

JRP-21GRD09

Metrology for the harmonisation of measurements of environmental pollutants in Europe

2022 - 2025

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of the European Partnership on Metrology research funding programme:

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JRP-21GRD09 2022 - 2025

Metrology for the harmonisation of measurements of environmental pollutants in Europe

Consortium: 12 NMI/DIs and 10 universities and research institutes

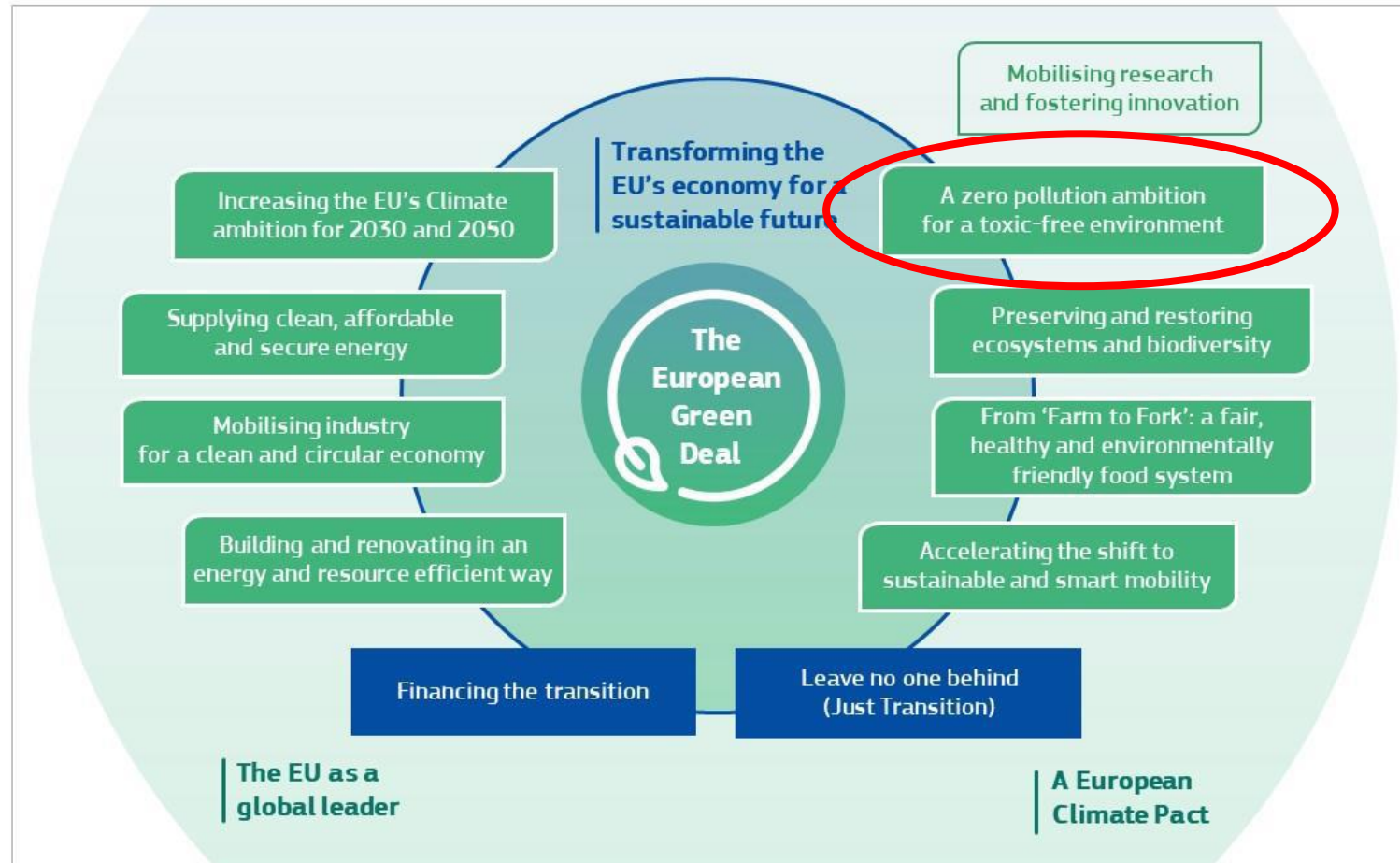


LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS



Metrology for the harmonisation of measurements of environmental pollutants in Europe

The European Green Deal, Document: "COM/2019/640 final"



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EURATOM, founded 25 March 1957:

Treaty establishing the European Atomic Energy Community, Document: “(2016/C 203/01)”

Article 35

Each Member State shall establish the facilities necessary to carry out continuous monitoring of the level of radioactivity in the air, water and soil and to ensure compliance with the basic standards.

The Commission shall have the right of access to such facilities; it may verify their operation and efficiency.

Other European Regulations:

Council Directive 2013/51/Euratom, Council Directive 2013/59/Euratom

Directive 2008/50/EC, Directive 2009/29/EC, Directive 2009/31/EC, Directive 2010/75/EU,

Results of continuous radioactivity monitoring

Earth Syst. Sci. Data, 11, 589–601, 2019
<https://doi.org/10.5194/essd-11-589-2019>
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Earth System
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Data

30 years of European Commission Radioactivity Environmental Monitoring data bank (REMdb) – an open door to boost environmental radioactivity research

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Abstract. The Radioactivity Environmental Monitoring data bank (REMdb) was created in the aftermath of the Chernobyl accident (1986) by the European Commission (EC) – Directorate-General Joint Research Centre (DG JRC), sited in Ispra (Italy). Since then it has been maintained there with the aim to keep a historical record of the Chernobyl accident and to store the radioactivity monitoring data gathered through the national environmental monitoring programs of the member states (MSs). The legal basis is the Euratom Treaty, Chapter III Health and Safety, Articles 35 and 36, which clarify that MSs shall periodically communicate to the EC information on environmental radioactivity levels. By collecting and validating this information in REMdb, JRC supports the DG for Energy in its responsibilities in returning qualified information to the MSs (competent authorities and general public) on the levels of radioactive contamination of the various compartments of the environment (air, water, soil) on the European Union scale. REMdb accepts data on radionuclide concentrations from EU MSs in both environmental samples and foodstuffs from 1984 onwards. To date, the total number of data records stored in REMdb exceeds 5 million, in this way providing the scientific community with a valuable archive of environmental radioactivity topics in Europe. Records stored in REMdb are publicly accessible until 2011 through an unrestricted repository “REM data bank – Years 1984–2006” <https://doi.org/10.2905/jrc-10117-10024> (De Cort et al., 2007) and “REM data bank – Years 2007–2011” <https://doi.org/10.2905/de42f259-fafe-4329-9798-9d8fab98de5> (De Cort et al., 2012). Access to data from 2012 onwards is granted only after explicit request, until the corresponding monitoring report is published. Each data record contains information describing the sampling circumstances (sampling type, begin and end time), measurement conditions (value, nuclide, apparatus, etc.), location and date of sampling, and original data reference. In this paper the scope, features and extension of REMdb are described in detail.

Statement in the publication:

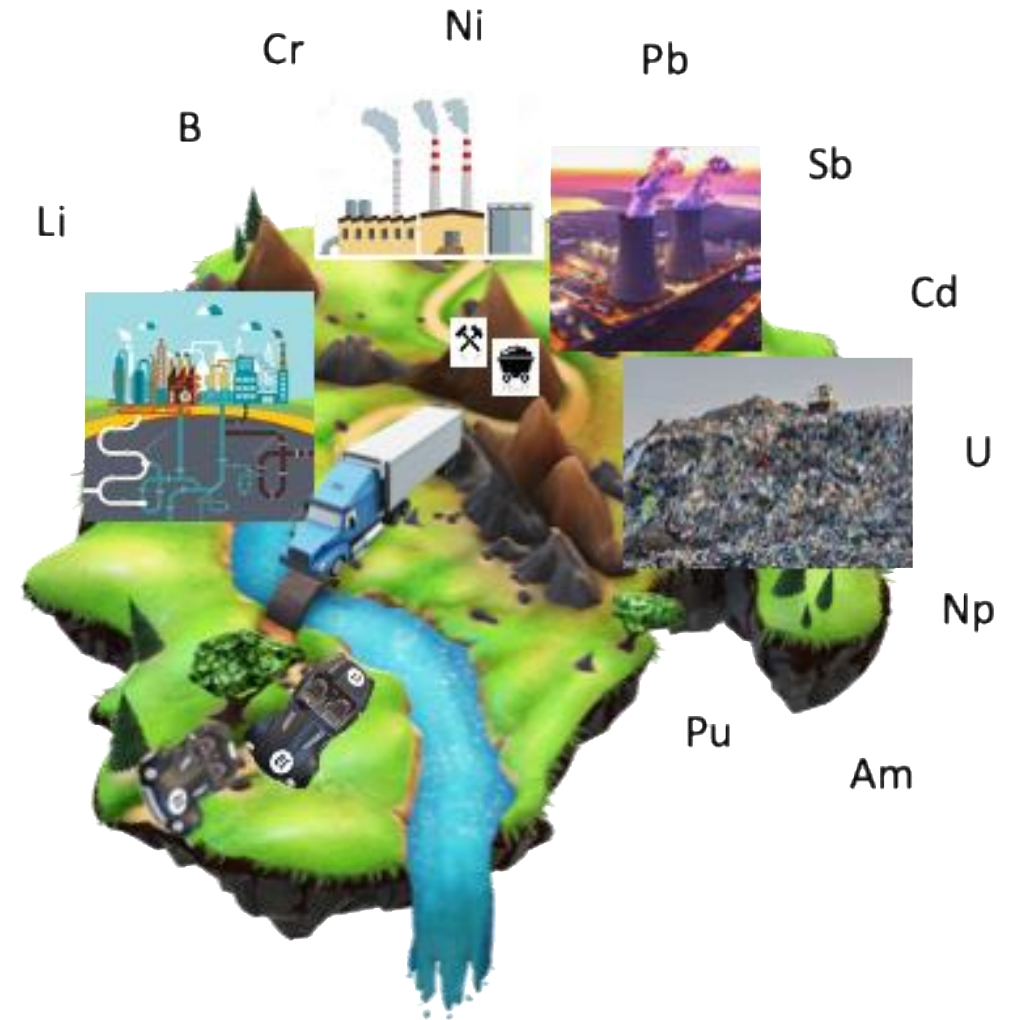
Artificial alpha-emitting aerosols are rarely measured by routine monitoring networks as they are usually undetectable, even close to the nuclear installations where they are produced.

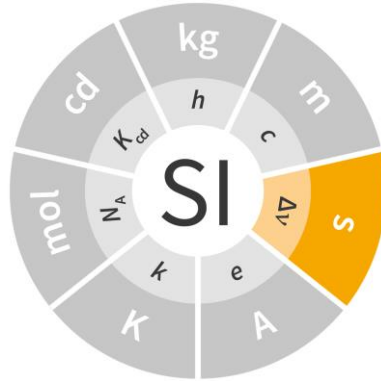
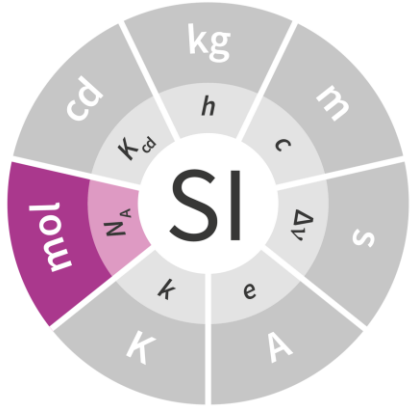
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Metrology for the harmonisation of measurements of environmental pollutants in Europe

Key Aspects:

- **The zero-pollution ambition promoted by the European Green Deal**, requires highly sensitive and state-of-the-art detection techniques for the measurement of ultra-low amounts of pollutants.
- **Mass spectrometry** is a key method,
 - ✓ with high potential for reducing measurement uncertainties and detection limits,
 - ✓ but there is no existing traceability chain for **radioactive elements**,
 - ✓ and there is a lack of SI-traceable isotope reference materials for **stable isotopes**.





THE SECOND

The second, symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta\nu_{\text{Cs}}$, the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be 9 192 631 770 when expressed in the unit Hz, which is equal to s^{-1} .

Derived quantity	Special name of unit	Unit expressed in terms of base units
activity referred to a radionuclide	becquerel	$\text{Bq} = \text{s}^{-1}$

THE MOLE

The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.022\,140\,76 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A , when expressed in the unit mol^{-1} and is called the Avogadro number.

The amount of substance, symbol n , of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.

$$\text{mol} \leftarrow n = \frac{A \times T_{1/2}}{N_A \times \ln 2} \quad \text{Bq}$$

n : amount of substance (mol)

A : activity in Bq (equiv. to s^{-1})

$T_{1/2}$: Half-life (s)

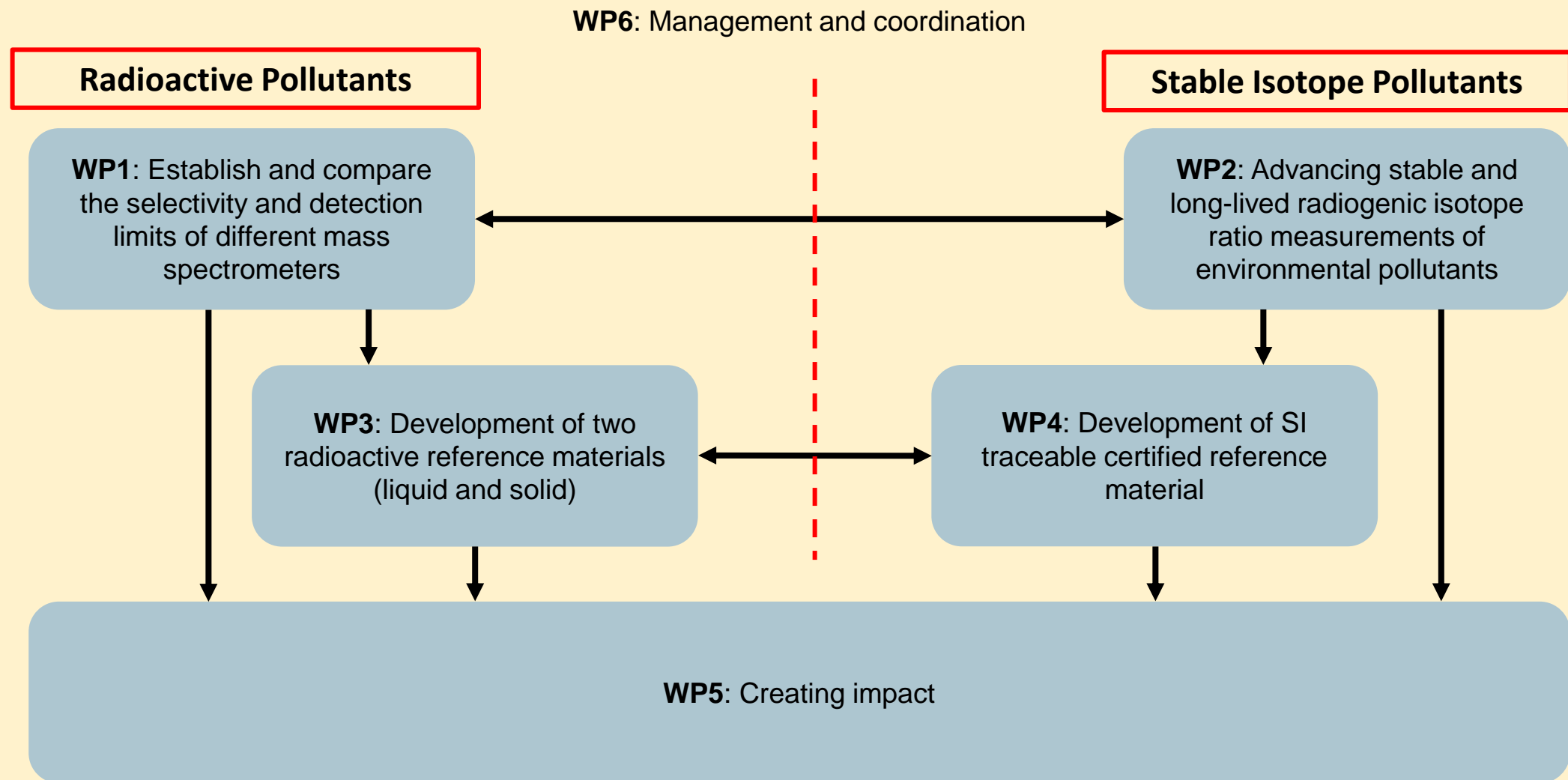
N_A : Avogadro constant (mol^{-1})

$$T_{1/2}({}^{238}\text{U}) = 1.4 \times 10^{17} \text{ s}$$

$$T_{1/2}({}^{240}\text{Pu}) = 2.1 \times 10^{11} \text{ s}$$

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Mass spectrometry systems included in the project

- **ICP-QMS** Inductively Coupled Plasma Quadrupole Mass Spectrometer
- **ICP-MS/MS** Inductively Coupled Plasma Tandem Mass Spectrometer
- **ICP-SFMS** Inductively Coupled Plasma Sector Field Mass Spectrometer
- **MC-ICP-MS** Multi-Collector Inductively Coupled Plasma Mass Spectrometer
- **SIMS** Secondary-Ion Mass Spectrometer
- **TIMS** Thermal Ionisation Mass Spectrometer
- **AMS** Accelerator Mass Spectrometer
- **ICP-TOF-MS** Inductively Coupled Plasma Time of Flight Mass Spectrometer
- **SNMS** Secondary Neutral Mass Spectrometer
- **HR-ICP-SF-MS** High Resolution Inductively Coupled Plasma Sector Field Mass Spectrometer
- **ICP-QQQ-MS** Triple quadrupole Inductively Coupled Plasma Mass Spectrometer

WP1: Establish and compare the selectivity and detection limits of different mass spectrometers

Objectives

- Define and prepare **traceable aqueous standards containing radioactive pollutants** (U, Np, Pu, Am, Sr, Ra).
- Establish the **advantages and limitations** of commercially available instruments and decay counting techniques.
- Produce **recommendations** for low-level radionuclide measurement using mass spectrometry.

Outputs

- Production of **traceable standards** and methods for single, mixed and isotopic ratio radionuclide measurements.
- **Comprehensive assessment** of mass spectrometry instruments for low-level radionuclide measurement.

WP3: Development of 2 radioactive reference materials (liquid & solid)

Objectives

- To develop **2 radioactive reference materials** (liquid & solid) containing radioactive pollutants (e.g. U, Np, Pu, Am)
- For use in **2 inter-laboratory comparisons** to assess measurement capabilities (e.g. detection limits & uncertainty budgets)

Outputs

- Extensive comparison of **instrument capabilities** (15 partners)
- **Harmonisation** of mass spectrometry **measurement methods**
- Addressing isotopic fractionation

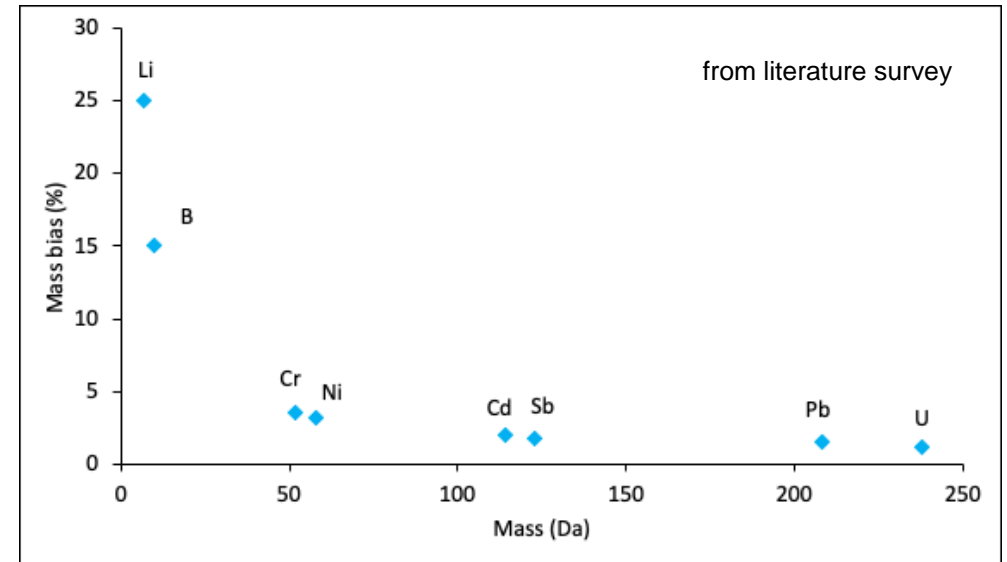
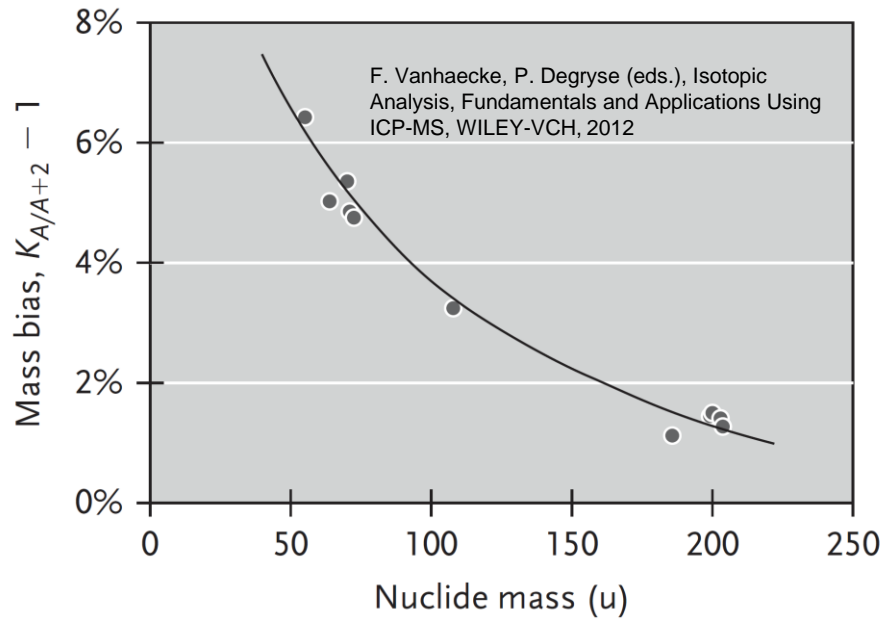
Metrology for the harmonisation of measurements of environmental radioactive pollutants

Major Outputs

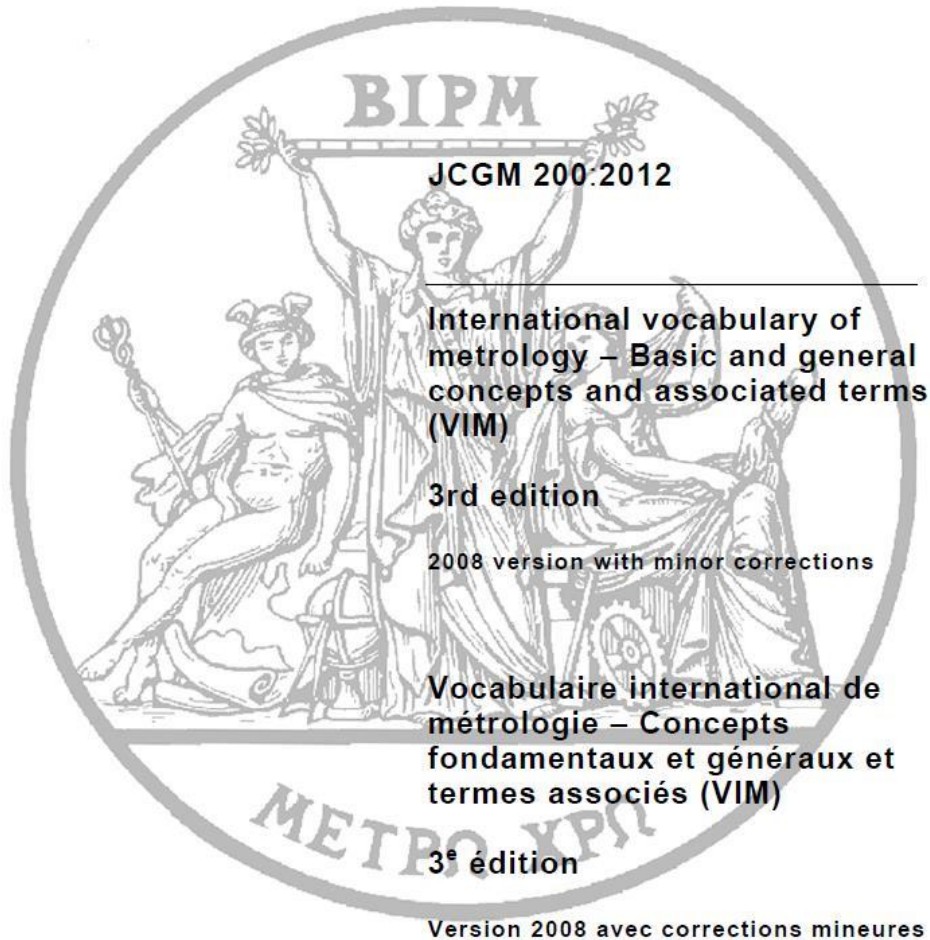
- Traceable aqueous radioactive standards: single, mixed and isotopic ratio standards
- 2 Reference Materials
- Guide on the use of mass spectrometry for low level radionuclide detection including detection limits & uncertainty budgets

The lack of SI-traceable isotope reference materials for stable isotopes

The **mass bias effect** (instrumental mass fractionation) breaks the traceability chain, especially for measurements with ICP-MS systems



The lack of SI-traceable isotope reference materials for stable isotopes



2.8

primary reference measurement procedure

primary reference procedure

reference measurement procedure used to obtain a **measurement result** without relation to a **measurement standard** for a **quantity** of the same **kind**

NOTE 1 The Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) uses the term “primary method of measurement” for this concept.

5.4 (6.4)

primary measurement standard

primary standard

measurement standard established using a **primary reference measurement procedure**, or **created as an artifact, chosen by convention**

The lack of SI-traceable isotope reference materials for stable isotopes

DE GRUYTER

DOI 10.1515/pac-2013-1023 — Pure Appl. Chem. 2014; 86(3): 425–467

IUPAC Technical Report

Willi A. Brand*, Tyler B. Coplen, Jochen Vogl, Martin Rosner and Thomas Prohaska

Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report)¹

Abstract: Since the early 1950s, the number of international measurement standards for anchoring stable isotope delta scales has mushroomed from 3 to more than 30, expanding to more than 25 chemical elements. With the development of new instrumentation, along with new and improved measurement procedures for studying naturally occurring isotopic abundance variations in natural and technical samples, the number of internationally distributed, secondary isotopic reference materials *with a specified delta value* has blossomed in the last six decades to more than 150 materials. More than half of these isotopic reference materials were produced for isotope-delta measurements of seven elements: H, Li, B, C, N, O, and S. The number of isotopic reference materials for other, heavier elements has grown considerably over the last decade. Nevertheless, even primary international measurement standards for isotope-delta measurements are still needed for some elements, including Mg, Fe, Te, Sb, Mo, and Ge. It is recommended that authors publish the delta values of internationally distributed, secondary isotopic reference materials that were used for anchoring their measurement results to the respective primary stable isotope scale.

Keywords: delta notation; delta values; geochemistry; inductively coupled plasma (ICP) mass spectrometry; isotopes; IUPAC Inorganic Chemistry Division; mass spectrometry; reference materials.

3.2 Lithium

Lithium has two stable isotopes, ^7Li and ^6Li , with isotopic abundances of 92.4 and 7.6 %, respectively, in naturally occurring terrestrial materials. Relative lithium isotopic ratios in geochemical and environmental studies commonly are reported as $\delta^7\text{Li}_{\text{RM8545}}$ values relative to the internationally distributed lithium carbonate isotopic reference material NIST RM 8545 ($\delta^7\text{Li} = 0$; LSVEC) in terms of $N(^7\text{Li})/N(^6\text{Li})$ ratios.

Table 3 The $\delta^7\text{Li}$ values of lithium isotopic reference materials.

Description	Material	$\delta^7\text{Li}_{\text{RM8545}}$	Uncertainty	References	Comment
<u>NIST RM 8545</u> (LSVEC)	Lithium carbonate	0 ^a	None	[58, 59]	^b
IRMM-016	Lithium carbonate	+0.35 ‰			Calc. from certificates
		-0.01 ‰	0.6 ‰	[58, 60]	Mean from GeoReM ^c
		-0.01 ‰	0.72 ‰	[58, 60–62]	
		+0.15 ‰	1.0 ‰	[63]	
		-0.2 ‰	0.5 ‰	[64]	
		+0.14 ‰	0.2 ‰	[65]	
NRC NASS-5	Seawater	+30.63 ‰	0.44 ‰	[66]	
		+30.7 ‰			Mean from GeoReM ^c
OSIL IAPSO	Seawater	+30.84 ‰	0.19 ‰	[66]	
		+31.1 ‰	0.3 ‰		Mean from GeoReM ^c
IRMM BCR-403	Seawater	+30.8 ‰	0.6 ‰		Mean from GeoReM ^c
NIST SRM 610	Silicate glass	+32.36 ‰	0.29 ‰	[67]	
		+32.5 ‰	0.02 ‰	[65]	
NIST SRM 612	Silicate glass	+35.26 ‰	0.79 ‰	[68]	
		+31.78 ‰	0.34 ‰	[67]	
		+31.2 ‰	0.1 ‰	[65]	
		+31.1 ‰	0.4 ‰	[69]	
NIST SRM 614	Silicate glass	+20.5 ‰	0.1 ‰	[65]	
BCR-2	Silicate glass	+2.87 ‰	0.39 ‰	[66]	
		+4.08 ‰	0.1 ‰	[65]	
JA-1	Andesite	+5.57 ‰	0.44 ‰	[66]	
		+5.79 ‰	0.65 ‰	[70]	
JB-2	Basalt	+4.78 ‰	0.47 ‰	[66]	
		+4.29 ‰	0.34 ‰	[70]	
JB-3	Basalt	+3.94 ‰	0.29 ‰	[70]	
BHVO-1	Basalt	+5.0 ‰	0.35 ‰	[66]	
		+5.31 ‰	0.18 ‰	[68]	
BHVO-2	Basalt	+4.5 ‰	0.5 ‰		Mean from GeoReM ^c
		+4.55 ‰	0.29 ‰	[68]	
		+4.33 ‰	0.33 ‰	[62]	
		+4.7 ‰	0.2 ‰	[65]	

^aExact value defining the $\delta^7\text{Li}_{\text{RM8545}}$ scale. For Li, the commonly used name is “RM 8545”. For carbon, the name “LSVEC” is more popular.

^bIsotope-amount ratio determined using synthetic isotope mixtures.

^cMean of values published in GeoReM (georem.mpch-mainz.gwdg.de/); last accessed 4/2013.



Cite this: *J. Anal. At. Spectrom.*, 2016, 31, 1440

Characterization of a series of absolute isotope reference materials for magnesium: *ab initio* calibration of the mass spectrometers, and determination of isotopic compositions and relative atomic weights†

Jochen Vogl,^{*a} Björn Brandt,^a Janine Noordmann,^b Olaf Rienitz^b and Dmitriy Malinovskiy^c

For the first time, an *ab initio* calibration for absolute Mg isotope ratios was carried out, without making any *a priori* assumptions. All quantities influencing the calibration such as the purity of the enriched isotopes or liquid and solid densities were carefully analysed and their associated uncertainties were considered. A second unique aspect was the preparation of three sets of calibration solutions, which were applied to calibrate three multicollector ICPMS instruments by quantifying the correction factors for instrumental mass discrimination. Those fully calibrated mass spectrometers were then used to determine the absolute Mg isotope ratios in three candidate European Reference Materials (ERM)-AE143, -AE144 and -AE145, with ERM-AE143 becoming the new primary isotopic reference material for absolute isotope ratio and delta measurements. The isotope amount ratios of ERM-AE143 are $n(^{25}\text{Mg})/n(^{24}\text{Mg}) = 0.126590(20) \text{ mol mol}^{-1}$ and $n(^{26}\text{Mg})/n(^{24}\text{Mg}) = 0.139362(43) \text{ mol mol}^{-1}$, with the resulting isotope amount fractions of $x(^{24}\text{Mg}) = 0.789920(46) \text{ mol mol}^{-1}$, $x(^{25}\text{Mg}) = 0.099996(14) \text{ mol mol}^{-1}$ and $x(^{26}\text{Mg}) = 0.110085(28) \text{ mol mol}^{-1}$ and an atomic weight of $A_r(\text{Mg}) = 24.305017(73)$; all uncertainties were stated for $k = 2$. This isotopic composition is identical within uncertainties to those stated on the NIST SRM 980 certificate. The candidate materials ERM-AE144 and -AE145 are isotopically lighter than ERM-AE143 by -1.6‰ and -1.3‰ , respectively, concerning their $n(^{26}\text{Mg})/n(^{24}\text{Mg})$ ratio. The relative combined standard uncertainties are $\leq 0.1\text{‰}$ for the isotope ratio $n(^{25}\text{Mg})/n(^{24}\text{Mg})$ and $\leq 0.15\text{‰}$ for the isotope ratio $n(^{26}\text{Mg})/n(^{24}\text{Mg})$. In addition to characterizing the new isotopic reference materials, it was demonstrated that commonly used fractionation laws are invalid for correcting Mg isotope ratios in multicollector ICPMS as they result in a bias which is not covered by its associated uncertainty. Depending on their type, fractionation laws create a bias up to several per mil, with the exponential law showing the smallest bias between 0.1‰ and 0.7‰ .

Received 14th January 2016
Accepted 14th April 2016

DOI: 10.1039/c6ja00013d

www.rsc.org/jaas

WP2: Establish and compare the selectivity and detection limits of different mass spectrometers

Objectives

- Develop **measurement methods for isotope ratios**, traceable to the SI by using multi-collector ICP-MS.
- **Apply** these methods on more commonly available techniques (ICP-MS/MS, ICP-QMS).
- Providing suitable **operating procedures** focusing on stable polluting elements (e. g. Li, B, Cr, Cd, Ni, Sb, Pb, U).
- Produce **recommendations** for sample processing, treatment, uncertainty budgets, and the quantification of the mass bias.

Outputs

- **SI traceable methods** for determination of isotope ratios of Li, B, Cr, Cd, Ni, Sb, Pb, U by MC-ICP-MS and single collector ICP-MS.
- **Analyte separation methods** for high precision analysis.
- **Evaluated instrumental mass fractionation** for ICP-based mass spectrometers.

WP4: Development of SI Traceable Certified Reference Material

Objectives

- To develop **one certified seawater reference materials** for stable inorganic pollutant elements:
 - ✓ Processing and production plan
 - ✓ Sampling and processing of raw material
 - ✓ Homogeneity and stability measurements
 - ✓ Characterization, value assignment and reporting

Output

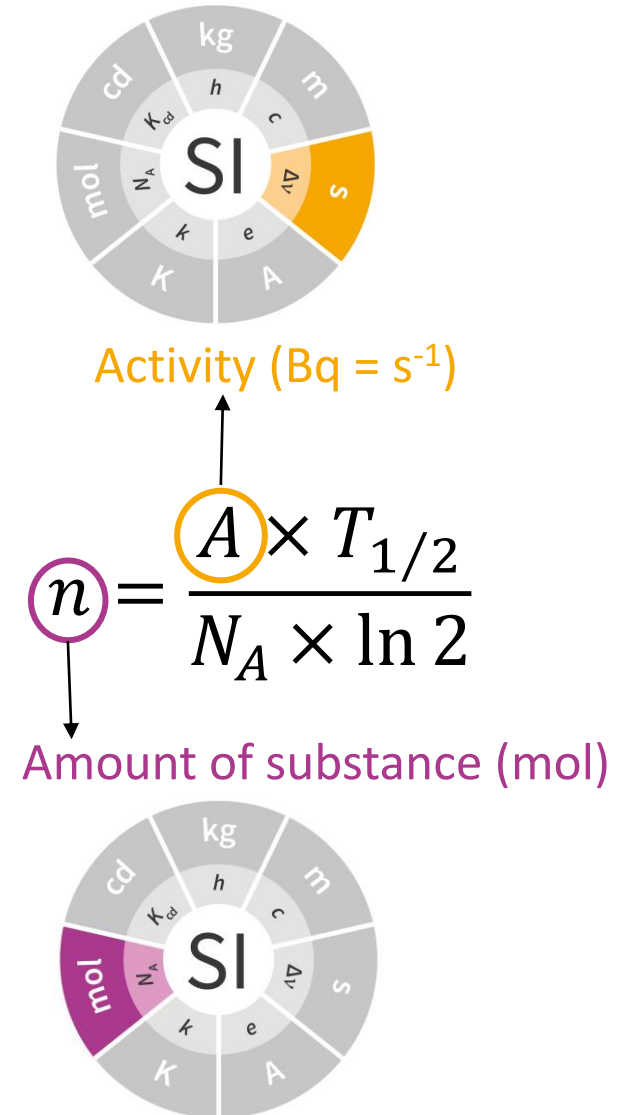
- Availability of **one certified seawater reference materials** for stable inorganic pollutant elements

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Impact:

- **Establish link** between radiometric techniques and mass spectrometry, bridging the gap between the activity (Bq) and the amount of substance (mol) of an isotope
- Close the **traceability gap** for isotope ratio measurement resulting from isotopic fractionation (mass bias)
- Guide on the use of mass spectrometry for **low level radionuclide detection**
- Report of different instrument's **advantages and limitations**
- Three Si-traceable **reference materials**
- Establish Si-traceable **calibration chain** for single collector ICP-MS
- **Harmonized methods** for measurement of polluting elements using mass spectrometric techniques

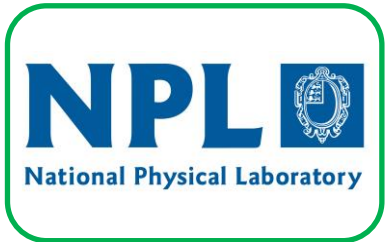


N_A : Avogadro constant (mol⁻¹) $T_{1/2}$: Half-life (s)

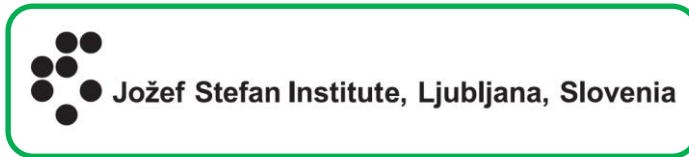
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WP leaders:



WP1: Ben Russell



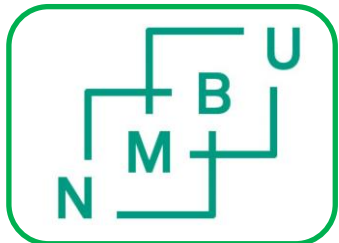
WP2: Tea Zuliani



WP3: Valérie Lourenço



WP4: Betül Ari



WP5: Simon Jerome



WP6: Dirk Arnold

Some facts about the project:

- The 22 partners will contribute with in total 320 months of work!
- The funding from the European Union will be 2.7 Million € !

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