Designation: C1255 – 18

Standard Test Method for Analysis of Uranium and Thorium in Soils by Energy Dispersive X-Ray Fluorescence Spectroscopy[1]

This standard is issued under the fixed designation C1255; 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 energy dispersive X-ray fluorescence (EDXRF) spectrochemical analysis of trace levels of uranium and thorium in soils. Any sample matrix that differs from the general ground soil composition used for calibration (that is, fertilizer or a sample of mostly rock) would have to be calibrated separately to determine the effect of the different matrix composition.

1.2 The analysis is performed after an initial drying and grinding of the sample, and the results are reported on a dry basis. The sample preparation technique used incorporates into the sample any rocks and organic material present in the soil. This test method of sample preparation differs from other techniques that involve tumbling and sieving the sample.

1.3 Linear calibration is performed over a concentration range from 20 to 1000 µg per gram for uranium and thorium.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units in parentheses are for information only.

1.5 *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.*

1.6 *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.*

[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials
C998 Practice for Sampling Surface Soil for Radionuclides
D420 Guide for Site Characterization for Engineering Design and Construction Purposes
D1452/D1452M Practice for Soil Exploration and Sampling by Auger Borings
D1586 Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils
D1587/D1587M Practice for Thin-Walled Tube Sampling of Fine-Grained Soils for Geotechnical Purposes
D2113 Practice for Rock Core Drilling and Sampling of Rock for Site Exploration
D3550/D3550M Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils
D4697 Guide for Maintaining Test Methods in the User's Laboratory (Withdrawn 2009)[3]
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves
E456 Terminology Relating to Quality and Statistics
E876 Practice for Use of Statistics in the Evaluation of Spectrometric Data (Withdrawn 2003)[3]
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

2.2 *Other Document:*

ANSI/HPS N43.2-2001 Radiation Safety for X-ray Diffraction and X-ray Fluorescence Equipment[4]

[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to the nuclear fuel cycle, refer to Terminology C859.

3.1.2 For definitions of terms relating to analytical atomic spectroscopy, refer to Terminology E135.

3.1.3 For definitions of terms relating to statistics refer to Terminology E456.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *escape peak*—a peak generated by an X-ray having energy greater than 1.84 keV (the energy of the k-alpha absorption edge for silicon) that enters the detector and causes the silicon detector crystal to fluoresce.

3.2.1.1 *Discussion*—If the silicon X-ray escapes the detector, carrying with it the energy of the silicon k-alpha X-ray, 2.79 E-16 Joules [J] (1.74 keV), the energy measured for the detected X-ray will be less than the actual X-ray energy by exactly 2.79 E-16 J (1.74 keV). Therefore, as counts accumulate for any major X-ray peak, an escape peak can be expected to appear at an energy of 2.79 E-16 J (1.74 keV) below the major peak. Escape peaks can be calculated and removed from the spectrum by most instrumentation software.

3.2.2 *flux monitor (FM) value*—the detected X-ray intensity within a specified spectral range from a metallic standard giving a high number of counts.

3.2.2.1 *Discussion*—The same excitation conditions as the sample analysis are used (except for the change in the current to achieve maximum efficiency of the data acquisition system). With all conditions remaining constant, the FM value is proportional to the X-ray energy flux being emitted from the X-ray tube or radioisotope source.

3.2.3 *flux monitor ratio (FMR)*—the ratio of the initial FM value (FMi) prior to calibration and sample analysis to current FM value (FMc) at the time of sample analysis.

3.2.3.1 *Discussion*—This ratio is used to correct the measured element intensity for changes in the X-ray energy flux.

4. Summary of Test Method

4.1 A representative sample of soil is obtained by first taking a sizeable amount (>100 g) and drying it, then running it through a crusher and placing it on a shaker/tumbler to homogenize it. A portion is then ground in a ball mill and pressed into a sample pellet. An energy dispersive X-ray fluorescence spectrometer is used to expose the sample to a monochromatic X-ray source capable of exciting the uranium and thorium L-alpha series lines. The X-rays emitted by the sample are detected via a solid state detector [Si(Li)] and counted in discrete energy channels on a multi-channel analyzer (MCA) to form an energy spectrum. The spectrum is then processed to obtain the peak intensities for uranium and thorium for calibration and quantitation.

5. Significance and Use

5.1 This test method was developed and the instrument calibrated using ground soils from the site of a nuclear materials plant. This test method can be used to measure the extent of contamination from uranium and thorium in ground soils. Since the detection limit of this technique (nominally 20 µg per gram) approaches typical background levels for these contaminants, the method can be used as a quick characterization of an on-site area to indicate points of contamination. Then after cleanup, EDXRF may be used to verify the elimination of contamination or other analysis methods (such as colorimetry, fluoremetry, phosphorescence, etc.) can be used if it is necessary to test for cleanup down to a required background level. This test method can also be used for the segregation of soil lots by established contamination levels during on-site construction and excavation.

6. Interferences

6.1 The following elements typically are found in an X-ray spectrum from soil in the spectral region of uranium and thorium: zinc (Zn), tungsten (W), lead (Pb), rubidium (Rb), strontium (Sr), and yttrium (Y).

6.2 Rubidium is the primary interference for uranium, overlapping the uranium L-alpha-1 peak, and lead is the primary interference for thorium, overlapping the thorium L-alpha-1 peak. At typical levels for these elements all of the peak interferences can be eliminated by using a Gaussian mathematical peak fitting and deconvolution software routine. (Such is usually part of EDXRF instrumental software.) However, if the lead level is high (greater than 500 µg per gram), due, for instance, to the contamination of the soil by lead paint, then the peak segregation can become impossible. (A complete discussion of interelement effects and the correction models used to compensate for these effects is outside the scope of this procedure.) Explanations are found in several sources (**1, 2**).[5]

6.3 Escape peaks (see 3.2.1) can interfere with the integration of the uranium and thorium L-alpha peaks and are therefore removed from the spectrum with a software operation (as is available with most instruments).

7. Apparatus

7.1 *Energy Dispersive X-Ray Fluorescence (EDXRF) System,* refer to manufacturer's literature for the selection of the X-ray spectrometer.

7.1.1 *Photon Excitation Source,* capable of producing monochromatic X-rays of an appropriate energy to efficiently excite uranium and thorium, that is, from 2.72 E-15 to 3.52 E-15 Joules [J] (from 17 to 22 keV). Either of the following sources is acceptable:

7.1.1.1 *Radioactive Source,* ^{109}Cd is well suited for efficient excitation. It should have an activity between 2.59 E + 08 and 3.70 E + 08 becquerels (between 7 and 10 millicurie).

7.1.1.2 *X-Ray Generator,* with high voltage power supply, rhodium target X-ray tube and a secondary target; molybdenum (Mo), rhodium (Rh) or silver (Ag) are suitable secondary targets.

7.1.2 *Solid State Detector [Si(Li)],* with preamplifier maintained at appropriate temperature and capable of 2.64 E-17 J

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

(165 eV) FWHM resolution or better using an ^{558}Fe radioisotope source with 1000 cps intensity of the emitted Mn K-alpha peak at 9.453 E-16 J (5.900 keV).

7.1.3 *Signal Processing and Data Acquisition Electronics,* includes: a bias power supply; a shaping amplifier or pulse processor using a 7.5 µs pulse shaping time constant; a pulse pileup rejector; an analog-to-digital converter (ADC); and multi-channel scaler.

NOTE 1—Automatic correction for count rate losses due to pulse pileup or electronics deadtime is achieved in the pulse processing electronics (as is available in most commercial X-ray units). Along with the automatic count rate correction, the maximum efficiency of the data acquisition system (that is, the preamplifier, pulse processor, and ADC) is achieved at a 50 % deadtime count rate. This is based on an electronic analysis of counting losses by the manufacturer. The X-ray tube current is therefore adjusted for a given sample matrix and set of excitation conditions to achieve a 50 % deadtime.

7.2 *Drying Oven,* controlled at 110 ± 5° Celsius.

7.3 *Analytical Jaw Tooth Crusher,* or equivalent, capable of crushing to 0.1 mm particle size.

7.4 *Laboratory Vacuum Cleaner,* with a high efficiency particulate air (HEPA) filter element.

7.5 *Shaker/Tumbler,* capable of blending a large volume of dry soil (at least 100 g) in a sample container. The shaker/tumbler may have a capacity to blend several containers.

7.6 *Impact Grinding/Mixing Mill,* capable of accepting the vial in 8.2.3. An equivalent process may be used to achieve the particle size specified in the sample preparation Section 11.

7.7 *Hydraulic Press,* 2.22 E + 05 N (25 ton-force) load capacity.

7.8 *Desiccator.*

8. Reagents and Materials

8.1 *Reagents*—None.

8.2 *Materials:*

8.2.1 *Evaporating Dishes,* glazed porcelain, size No. 7 or larger, with a 2.00 E-4 m^3 (200 mL) capacity.

8.2.2 *Watch Glasses,* size appropriate to cover the evaporating dish.

8.2.3 *Grinding/Mixing Vial Set,* with two mixing balls, made of steel or tungsten carbide, ball diameters of nominally 13 mm (0.5 in.), with a grinding sample capacity of 10 cm^3. An equivalent process and set of materials may be used to achieve the same particle size specified in the sample preparation section.

8.2.4 *Die Press Set,* 31 mm diameter with a maximum load capacity in excess of 2.22 E + 05 N (25 ton-force), or as required for the instrument in use.

8.2.5 *Retaining Cup,* aluminum, 32 mm diameter, suitable for the die press, or as required for the instrument in use.

9. Hazards

9.1 XRF equipment analyzes by the interaction of ionizing radiation with the sample. Applicable safety regulations and standard operating procedures must be reviewed prior to the use of such equipment. All modern XRF spectrometers are equipped with safety interlocks to prevent accidental penetration of the X-ray beam by the user. Do NOT override these interlocks without proper training or a second knowledgeable person present during sup operation. (See ANSI/HPS N43.2-2001.)

9.2 When cleaning out the grinder and sample mixing vials with course sand or crushed glass, the resultant finely powdered glass is a health hazard if inhaled; crystalline silica can cause silicosis if exposure occurs on a regular basis. All such operations must be performed in a properly functioning exhaust hood.

10. Sampling, Test Specimens, and Test Units

10.1 Practice C998 gives a practice for sampling of surface soil to obtain a representative sample for analysis of radionuclides. Guide D420 provides a guide for investigating and sampling soil and rock materials at subsurface levels but is mainly concerned with geological characterization. The method described in Test Method D1587/D1587M may be used to sample the soil using a thin-walled tube. If the soil is too hard for pushing, the tube may be driven or Practice D3550/D3550M may be used. The method described in Test Method D1586 may also be used to sample the soil and includes discussion on drilling procedures and collecting samples which are representative of the area. In the case of sampling rocky terrain, diamond core drilling may be used (see Practice D2113). Where disturbed sampling techniques can be afforded, Practice D1452/D1452M can be used, that is, using an Auger boring technique. The size of the sample is based on achieving a representative sample. Tube samples can be composited to achieve such a sample. Refer to the standards mentioned above that discuss obtaining a representative sample.

11. Sample Preparation

11.1 As stated in the scope, the analysis is performed on a dry weight basis, however, the percent moisture of the soil sample can be determined during the following steps by measuring the weight before and after drying. This provides the opportunity to calculate and report the data on an as-received basis or the percent moisture can be reported separately. Transfer the laboratory soil sample into an evaporating dish and cover the dish with a watch glass. Place the evaporating dish into a drying oven maintained at 105° Celsius. Allow it to dry for a minimum of 18 h. Remove the dish from the oven and allow it to cool to room temperature.

NOTE 2—It is recommended that a sample preparation log be developed and implemented by the user which details and tracks the steps of preparation for each sample. For each sample, the sample preparation log would list: the jaw tooth crusher; mixing vial number; grinder/mixing mill; and die press set used, as well as the preparer's name, and the date and time of preparation. Such a log is useful in backtracking cross contamination or sample carry over problems that are detected from the blank, standard, and control sample data (see 13.2). When multiple pieces of equipment are used for any one of the processing steps, the equipment should be numbered and the vials and die sets should be scribed with numbers for tracking purposes.

11.2 A Geiger-Muller counter may be used to survey the dried soil as a means of segregating any with a high level of contamination. High activity level samples can then be prepared on a separate jaw tooth crusher, if available, and the cleaning process can be done twice to ensure against cross contamination.

NOTE 3—The count rate used to denote a high level sample will depend on the model of instrument used and its counting efficiency.

11.3 Adjust the particle size setting on the jaw tooth crusher to 0.1 mm.

NOTE 4—It is recommended that all crushing, tumbling, and mixing be performed in a properly functioning laboratory hood. Follow the vendor's instructions on the use of the jaw tooth crusher, shaker/tumbler, and the impact grinding/mixing mill devices. An equivalent process to the one described below using the jaw tooth crusher may be used to homogenize the soil and grind it to a particle size of U.S. Sieve 150 mesh with an aperture of 106 µm.

11.4 Prior to the initial use and after each consecutive use of the jaw tooth crusher, clean it out by running about 150 g of course sand through it. Then use a laboratory HEPA vacuum cleaner to vacuum out all residual sand from the collection tray, sample insertion region, etc.

11.5 Remove each sample from the evaporating dish and run it through the jaw tooth crusher, cleaning as directed above after each use. Collect the sample in a sample container suitable for tumbling, such as an 8 oz jar or disposable polyethylene container. The container must be less than three-fourths full to allow for adequate mixing in the tumbling process.

11.6 Place the sample on a shaker/tumbler for an appropriate amount of time to allow for complete mixing. Consult the manufacturer's instructions to establish an appropriate mixing time.

11.7 Place approximately 15 cm^3 of sample into a mixing vial with two mixing balls and place the vial inside the grinding/mixing mill. Grind the sample for approximately 1500 s (25 min). An appropriate amount of time can be established from a series of test samples (**3**, **4**) taken from a single homogenous sample with concentrations near the mid-range. The test samples would be prepared at incrementally longer grinding times and then analyzed. The appropriate grinding time would be at the point in which any further increase in grinding time does not result in an appreciable increase in X-ray peak intensity.

11.8 The mixing vials are cleaned out after each use as follows:

11.8.1 Disassemble and rinse the vial components with water.

11.8.2 Blow or air dry the components and then reassemble the vial.

11.8.3 Place course ground glass or sand in the vial and run it on the grinding/mixing mill.

11.8.4 Remove the glass from the vial and wipe or blow out under a hood, the residual glass powder.

11.9 Place the finely powdered sample, or a portion of it, into the die press with an aluminum retaining cap. The cap helps to support the sample when pressed.

NOTE 5—The amount of sample placed into the die press is not critical for use in an EDXRF instrument in which the sample is inverted facing a lower mounted X-ray tube and detector, as long as the pellet is sufficiently thick to completely absorb the X-ray penetration.

11.10 Place the die press on the hydraulic press at a force of 2.22 E + 05 N (25 ton-force) for a minimum of 60 s, or as required for the instrument in use. Then remove the pressed sample from the die. Mark the sample inside diameter (ID) on the back of the aluminum cap and handle the samples carefully so as not to abrade or disturb the surface.

11.11 Wipe out any remaining powder residue from the die with a wetted paper towel.

12. Preparation of Apparatus

12.1 The X-ray spectrometer must be allowed to reach the level of stability as specified by the manufacturer's instructions.

12.2 The detector supply of liquid nitrogen (if required) must be maintained.

12.3 Typical operating conditions are given in Table 1. These conditions are instrument dependent; the manufacturer's guidelines should be followed.

13. Calibration and Standardization

13.1 *Apparatus:*

13.1.1 *Peak Energy Calibration*—Calibrate the gain and offset on the pulse processor to ensure proper peak position according to manufacturer's instructions.

13.1.2 *X-Ray Energy Flux Monitoring*—Before a calibration is determined a factor, called the flux monitor ratio (FMR), is established to adjust for changes in the X-ray tube output or the X-ray energy flux. Refer to the terminology section for the definition of a flux monitor value and the flux monitor ratio. This factor can also be used to adjust for the rate of decay if a radioisotope source is used. The flux monitor ratio is the ratio of the initial flux monitor value (FMi) and the current flux monitor value at the time of sample analysis (FMc). Changes in the X-ray energy flux may occur as the tube ages and may

TABLE 1 Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer Operating Conditions

For use of an X-ray Generator Excitation Source:	
X-ray tube anode target	Rhodium
Anode voltage (kV)	32
Anode current (mA)[A]	2.8
Secondary target	Molybdenum
Filter and thickness (mm)	Ag-(0.050)
For Use of a Radioisotopic Excitation Source:	
Radioisotope	Cadmium-109
Activity	2.59 E + 08 and 3.70 E + 08 becquerels
General Conditions:	
Atmosphere	vacuum (<70 Pa)
Counting live time (seconds)	1000
Energy range (keV)	0 to 20
Time constant (µseconds)	7.5
Detector columnator	Silver

[A] The anode current will vary between instruments. It should be set according to the manufacturer's instructions to achieve maximum efficiency of the data acquisition system (that is, the preamplifier, pulse processor, and ADC).