
Δt = elapsed time between measurement and reference times, and
$T_{1/2}$ = half-life of the radionuclide, in the same time unit as Δt.

11.4.1 A_o will be in the same unit as A.

11.4.2 When a reference time is later than the time of measurement, calculate the activity at this reference time by:

$$A_o = A \times e^{-0.69315\Delta t/T_{1/2}} \tag{14}$$

11.5 Calculate the minimum detectable concentration (**12**), *MDC*, of the analyte in becquerels per litre (Bq/L) by:

$$MDC = \frac{2.71 + 4.65 \times [(B \times (t_S/t_B)^2 + I)]^{1/2}}{RE \times t_S \times V \times D_S} \tag{15}$$

12. Precision and Bias

12.1 The precision and bias associated with alpha-particle spectrometry depend on several factors. These include: the quantity of radioactivity being measured, the number of alpha-particle-emitting radionuclides present and the energies of their emissions, the background count rate of the detector, the uncertainty in the values of the calibrating standards, the resolution of the spectrum, and the length of the counting period.

12.2 See the precision and bias statements in Test Methods D 3865 and D 3972.

12.3 See Section 8 of Practice D 3648 for information about establishing counter characteristics and preparing counter control charts. See Section 9 of Practices D 3648 for information about counting statistics, including confidence levels, precision, uncertainties associated with a measurement, and minimum detectable activity.

13. Quality Control

13.1 Whenever possible, the project leader, as part of the external quality control program, should submit quality control samples to the analyst along with routine samples in such a way that the analyst does not know which of the samples are the quality control samples. These external quality control samples, which usually include duplicate and blank samples, should test sample collection and preparation as well as sample analysis whenever this is possible. In addition, analysts are expected to run internal quality control samples that will indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples should be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types; blank samples, replicate samples, reference materials, control samples, and spiked samples.

14. Keywords

14.1 alpha-particle; alpha-particle spectrometry; alpha pulse-height analysis; pulse-ionization chamber; radioactivity; semiconductor detector; water

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