

TABLE 4c – Uranium and Thorium Mass Fraction (NDA)

Method/measurement system (including software): XRGs / XMCX / GEM

Application: In-Situ Measurements of Uranium Content in Non-Equilibrated and Aged Bulk Materials with Known Enrichment

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the concentration meter principle [1] that derives the U content from the count rate in the 185.7 keV peak of ^{235}U in a gamma-spectrum measured under <u>quasi-infinite thickness</u> conditions. The method is applicable for low-U materials with contents <25 wt%. The spectrum processing and derivation of the U content are performed using the IAEA's GEM (General Enrichment Measurements) software [2]. The detector types include NaI(Tl), LaBr₃(Ce), CZT, and HPGe. The method requires one-point calibration in the case of fixed container wall thickness or two-point calibration at arbitrary container wall thickness. The method requires <u>knowledge of the ^{235}U enrichment</u>, e.g. as declared by the facility operator or defined by a technological process. The IAEA applies the method for in-situ measurements of in-process materials, low-concentrated sub-products, scraps and wastes at NU conversion and purification plants. A typical measurement system includes a collimated detector, an integrated or stand-alone digital MCA, and an instrumentation laptop. The employed detector arrangements are as follows: (i) electrically cooled HPGe with Ø50 mm × 30 mm crystal and Ø50 mm × 8 mm collimator dimensions; (ii) ≥1.5 cm³ CZT with Ø15 mm × 7 mm or larger collimator; (iii) Ø50.8 mm × 12.7 mm LaBr₃(Ce) or NaI(Tl) with Ø44 mm × 20 mm collimator. Typical measurement live times are 500-1000 s.
Factors affecting the method performance
The method assumes low-Z material. Presence of unknown amounts of high-Z elements may bias the measured U content to low values. Other constraints: fulfillment of the quasi-infinite thickness geometry conditions and material homogeneity. The measurement uncertainty may degrade at high ambient radiation background, e.g. when measurements are performed in process or storage areas. Analysis of low-U samples taken from waste streams of the UOC refining process may suffer from the elevated contents of Ra-226 and other decay products of uranium isotopes.
Method references
[1] J.L. Parker, T.D. Reilly, The enrichment meter as a concentration meter, in: Nuclear analysis research and development, Program Status Report, September-December 1972, G. Robert Keepin Comp., Los Alamos Scientific Laboratory report LA-5 197-PR (1972), p. 11. [2] A. Berlizov, GEM: A Next Generation Gamma Enrichment Measurements Code, Proceedings of the International Workshop on U/Pu Isotopics Analysis for Nuclear Safeguards, February 2021, Vienna, Austria. [3] A. Berlizov, U. Repinc, M. Sturm, K. Henderson, S. Baumann, V. Mayorov, Validation of the Concentration Meter Principle for Nondestructive Assay of Uranium in Low-Concentrated Materials, Proceedings of the International Workshop on U/Pu Isotopics Analysis for Nuclear Safeguards, February 2021, Vienna, Austria.

Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were evaluated based on the results of the validation study [3], which was performed in the IAEA Safeguards Analytical Laboratory.

Prepared by: A. Berlizov (IAEA SGTND)

Date: 2021-05-17

Method/measurement system (including software): HRGS / XMCG / GEM-FRAM- MGAU**Application:** In-Situ Measurements of Uranium Content in Aged Bulk Materials

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the concentration meter principle [1] that derives the U content from the count rate in the 185.7 keV peak of ^{235}U in a gamma-spectrum measured under <u>quasi-infinite thickness</u> conditions. As the method requires the knowledge of ^{235}U enrichment, it is combined with one of the peak-ratio methods (FRAM [2] or MGAU [3]) to measure the ^{235}U enrichment using the same or separately acquired gamma-spectrum. The method is applicable for low-U materials with contents <25 wt%. The spectrum processing and derivation of the U content are performed using the IAEA's GEM (General Enrichment Measurements) software [4]. The IAEA applies the method for in-situ measurements of in-process materials, low-concentrated sub-products, scraps and wastes at conversion and fuel fabrication plants. A typical measurement system includes a collimated HPGe detector (planar type with $\geq 1000 \text{ mm}^2$ active area or coaxial type with rel. efficiency > 10%), an integrated or stand-alone digital MCA, and an instrumentation laptop. Typical measurement live times are 500-1000 s.
Factors affecting the method performance
The method assumes low-Z material. Presence of unknown amounts of high-Z elements may bias the measured U content to low values. Other constraints: fulfilment of the quasi-infinite thickness geometry conditions, material homogeneity, radioactive equilibrium (materials must be aged for ≥ 4 months after chemical separation or purification). The measurement uncertainty may degrade at high ambient radiation background, e.g. when measurements are performed in process or storage areas. Analysis of low-U samples taken from waste streams of the UOC refining process may suffer from the elevated contents of Ra-226 and other decay products of uranium isotopes.
Source of bottom-up value (<u>only for prospective ITV not based on historical data</u>)
ITVs were evaluated based on the results of the validation studies [5] and [6].
Method references
[1] J.L. Parker, T.D. Reilly, The enrichment meter as a concentration meter, in: Nuclear analysis research and development, Program Status Report, September-December 1972, G. Robert Keepin Comp., Los Alamos Scientific Laboratory report LA-5 197-PR (1972), p. 11. [2] T.E. Sampson, T.A. Kelley, PC/FRAM: a code for the nondestructive measurement of the isotopic composition of actinides for safeguards applications, Appl. Radiat. Isot. Vol. 48 (1997) 1543-1548. [3] R. Gunnink, W.D. Ruhter, P. Miller, J. Goerten, M. Swinhoe, H. Wagner, J. Verplancke, M. Bickel, S. Abousahl, MGAU: A new analysis code for measuring U-235 enrichments in arbitrary samples, LLNL Report UCRL-JC-114713, January 1994. [4] A. Berlizov, GEM: A Next Generation Gamma Enrichment Measurements Code, Proceedings of the International Workshop on U/Pu Isotopics Analysis for Nuclear Safeguards, February 2021, Vienna, Austria.

- [5] A. Berlizov, U. Repinc, M. Sturm, K. Henderson, S. Baumann, V. Mayorov, Validation of the Concentration Meter Principle for Nondestructive Assay of Uranium in Low-Concentrated Materials, Proceedings of the International Workshop on U/Pu Isotopics Analysis for Nuclear Safeguards,
- [6] D. Vo, M. Yoho, Optimization and Verification of FRAM 6.1 Parameter Sets, LANL Report LA-UR-19-30676, 2019-10-21, 53 p.

Prepared by: A. Berlizov (IAEA SGTND)

Date: 2021-05-17

Method/measurement system (including software): HRGS / XMCG / GRASS2**Application:** Uranium Content Determination in Freshly Separated Materials

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)

The method is based on the gamma-spectrometric assay of sampled material in a fixed “thin-layer” geometry [1] and requires knowledge of the ^{235}U enrichment (e.g., as declared by operator or known from the technological process). A quantitatively taken ~2 g powder is homogenized and then pressed into a uniform disk (~1 mm thick) using a special stainless-steel container with a screw-cap plug. In the case of liquids, a 10 mL aliquot is loaded into a polystyrene container using a fixed volume pipette. The taken sample net mass is determined by container weighing before and after loading. Gamma-spectrometric measurements are performed in a well-defined geometry, which is pre-calibrated in SGAS-NML using secondary standards. Spectrum evaluation is done using the IAEA’s GRASS2 (Gamma-Ray ASSay of Thorium and Uranium) software [2]. The software extracts count rate in the 185.7 keV (^{235}U) peak from a measured spectrum, evaluates material density based on the measured sample layer thickness / volume and sample net mass, and solves a non-linear equation for U content. The solution is aided by on-line Monte Carlo computations of the detector efficiency.

The method is applied by the IAEA at refining and conversion facilities that operates with Nu feed. Typical field setup includes an electrically cooled HPGe detector (active area $\geq 1000 \text{ mm}^2$, thickness $\geq 15 \text{ mm}$), radiation shielding with a sample positioning cavity (sample to detector end cap distance ~10 mm), a digital MCA, and an instrumentation laptop. Spectrum counting live times: 1000 s (>50 wt% powder, >200 g/L solution), 2000 s (20-50 wt% powder, 50-200 g/L solution), 3000 s (<20 wt% powder, <50 g/L solution). Additional equipment includes an electronic balance with ≥ 2 -digit precision, control weights and a 5 mL fixed volume pipette.

Factors affecting the method performance

Unknown contents of high-Z elements in sample matrix may lead to an underestimation of the measured U content. Material inhomogeneity may bias measurement results. Coincidence summing effects are reduced by the use of stainless-steel containers that effectively absorb coinciding low-energy gamma and characteristic X-ray emissions. Weighing and aliquoting inaccuracies. Reproducibility of sample positioning. High ambient radiation background, e.g. when measurements are performed in a process or in a storage area. Freshly separated products do not contain Ra-226 in quantities that could pose a bias. Analysis of low-U samples taken from waste streams of the UOC refining process may suffer from the elevated contents of Ra-226 and other decay products of uranium isotopes.

Method references

- [7] A. Berlizov, Gamma-Spectrometric Assay of Uranium in Support of Partial Defect Verification of In-Process Material, Technical Procedure, SG-TP-15270, 2019-07-08, 39 p.
- [8] A. Berlizov, F. Rorif, V. Unsal, A. Bopape, J. Million, On-Site Gamma-Spectrometric Assay of Uranium and Thorium in Support of Safeguards Verifications at Bulk Handling Facilities, RANC-2016, April 10-16, Budapest, Hungary.

Source of bottom-up value (only for prospective ITV not based on historical data)

ITVs were evaluated by the IAEA using top-bottom analysis of the operator-inspector differences and results of the method's performance testing at SGAS-NML. The analyzed sets contained 42 data points for clean UO_2 , U_3O_8 , UO_3 , UF_4 UOC powders with $C_U=70\text{-}80$ wt% and 45 data points for solutions with $C_U=40\text{-}570$ gU/L.

Prepared by: A. Berlizov (IAEA SGTND)

Date: 2021-05-16

Method/measurement system (including software): HRGS / XMCG / GRASS2- FRAM-MGAU**Application:** Uranium Content Determination in Aged Materials

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the gamma-spectrometric assay of sampled material in a fixed “thin-layer” geometry [1]. A quantitatively taken 50-100 g powder is homogenized and then quantitatively loaded up to the top of a 30 mL polystyrene container. In the case of liquids, a 30 mL aliquot is loaded. The sample net mass is determined by container weighing before and after loading. Gamma-spectrometric measurements are performed in a well-defined geometry, which is calibrated in the field using secondary standards. Spectrum evaluation is done using the IAEA’s GRASS2 (Gamma-Ray ASSay of Thorium and Uranium) software [2]. The software extracts the count rate in the 1001 keV ($^{238}\text{U}/^{234\text{m}}\text{Pa}$) peak from a measured spectrum, evaluates material density based on the sample mass and volume, and solves a non-linear equation for U content. The solution is aided by on-line Monte Carlo computation of detector efficiency and determination of the ^{235}U enrichment using peak ratio method (MGAU/FRAM) from the same spectrum. The method is applied by the IAEA at fuel fabrication plants. A typical measurement setup includes a shielded uncollimated HPGe detector with $\geq 20\%$ relative efficiency, a holder for reproduceable sample positioning at a fix distance from the detector (usually 10-15 cm), a digital MCA and instrumentation laptop. Spectrum counting live time: 2000 s. Additional equipment includes electronic balance with ≥ 2-digit precision, control weights and a 5 mL fixed volume pipette.
Factors affecting the method performance
The method is applicable to materials aged for >4 months since last chemical separation or purification. Non-equilibrium materials will be subject to biasing to higher U contents. Unknown amounts of high-Z elements in sample matrix may lead to an underestimation of the U content. The material inhomogeneity and coincidence summing effects are significantly reduced due to sufficiently large sample-to-detector distance. Other factors include weighing and aliquoting inaccuracies, reproducibility of sample positioning, high radiation background, e.g. when measurements are done in a process or storage area.
Method references
[9] A. Berlizov, Gamma-Spectrometric Assay of Uranium is Support of Partial Defect Verification of Scrap Material, IAEA, Department of Safeguards, Technical Procedure, SG-TP-13872, 2015-11-17, 25 p. [10] A. Berlizov, F. Rorif, V. Unsal, A. Bopape, J. Million, On-Site Gamma-Spectrometric Assay of Uranium and Thorium in Support of Safeguards Verifications at Bulk Handling Facilities, RANC-2016, April 10-16, Budapest, Hungary.
Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were derived by the IAEA using top-bottom analysis of the operator-inspector differences. The analyzed set contained 20 field measurements of homogeneous LEU scrap powders with uranium contents from 17 wt% to 88 wt%.

Prepared by: A. Berlizov (IAEA SGTND)

Date: 2021-05-16

Method/measurement system (including software): HRGS / XMCG / GRASS2**Application:** Thorium Content Determination in Powders and Liquids

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the gamma-spectrometric assay of sampled material in a fixed “thin-layer” geometry [1]. A quantitatively taken 10 g powder is homogenized and then pressed into a uniform disk using a special stainless-steel container with a screw-cap plug. 10 mL liquid samples are loaded by volume into a polystyrene container using a fixed volume pipette. Measurements are done in a well-defined geometry, which is pre- or field calibrated using secondary standards. Spectrum evaluation is done using IAEA’s GRASS2 (Gamma-Ray ASSay of Thorium and Uranium) software [2]. The software extracts background corrected count rates in the 583 keV (^{208}Tl) and 911 keV (^{228}Ac) peaks. Material density is evaluated based on the sample layer thickness / volume and sample mass. A system of two non-linear equations is solved for Th content. The solution is aided by Monte Carlo. Coincidence summing corrections are implemented as function of sample fill height. Evaluation modes include analysis of untreated ore or aged materials, analysis of non-equilibrated materials with unknown separation date, and analysis of materials with known separation date. Typical field setup includes an electrically cooled HPGe detector (active area $\geq 1000 \text{ mm}^2$, thickness $\geq 15 \text{ mm}$), radiation shielding with a sample positioning cavity (sample to detector end cap distance $\sim 10 \text{ mm}$), a digital MCA, and an instrumentation laptop. Spectrum counting live time: 1000 s ($>20 \text{ wt\%}$), 2000 s ($1\text{-}20 \text{ wt\%}$), 3000 s ($<1 \text{ wt\%}$). Additional equipment includes an electronic balance with ≥ 2-digit precision, control weights and a 5 mL fixed volume pipette.
Factors affecting the method performance
Unknown content of high-Z elements in sample matrix may lead to an underestimation of the measured Th contents. At low Th contents ($< 1 \text{ wt\%}$), the unknown matrix properties may lead to increased systematic uncertainties. Material inhomogeneity may bias measurement results. Presence of radioactive equilibrium is checked and taken into consideration by the GRASS2 software. Therefore, no significant effects on the measurement accuracy from the absence of radioactive equilibrium is expected.
Method references
[1] A. Berlizov, Gamma-Spectrometric Assay of Thorium Using Electrically Cooled Gamma-Spectrometer (ECGS), Technical Report, SG-RP-13429, IAEA, Department of Safeguards, ver. 1, 2015-03-02, 31 p. [2] A. Berlizov, F. Rorif, V. Unsal, A. Bopape, J. Million, On-Site Gamma-Spectrometric Assay of Uranium and Thorium in Support of Safeguards Verifications at Bulk Handling Facilities, RANC-2016, April 10-16, Budapest, Hungary

Source of bottom-up value (only for prospective ITV not based on historical data)

ITVs were evaluated based on the laboratory tests performed using reference standard materials with known Th content in the range from 0.05 wt% to 100 wt%. The dataset of >60 spectra taken from >20 samples was evaluated by ANOVA to yield systemic and random measurement uncertainties for the Th content intervals: <1 wt%, 1-20 wt%, and >20 wt%. The obtained ITVs are expected to be applicable to both powders and liquids.

Prepared by: A. Berlizov (IAEA SGTND)

Date: 2021-05-15

Method/measurement system (including software): HRGS / XMCG / ISOCS**Application:** Thorium Content Determination in Powders

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the measurement of powdered material using a laboratory gamma-spectroscopy system equipped with an ISOCS [1] characterized high purity germanium detector inside a 10 cm thick lead shield. Prior to each measurement 20 g of homogenized thorium containing powder is loaded in a 25 mL glass vial and weighed using a high-precision laboratory scale (≥ 0.001 g precision). The sample is then measured in close proximity to the detector using a well-defined counting geometry. The counting time is selected to ensure good counting statistics ($\sim 30,000$ counts) in the 911 keV peak of ^{228}Ac for all samples. Following the measurement, activity of ^{232}Th is determined by averaging measured activities of ^{228}Ac and ^{208}Tl, which are assumed to be in secular equilibrium with ^{232}Th. Thorium concentration in the sample is then calculated by dividing measured thorium mass, which corresponds to the observed ^{232}Th activity value, by the total sample mass. Spectra evaluation is performed using a general gamma-spectroscopy software, e.g., Canberra's Genie 2000. During spectrum evaluation the efficiency calibration is performed using the Canberra's ISOCS calibration software. For each measurement the final efficiency calibration is optimized through several iterations using benchmarks available directly from the measured spectra. The benchmarks include the line activity consistency evaluation for several individual peaks of ^{228}Ac (911, 969, and 338 keV) and ^{208}Tl (583 and 2615 keV), as well as comparison between measured and ISOCS modelled thorium concentration.
Factors affecting the method performance
Material inhomogeneity may bias measurement results. Presence of radioactive equilibrium is assumed, which can be confirmed by comparing measured activities of ^{228}Ac and ^{208}Tl. If not properly corrected for, significant ($>10\%$) bias due to true coincidence summing (TCS) effect can be observed for ^{228}Ac and ^{208}Tl measured activity values when samples are measured close ($<5\text{cm}$) to the detector end-cap.
Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were evaluated based on the laboratory tests performed using reference standard materials with known Th content in the range from 0.1 wt% to 88 wt%. The dataset of 184 spectra taken with 16 samples was evaluated by ANOVA to yield systematic and random measurement uncertainties for the Th content intervals: 0.1 - 1 wt% and >1 wt%.
Method references
[1] Venkataraman R, Bronson F, Atrashkevich V, Field M, and Young B; Improved Detector Response Characterization Method in ISOCS and LabSOCS; Journal of Rad. Nucl. Chem., Vol. 264, No.1, 213-219, 2005.

Prepared by: A. Bosko (IAEA SGAS)

Date: 2021-06-14

Method/measurement system (including software): HRGS / XMCG / A-ISOCS**Application:** Uranium Content Determination in Powder, Scrap.

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
Advanced-ISOCS or Advanced ISOCS Uncertainty Estimator (A-IUE) was developed by Canberra Industries for IAEA's use. A-ISOCS is an efficiency adjustment tool. A-ISOCS varies the "not well-known" parameters in the ISOCS model such as the matrix composition, density, fill height etc and adjusts the efficiency calibration by benchmarking the efficiency shape and magnitude to the data available in the analyzed gamma ray spectra. The benchmarks include relative efficiency results from MGA, MGAU, FRAM analysis, or declared isotopics information, the consistency of line activities from a given multiple-line nuclide, the consistency between measured and modeled uranium or plutonium mass, and the consistency of activities from multiple measurements of the same item. The results presented in this spreadsheet are drawn from 2 reports that were submitted by Canberra Industries to the IAEA, at the end of Phase 2 and Phase 3 of the project. For performance testing A-ISOCS, the IAEA provided 18 measured gamma ray spectra to Canberra, some of which were from the field. These spectra spanned a wide range of enrichments as well as uranium masses. The mass and enrichments were blinded to Canberra. Phase 2 results were obtained using the so called "Best Random Fit" approach for optimizing the efficiency. This was based on creating a large number of models by varying the not-well known parameters within specified uncertainty limits, and find the best model that fit the measured data. Phase 3 results were obtained by optimizing the efficiency using downhill simplex routine.
Factors affecting the method performance
The heterogeneity of source matrix and the non-uniformity of source distribution will impact the results. Performing multiple measurements of a given item from different angles/orientations will help mitigate the bias due to non-uniformities.
Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were evaluated using a top-down approach. The A-ISOCS analysis was carried out using 4 different combinations of optimization benchmarks, and 2 different optimization methods. The 4 benchmarks used were: (i) Relative efficiency from MGAU + ratio of modeled/measured U mass, (ii) User-defined isotopics + ratio of modeled/measured mass, (iii) Relative efficiencies from FRAM + ratio of modeled/measured mass, (iv) Line activity consistency. The 2 different methods used were Best Random Fit and Downhill Simplex. Pooling the results from all 8 different analyses, the random uncertainty $u(r)$ was determined as the standard deviation of the relative deviation of U concentration (or U mass) measurement results w.r.t. the corresponding declared values. The systematic uncertainty $u(s)$ was determined as the standard deviation of the average relative deviations for each of the 8 analysis methods.

Method references

- [1] Andrey Bosko, "Advanced ISOCS for the IAEA - Phase 2: A-IUE Geometry Optimization Software Performance Testing Report", Canberra Industries report, November 2010.
- [2] Gabriela Ilie, "Advanced ISOCS for the IAEA - Phase 3: Performance Testing Report of the Downhill Simplex Optimization Option", Canberra Industries report, May 2013.
- [3] R. Venkataraman, A. Bosko, L.C. Bourva, W. Russ, F. Bronson, A. Berlizov, V. Nizhnik, S. Yoon, A. Lebrun, "Advanced Mathematical Methods for Gamma Ray Based Nuclear Safeguards Measurements", Proc. International Symposium on Nuclear Safeguards, Vienna, October 2014.

Prepared by: R. Venkataraman, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

Date: 2021-06-04

Method/measurement system (including software): XRF / T4/ ED-XRF**Application:** Uranium and Thorium Content Determination in Powders and Liquids

Short Description of the method/measurement system and typical measurement conditions (measurement time, etc.)

The method of X-ray fluorescence analysis (XRF) is suitable for rapid non-destructive analysis to detect and measure the concentration of elements in solid and liquid samples. An XRF analyzer consists of four basic components, X-ray tube, X-ray detector, multi-channel analyzer, and a computer. The energy of each fluorescent X-ray is characteristic of the element excited. The energy dispersive XRF (EDXRF) uses a less powerful X-ray tube (of the order of few hundred watts) to excite the sample and the emitted X-rays are viewed by the detector uncollimated.

The EDXRF spectrometer used for the measurements was a Jordan Valley EX-3600TEC with a Rh target operated at 40 kV and the data is processed using the nEXt program provided with the instrument. The EDXRF measurements are based on an internal standard method to determine uranium and thorium concentrations. In this method, a known amount of internal standard yttrium (Y) was added to either a pelletized sample or to a liquid solution that is deposited onto a filter paper. The U $L\alpha$, Th $L\alpha$ characteristic lines, and Y $K\alpha$ line were used for obtaining the calibration plots as well as for the determination of U and Th in the samples. Calibration plots and U/Th concentrations can be made by either plotting U/Y, U/Th and Th/Y amount ratios against the respective intensity ratios of Th $L\alpha$, U $L\alpha$ and Y $K\alpha$ or conversely by plotting the intensity ratios of the analytes and the yttrium X-ray lines against the amount ratios.

The powder samples are prepared by using a mixture of uranium and thorium oxides and a fixed amount of yttrium oxide pressed into a pellet. The liquid samples are a result of solutions of uranyl nitrate and thorium nitrate mixed with dissolved yttrium oxide in nitric acid. An aliquot of the liquid solution can be transferred onto a filter paper or other absorbent sheets and dried before measurement.

Factors affecting the method performance

Random error can be reduced by averaging results of repeated measurements. Systematic errors can be reduced by calibration and carefully following established measurement procedures. For thicker samples, additional uncertainty sources have to be taken into account for the determination of the total mass per unit area and the potential non-uniform thickness of the sample. The absorption factor is obtained from a set of transmission measurements of each individual sample and a reference target, and the associated uncertainty is obtained from the measurement uncertainties. The EDXRF is a versatile method for measurements requiring small amounts of sample, minimal sample preparation, and short measurement times. Depending on the concentration range, measurement times can vary from 100s up to 1000s.

Source of bottom-up value (only for prospective ITV not based on historical data)

ITVs were evaluated based on the laboratory tests performed using Yttrium as an internal standard added to mixed samples with known Th and U content in the range from 0.1 wt% up to 25 wt%. The obtained ITVs are expected to be applicable to both powders and liquids.

Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were evaluated based on the laboratory tests performed using Yttrium as an internal standard added to mixed samples with known Th and U content in the range from 0.1 wt% up to 25 wt%. The obtained ITVs are expected to be applicable to both powders and liquids.
Method references
1. An EDXRF method for determination of uranium and thorium in AHWR fuel after dissolution. X-Ray Spectrometry, Vol. 38, 2009, 112-116 2. A comparative study on determination of uranium and thorium in their mixed oxides by EDXRF using tube and radioisotope X-ray sources. X-Ray Spectrometry, Vol. 40, 2011, 379-384

Prepared by: N. St-Amant

Date: 2022-03-4

Method/measurement system (including software): XRF / WDXRF / CAL**Application:** Uranium Content Determination in Solutions Using WDXRF

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
Uranium bearing solutions are irradiated by an X-ray tube in a wavelength dispersive X-ray fluorescent X-ray spectrometer (WDXRF). A LiF220 crystal is used to refract and selectively detect the fluorescent X- rays from the sample. The counts are used from the U Lα1 ($2\theta = 37.353^\circ$) line for the calibration. The spectrometer used was the PANalytical Philips Magix Pro PW2440 sequential instrument with a single goniometer, which is equipped with the X-ray tube (Rh anode) providing a maximum voltage/current of 60 kV/125 mA at a maximum power level of 4 kW. The samples covered by this method represent high concentration uranium solutions in an acidic matrix. A set of reference uranium solution samples is required to produce a calibration curve. This calibration curve represents a linear dependence between the raw counts observed for uranium in the WDXRF spectra and uranium concentration in reference solutions. Several reference solutions are typically needed in order to generate a calibration curve that covers the range of concentrations up to 50 gU/L. The sample solutions with concentrations within the calibration range can be analyzed directly, while samples with higher concentration require to be diluted.
Factors affecting the method performance
As WDXRF analysis is performed using the very low energy X-ray lines the sample preparation becomes a critical factor affecting the accuracy of the result. Any deviation in sample composition between the reference samples used for generating the calibration curve and unknown samples to be analyzed may affect the measured result. Additional factors include spectral interferences, instrument instability (drift), counting statistics, etc.
Source of bottom-up value (only for prospective ITV not based on historical data)
Multiple WDXRF measurements of the quality control samples at one of the uranium refinery facilities were used to evaluate the method performance. The calibration was performed by measuring eight reference uranium solution samples in the range of 5 to 50 gU/L, and using raw counts to produce a linear calibration curve. The control solutions had concentrations of ~100 gU/L and ~400 gU/L, and therefore required ~10 times dilution in order to fall within the calibration range.
Method references
n/a

Prepared by: A. Bosko (IAEA SGAS)

Date: 2022-03-22

Method/measurement system (including software): XRF / WDXRF / FP

Application: Thorium Content Determination in Powders Using WDXRF

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The method is based on the measurement of a powdered material using a laboratory Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF). The samples for WDXRF measurements are typically prepared in the form of loose powder, press pellet, or fused glass bead. The WDXRF spectrometer used to evaluate the method performance was the PANalytical Philips Magix Pro PW2440 sequential instrument with a single goniometer, which is equipped with the X-ray tube (Rh anode) providing a maximum voltage/current of 60 kV/125 mA at a maximum power level of 4 kW. Data acquisition and analysis for the purpose of method evaluation were performed with the PANalytical SuperQ v5.3 software using the Omnian “standardless” analysis (fundamental parameters (FP) method). The FP method [1-3] is based upon the theoretical relationship between measured X-ray intensities and the concentrations of elements in the sample. During analysis process the theoretical X-ray intensity for each identified element is iteratively compared to the theoretical value, which is calculated by combining the physical X-ray production processes and the measured sample composition using known fundamental atomic parameters (attenuation/absorption factors, X-ray energies, relative intensities, etc.).
Factors affecting the method performance
As WDXRF analysis is performed using the very low energy X-ray lines the sample preparation becomes a critical factor affecting the accuracy of the result. The following sample parameters will influence the method performance: • quality of the sample surface • sample homogeneity • sample thickness (must be “infinitely” thick for the most accurate result) Additional factors include spectral interferences, instrument stability (drift), counting statistics, etc.
Source of bottom-up value (only for prospective ITV not based on historical data)
ITVs were evaluated based on the laboratory measurements performed using a set of 10 reference materials with known Th content in the range from 0.05 wt% to 10.2 wt%. The samples for these measurements were prepared by mixing the sample powder with Flux 66-34 and fusing it into a glass bead. The dataset of 5 independent measurement results taken with each of 10 samples was evaluated by ANOVA to yield systematic and random measurement uncertainties for the Th content.

Method references
1. Sherman J. The theoretical derivation of fluorescent X-ray intensities from mixtures. <i>Spectrochimica Acta</i>; 7: 283-24 (1955). 2. R. Jenkins, R.W. Gould, and D. Gedcke, <i>Quantitative X-Ray Spectrometry</i>, 2nd edition (1995). 3. R. Tertian and F. Claisse, <i>Principles of Quantitative X-Ray Fluorescence Analysis</i> (1982).

Prepared by: A. Bosko (IAEA SGAS)

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