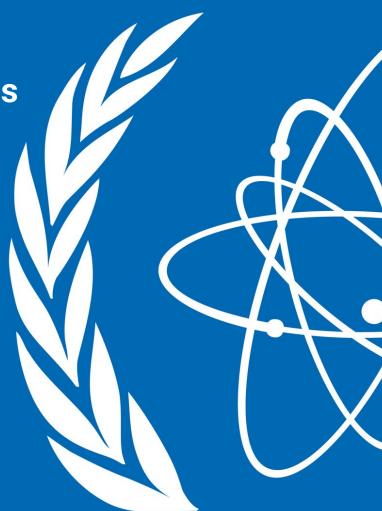
Radionuclide Reference Materials

Terrestrial Environmental Radiochemistry (TERC) Laboratory Division of Physical and Chemical Sciences-NAPC Department of Nuclear Sciences and Application International Atomic Energy Agency - IAEA

Ivana Vukanac Radiation Detection Specialist, TERC

BIPM Webinar 28 March 2025



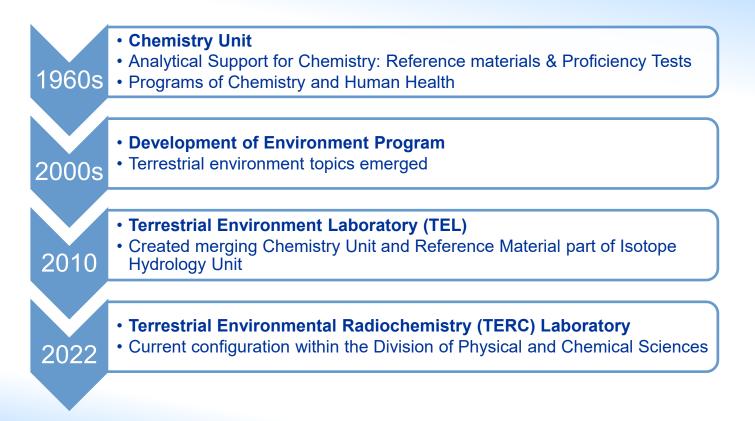


Summary

- TERC laboratory introduction
- Reference materials definition, usage, role in measurement process
- Reference material production (ISO 17034:2016)
- Reference materials in TERC
- TERC`s Worldwide Proficiency Testing exercise
- Conclusion

TERC History





TERC`s Mission

The key task of the TERC Laboratory is to provide expertise, training and support to the Member States (MS) dealing with radioactive, industrial and other pollution and to assists MSs in preparing for emergencies.

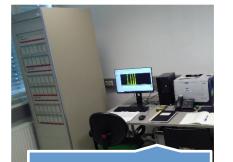
TERC supports the MS's laboratories in improving their measurement capabilities in environmental monitoring and in providing reliable analytical results:

- By providing Reference Materials (RMs) on both radionuclides and stable isotopes to laboratories worldwide
- By organizing Worldwide Proficiency Testing (PT) exercise (once per year).

- Expertise
- Training
- Support
- Reference Material Production (ISO17034)
- Organization of a Worldwide Proficiency
 - Testing exercise

Laboratory infrastructure





Alpha-particle spectrometry



Liquid scintillation counting



Radiochemistry laboratory



Gamma-ray spectrometry



Inductively-coupled plasma mass spectrometry



Isotope ratio mass spectrometry



Reference material production



Reference material storage and distribution

TERC`s measurement capabilities



Stable Isotopes Trace Element Radionuclide Analysis Analysis Analysis Mass Spectrometry; Gamma-ray Spectrometry ICP - Mass **Infrared Laser** (7 HPGe detectors) Spectrometry spectrometry Alpha-particle & Beta Spectrometry (36 alpha detectors; 3 LSCs) Radiochemistry labs Low background gross

alpha/beta counting (2 gas-flow proportional counter)



Reference materials (RM)

- Definitions
- Usage and role in measurement process

RM related definitions



ISO 17034:2016

General requirements for the competence of reference material producers

JCGM 200:2012

International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM) <u>JCGM_200_2012.pdf</u>

(Joint Committee for Guides in Metrology JCGM-WG2, 2021 International Vocabulary of Metrology VIM4; <u>VIM4_CD_210111c.pdf</u>)

ISO Guide 30:2015 Reference materials – Selected terms and definitions

ISO 17034:2016



INTERNATIONAL STANDARD 17034

ISO

First edition

Reference number ISO 17034:2016(E)

0150 2016

Reference material (RM) - material sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.

General requirements for the competence of reference material producers

iénérales pour la compétence des proc matériaux de référence

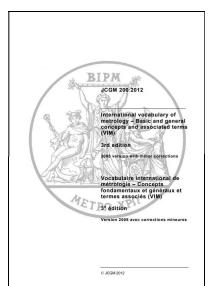
Certified Reference material (CRM) – RM characterized by a metrologically valid procedure for one or more specified properties, accompanied by a RM certificate that provides the value of the specified property, its associated uncertainty, and statement of metrological traceability.

ISO

Certified Value – value assigned to a property of a RM that is accompanied by an uncertainty statement and a statement of metrological traceability, identified as such in the RM certificate.

International Vocabulary of Metrology





Reference material (RM) -

- RMs can be used for measurement precision evaluation and quality control
- RM to be used as a measurement standard for calibration purposes it needs to be a CRM
- A given RM can only be used for one purpose in a measurement, either calibration or quality control, but not both.

Certified Reference material (CRM) -

- Metrologically valid approaches for characterization of RMs are given in ISO 17034:2016
- Only CRMs can be used for calibration or for assessing measurement trueness.



International Vocabulary of Metrology





Metrological traceability – property of measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.

- Metrological traceability requires an established calibration hierarchy
- For measurements with more than one input quantity in the measurement model, each of the input values and their uncertainties should itself be metrologically traceable
- Metrological traceability of a measurement result does not ensure that the measurement uncertainty is adequate for a given purpose or that no mistakes have been made
- ✓ ILAC considers the elements for confirming the measurement traceability to be unbroken metrological traceability chain to an international or a national measurement standard, a documented measurement uncertainty and procedure.

Use of RM - ISO 17034:2016

ISO

17034



General requirements for the competence of reference material producers

INTERNATIONAL

STANDARD

Exigences générales pour la compétence des producteurs de matériaux de référence **Reference material (RMs)** are used in all stages of measurement process, including for method validation, calibration and quality control. RMs are also used in Interlaboratory comparisons for method validation and for assessing laboratory proficiency.

ISO

Reference number ISO 17034:2016(E) 0 ISO 2016

ISO/IEC 17025:2017 - General requirements for the competence of testing and calibration laboratories - Normative Reference in ISO 17034.

Use of RM - ISO 17025:2017





6. Resource requirements

- Measuring equipment shall be calibrated
- Metrological traceability of measurement results shall be maintained
- ✓ Measurement results shall be traceable to the International System of Units (SI) through ...
 - Certified values of CRMs provided by a competent RM producer with stated metrological traceability to the SI

Bq

kg

 \checkmark

Traceability of IAEA Radionuclide RMs

National Standard of Activity of Radionuclide (efficiency calibration of gamma spectrometer) National Standard (regularly calibrated balance)

Use of RMs - Calibration

International Vocabulary of Metrology

Calibration – operation performed on measuring system that establishes a relation between values with measurement uncertainty provided by standards and corresponding indications with associated measurement uncertainty and use this information to obtain measurement result from an indication.

Gamma-ray spectrometry

- Experimental
- Numerical
- Semi-empirical



Traceability

(C)RMs for validation/verification of method (including efficiency calibration) CRMs for efficiency calibration

Use of RM - ISO 17025:2017





7. Process requirements

- ✓ Selected method fit for purpose
- Method verification
- Validation of non-standard methods, lab-developed methods and standard methods modified or used outside their intended scope
- Method validation
 - ✓ ...

 \checkmark

- ✓ Calibration or evaluation of bias and precision using reference standards or RM
- ✓ Assurance of the validity of the results
 - ✓ Use of RM or QC samples
 - Use of check or working standards with control charts
 - ✓ Intermediate checks on measuring equipment

Use of RM - ISO 17025:2017



INTERNATIONAL STANDARD	ISO/IEC 17025
	Third edition 2017-11
General requirements for competence of testing and laboratories	the d calibration
Exigences générales concernant la compétenc d'étaionnages et d'essais	e des laboratoires
	Reference number ISO/IEC 17025-2017(E)
ISO IEC.	6 ISO/IEC 17025-2017(E)

- Calibration (CRM)
- QA/QC activities
 - Method verification
 - Method validation

Reference Material Production



Bundesministerium
 Digitalisierung und
 Wirtschaftsstandort



Die Nationale Akkreditierungsstelle / The National Accreditation Body:

AKKREDITIERUNG AUSTRIA

bestätigt die Akkreditierung der Rechtsperson / confirms the accreditation of

International Atomic Energy Agency

Wagramer Straße 5, 1400 Wien

Identifikationsnummer / ID-number: 0415 als / as Referenzmaterial-Hersteller / Reference Material Producer gemäß / occording to EN ISO 17034-2016 Datum der Erstakreditierung / Initial date of occreditation: 18.05.2022

Standorte/Organisationseinheiten / sites/umits: International Atomic Energy Agency - Marine Environment Laboratories, 4 Qual Antolne Ler, 98000 Monaco International Atomic Energy Agency - Terrestrial Environmental Radiochemistry Laboratory, Friedensstraße 2, 2444 Seibersdorf

Informationen zum Akkreditierungsumfang und zu Akkreditierung Austria / Information about the accreditation scope and Akkreditierung Austria <u>https://www.bmdw.gv.at/akkreditierung</u>

Die Akkreditierung wurde mittels Bescheid erteilt und damit bestätigt, dass die Konformitätiswertungsstelle die angehinhten Anforderingen erfüllt. Diese Bestätigung darf nur unverändert weiterverbreitet werden. / The accreditation was granted by a decree which confirms, that the Conformity Assessment Body Juffis the given requirements. This confirmation of accreditation may not be regroadwed other than in full.

Elektronisch gefertigt / Signed electronically

Dipl.-Ing. Dr. Norman Brunner Wien, am 23, Juni 2022

ISO 17034:2016

General requirements for the competence of reference material producers

TERC – Accredited RM producer (2022)

Reference Material Production



Scope

production of matrix CRMs characterized for activity concentration of (gamma-ray emitting) radionuclides

supported by analytical techniques, operated in accordance with ISO 17025:2017 requirements: gamma-ray spectrometry particle size analysis dry-weight determination

Purpose

- to ensure **consistent quality** of IAEA CRMs provided to MS laboratories through **internal harmonization** and documented processes and requirements
- international harmonization through compliance with ISO 17034 requirements

Objective

to be **accredited as a reference material producer** as per requests from MS laboratories. They will benefit from the added value to the CRMs the IAEA provides (e.g., for their own accreditation as testing laboratories).

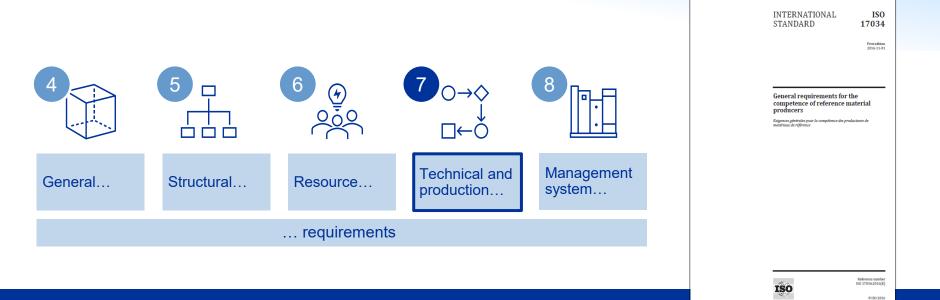
Quality Management System

Well-established QMS

- To support RM production
- To ensure fulfillment of the scope and objective of accreditation



Internationally harmonized requirements (ISO)

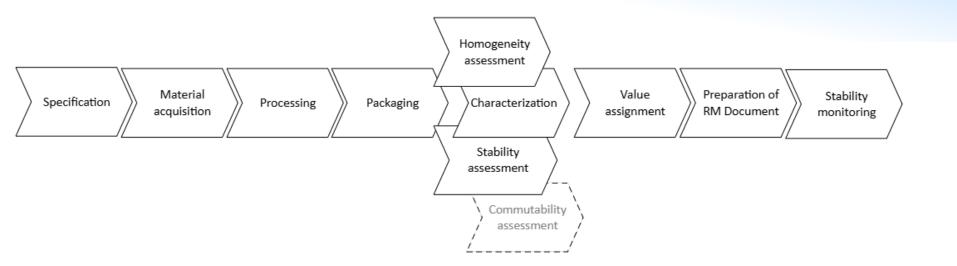




Overview of Clause 7







Project design



Adapted from ISO 33405:2024, Figure 1

Planning



- Documented production plan
- · Processes which directly affect quality of RM
- 21 items to be addressed

environmental conditions labelling equipment calibration homogeneity acceptance criteria stability testing uncertainties characterization storage post-distribution services

Reference Material Project Planning Form NAEL RM F.001.01 Rev.04 1. General information on the candidate CRM IAEA-XXX Code Planned name Short name Description Short description, e.g. analyte type; matrix; origin 2. Project Management Details Function Name Responsible project officer Alternate project officer Project team members Project approval 3. Selection and specification of candidate CRM 3.1. Origin of production request and justification Requested by ..., reason for preparation (reference to customer needs) 3.2. Matrix and sampling information Description, including origin of bulk material, sampling details, supplier, etc. 3.2.1. Verification of identity Short description, e.g.: based on accompanying documents, visual check, ... 3.3. Planned measurands Measurand: please specify, e.g. activity concentration, mass fraction, isotope amount ratio, activity ratio,... Measurand/Analyte Target value range Target uncertainty Metrological grade unit unit Choose Choose Choose Choose Choose Choose

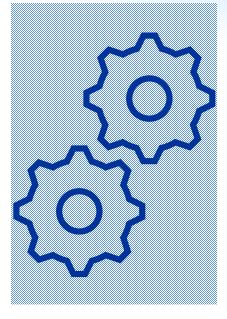
Material handling and storage

- Ensure integrity of candidate RMs throughout production process
- Adequate packaging and labelling
- Appropriate storage location controlled conditions
- Assessment of condition of RM at appropriate intervals throughout storage period



Material processing

- Drying
- Milling/grinding
- Sieving
- Homogenization (bulk homogeneity assessment)
- Protection from contamination
- Stabilization (sterilization by irradiation)
- Packaging (bottling)





Measurement procedures & equipment



In accordance with relevant requirements of ISO/IEC 17025:2017

Calibration

Method verification/validation

Ensuring the validity of results

Quality control of analytical results

- Internal QC (control charts, background monitoring, ...)
- Participation in external quality assurance (e.g., proficiency testing)

Uncertainty of measurement

- Metrological traceability
- Reporting

Data integrity and evaluation





- Data security
- Calculations and data transfers \rightarrow appropriate checks

\rightarrow Four-eye principle

• Validation of spreadsheets and software

NAEL.RM.F.006.03 Uncertainty Calculations Template - Formulation property values													
Material code	IAEA-482			Data Entry		Name		Date					
Matrix	Fish			Prepared by		Sian Patterson		2/29/2024					
Spiking reference (MSS/DRSS preparation)				Checked by			Ivana Vukanac	;		5/30/2024			
Radionuclide	К-40	Cs-134	Cs-137	Pb-210	Ra-226	Ra-228	Th-228						
Uncertainty components (coverage factor k=1)													

Assessment of homogeneity

- prior evidence ↔ experimental assessment
- '...in its final packaged form...'

in most cases necessary

- '...every property of interest...' (exception: evidence of similarity)
- '...measurement of a representative number of randomly chosen units...'
- validated measurement procedures
- between-unit and within-unit homogeneity
 - between-unit to ensure all units are equal
 - within-unit to ensure uniformity when using subsamples
- determination of minimum sample size
- [cert. values] uncertainty contributor from heterogeneity (or shown to be negligible)





Stability of assigned property values

- Assessment of stability during transport
 - short-term (≥ transport time)
 - transport conditions (e.g., elevated temperature)
- Assessment of stability during storage
 - long-term (typically \geq ~12 months)
 - storage conditions

Experimental design

- selection of representative subset of RM units
- choice of suitable measurement procedure (precision, selectivity)
- measurements under repeatability conditions
- statistical evaluation

- Estimate the uncertainty of certified value due to instability
- Predict shelf-life / assign appropriate period of validity / monitoring scheme to detect any changes in a timely manner
- Establish instructions for users
 - storage conditions,
 - repeated use (aliquots from one unit)

33405

SO

Stability of assigned property values





Long term stability monitoring – appropriate scheme

- Control measurements confirmation of certified values
- Extension of validity

Characterization



- Determination of the property values
- Determination of associated uncertainty
- Provide evidence of the metrological traceability

Examples for appropriate characterization strategies

- 1. using a single **reference measurement procedure** in a single laboratory
 - a) without direct comparison to a similar CRM
 - b) value transfer from an RM to a closely matched candidate RM performed using a single measurement procedure performed by one laboratory;
- 2. characterization of a non-operationally defined measurand using **two or more methods** of demonstrable accuracy in **one or more competent laboratories**
- 3. characterization of an operationally-defined measurand using a **network of competent laboratories**
- 4. characterization based on mass or volume of ingredients used in the preparation of the RM

Characterization considerations



- measurement plan with clear description and communication
- demonstrated competence of involved laboratories
 "by using data from each laboratory that was not obtained on the material to be characterized"
- ≥ 2 substantially different measurement principles (case 2) where possible
- Technical evaluation of received data and documents to confirm adherence to the measurement plan

Assignment of property values and uncertainties



Directly dependent on choice of characterization approach

Value assignment by formulation

Value assignment by characterization (e.g. network of expert laboratories)

Description

- experimental design and statistical techniques
- policies on treatment of **anomalous** results
- use of weighting techniques (considering different procedures / different measurement uncertainties)

Consider available technical information including reported uncertainty information and evidence of laboratory performance

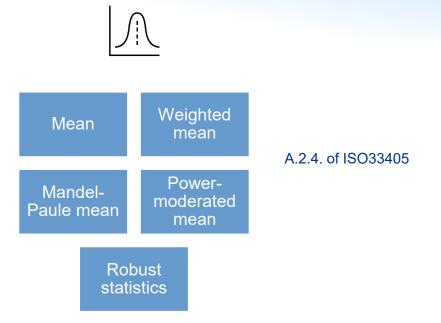
Assignment of property values and uncertainties



Statistical techniques

Choice depends on study design and obtained dataset

- number of datapoints
- independence of individual points
- Comparability of uncertainties of measurement / variability



Certified value shall be a good estimate of a true value and not just the average of a population.

Uncertainty of certified values

- Identify uncertainty contributors as a minimum from:
 - u_{char} characterization
 - u_{het} between-unit and within-unit heterogeneity
 - u_{lts} changes of property values during storage
 - u_{sts} changes of property values during transport

$$u_{CRM} = \sqrt{u_{char}^2 + u_{het}^2 + u_{lts}^2 + u_{sts}^2 [+u_{other}^2]}$$

$$U_{CRM} = k \cdot u_{CRM}$$





RM Document

Certificate (CRM)

• Content in accordance with ISO 33401:2024

Reference sheet (RM)

• Containing all information essential to the use of RM

Certification Report (not requirement of ISO17034)

• Containing information essential to the use and production of RM

- Title
- CRM identification and name
- Material description
- Assigned property values and uncertainties
- Metrological traceability statement
- Period of validity
- Instructions for storage and handling
- Producer information
- Name and function of approving officer
- page 1 of n

. .

Reference Materials-Radionuclides



Certified Reference Material

CERTIFICATE

IAEA-464

RADIONUCLIDES IN BROWN RICE

Certified values for activity concentration

(based on dry mass)

Radionuclide	Certified value ^(a) [Bg kg ⁻⁵]	Uncertainty [®] [Bq kg ⁻¹]	Half-life [1]	Remark
40K	72.1	3.2	1.2504(30)×10 ⁹ years	
127Cs	38.6	0.8	30.018(22) years	

(a) Certified values are calculated from the accepted data sets, each being obtained by a different laboratory following ISO 33405 [2].

(b) The uncertainty is expressed as a combined standard uncertainty (coverage factor k = 1) estimated in accordance with the JCGM 100:2008 [3] and ISO 33405 [2].

Information values for activity concentration

(based on dry mass)

Radionuclide	Information value ^[4] [Bg kg ⁻¹]	[Bq kg ⁻¹]	Half-life [1]
tH Cs	12.0	0.4	2.0644(14) years

(a) Information values are calculated from the accepted data sets, each being obtained by a different laboratory following ISO 33405 [2].

(b) The uncertainty is expressed as a combined standard uncertainty (coverage factor k = 1) estimated in accordance with the JCGM 100:2008 [3] and ISO 33405 [2].

Reference date for all specified radionuclide decay corrections: 01 January 2015



Page 1 of 5

- Radionuclides
 - Reference Materials under ISO 17034 accreditation
 - Certified Reference Materials
 - Reference Materials



Certified Reference Material

CERTIFICATE

IAEA-434

RADIONUCLIDES IN PHOSPHOGYPSUM

Certified values for activity concentration

(based on dry mass)

Radionuclide	Certified value [Bq kg ⁻¹]	Uncertainty ^(a) [Bq kg ⁻¹]	Half-life [1]
210Pb	680	58	22.23(12) years
226Ra	780	62	1600(7) years
²³⁰ Th	211	9	7.54(3) x 10 ⁴ years
234	120	9	2.455(6) x 10 ^s years
238U	120	11	4.468(5) x 10 ⁹ years

(a) The uncertainty is expressed as a Mixture model median based standard deviation S(MM-median) at 95% confidence level [2].

Reference date for all specified radionuclide decay corrections: 01 January 2008

Origin and preparation of the material

The material was obtained from a processing plant located in Gdansk (Poland) in 2003. The material was dried and milled by an air jet mill to less than 100 um and homogenized.

Bottling of IAEA-434 was carried out under normal laboratory conditions, taking all precautions to avoid segregation. Portions of 250 g were dispensed into plastic bottles sealed with security polyethylene caps and labelled with the code IAEA-434. After bottling the material was sterilized by gamma-ray irradiation with a total dose of 25 kGy using a Co-60 source to ensure long-term stability of the material by inhibiting microbial action.

Homogeneity of the material

For the homogeneity study, 10 bottles covering the whole bottling range were randomly selected, three independent sample portions at 12.5 g from each bottle were analyzed using gamma-ray spectrometry for 210 Pb, 226 Ra, 200 Th, 236 U and 238 U. The homogeneity of 226 Ra was also tested by analyzing three sample portions of one gram from five bottles using alpha

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RS IAEA-434 Rev.01 / 2023-02-06

NAEL RM.F.007.01 Rev.04_Template for Certificate (Radionuclides)



International Atomic Energy Agency Analytical Quality Control Services Wagramer Strasse 5, RO.Box 100, A-1400 Vienna, Austria

REFERENCE SHEET

REFERENCE MATERIAL

IAEA-312

226Ra, Th and U IN SOIL

Date of issue: January 2000®

Recommended Values (Based on dry weight)

Reference Date: 30th January 1988

Element	Recommended Value Bq/kg	95% Confidence Interval Bq/kg	N*
226Ra	269	250 - 287	25

Element	Recommended Value mg/kg	95% Confidence Interval mg/kg	N*
Th	91.4	81.3 - 101.5	32
U	16.5	15.7 - 17.4	29

Number of accepted laboratory means which were used to calculate the recommended values and confidence interval

. Revision of the original reference sheet dated January 1991

The values listed above were established on the basis of statistically valid results submitted by laboratories which had participated in an international intercomparison exercise organized during 1990. The details concerning the criteria for qualification as a recommended value can be found in the report (IAEA/AL/036) "Report on the Intercomparison Run IAEA-312: 228Ra, Th and U in Soil" [1]. This report is available free of charge upon request.

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IAEA Reference Material Certification Committee (RMCC)

Clause 7.2.1 of ISO 17034:2016: RM producer can establish a technical advisory group to make recommendations on part or all of the processes, i.e., to check that all work, data and documents (related to a certain reference material) are fit for their purpose.

- To overview all aspects of RM production (characterization, selection of subcontractors, homogeneity and stability testing);
- To approve certified or information values;
- To approve release of the IAEA RMs;
- To ensure that RMs comply with ISO standards and related internal QMS documents;
- To assign the selling prices of the IAEA RMs;
- To check and revise the status of RM over the material lifetime (extending, withdrawing from sale, discontinuing, introducing a revision of reference sheets, requests for re-characterization)

RMP in TERC

- Long tradition (since the 1960s)
- Worldwide provider of CRM and RM
- Accredited RM producer (since 2022)
- The TERC holds the primary reference materials for H, C, O, N and S stable isotope ratios

... in preparation ...







Reference Material activities in TERC



- Web-shop for RMs
- Storage, logistics & dispatching
- Production, processing, splitting
- Monitoring existing RMs
- Replacement RMs
- Planning new RMs
- Feasibility studies, homogeneity and stability tests & characterization of new RMs



Reference materials can be ordered at: https://nucleus.iaea.org/sites/ReferenceMaterials/



Reference Products for Environment and Trade

The IAEA provides reference materials (RMs) to laboratories world-wide to assist them in the quality assurance of the results they obtain by nuclear analytical techniques. More than 90 different reference materials are distributed by the Agency. Each of these is characterised for analytes belonging to one of the following groups: Radionuclides, Trace Elements and Methyl Mercury, Organic Compounds, Stable Isotopes. The IAEA is the world's largest supplier of matrix reference materials characterised for radionuclides. Some of the IAEA reference materials characterized for isotope ratios are at the highest metrological level as international measurement standards.

Reference Materials Catalogue

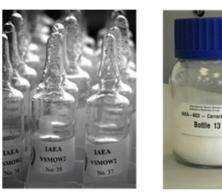
Reference materials characterized for:

- Trace Elements (and Methyl Mercury)
- Radionuclides
- <u>Stable Isotopes</u>
- Organic Compounds

Documentation for Reference Materials that are no longer available

Archive

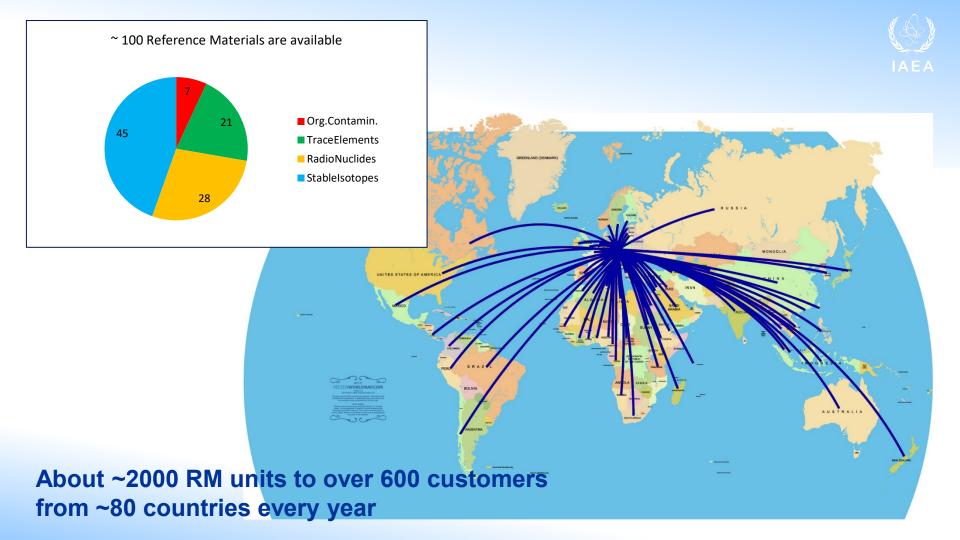
Note: For general inquiries, please continue to use our contact point at: Analytical-Reference-Materials.Contact-Point@iaea.org



Radioactive (top) and stable isotope (bottom) reference materials







TERC`s Worldwide Proficiency Testing exercise

- Support the MS's laboratories in improving their measurement capabilities in environmental monitoring and in providing reliable analytical results
- One of the first services to Member States since the IAEA had been established (*Intercomparison*)
- Connection to the RMP (value assignment through organized interlaboratory comparison)
- It supports quality assurance within the laboratory including ISO17025
- Facilitates continuous development in analytical quality
- Provides new challenges such as simulating nuclear emergencies or demonstration of real environmental situations
- Gap analysis and follow-up training
- PT 2024 ~ 500 laboratories

Proficiency Tests can be ordered at:

Reference Materials-Proficiency Tests





A proficiency test sample kit (top) and sample kits ready for dispatch (bottom)



Conclusions



- RMs play an important role in measurement process used in all stages, including for method validation/verification, calibration, quality control and quality assurance
- The quality of the RMs used in the analytical laboratory directly reflects on the quality of the obtained results
- High quality of RMs is ensured through compliance of RM production process
 with relevant standards and recommendations
- Certified RMs must meet high requirements regarding homogeneity and stability, as well as the uncertainty and traceability of certified values
- Usage of RMs contributes to ensuring accurate and reliable results for environmental radioactivity measurements – providing a basis for informed decision making in management of environmental contamination or to ensure the safety of food and drinking water

References

- ISO 17034:2016 General requirements for the competence of reference material producers
- ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories
- ISO Guide 30:2015 Reference materials Selected terms and definitions
- ISO 33401:2024 Reference materials Contents of certificates, labels and accompanying documentation
- ISO 33405:2024 Reference materials Guidance for characterization and assessment of homogeneity and stability
- JCGM 200:2012 International Vocabulary of Metrology Basic and General Concepts and Associated Terms (VIM)



Thank you!