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The CCRI Task Group on the Use of Mass Spectrometry in Radionuclide Metrology

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The CCRI Task Group on the Use of Mass Spectrometry in Radionuclide Metrology

Ben Russell[a], Lisa Karam[b], Dirk Arnold[c], Janine Eberhardt[c], Jacqueline Mann[b], Mark Tyra[b], Richard Essex[d]

[a] National Physical Laboratory, Queens Road, Teddington, Middlesex TW11 0LW, United Kingdom

[b]National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, United States of America

[c] [a]Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

[d]US Department of Energy, 1000 Independence Avenue, Southwest Washington, DC 20585, United States of America

Abstract

The CCRI(II) has formed a new Task Group to support the increasing use of mass spectrometry in radionuclide measurement applications across areas including nuclear decommissioning, environmental monitoring, and nuclear forensics. The Task Group is exploring current and potential roles for mass spectrometry in radionuclide metrology, including the identification of priority radionuclides, development of methods, instrumentation, standards, and relevant reference materials, as well as identifying the best approaches for the exchange of information. Collaborations with other communities are establishing where radionuclide measurement by mass spectrometry can add value, including earth and climate science, food safety, environmental monitoring, and emergency response.

Keywords

Atom counting; long-lived radionuclide metrology; low-level measurement; nuclear decay data; reference materials

Introduction

Background and history

Mass spectrometry development started in the late 1890's using a discharge tube with a vacuum, with cathode rays deflected using an electric field. One of the earliest examples of radionuclide measurements by mass spectrometry was the determination of the relative abundance of uranium isotopes by Alfred Nier in 1938 (Nier, 1939). These data, combined with alpha-particle counting experiments were used to calculate the decay constants and the half-lives of the U isotopes.

Since the early 1980s, mass spectrometric methods have been recognized as a useful tool in determining the composition and concentration of radionuclides (Halverson, 1984; Brown, 1988; Walther and Wendt, 2020). This was enhanced by the commercial availability of instruments, such as inductively coupled plasma mass spectrometry(ICP-MS) in 1983. Early examples of radionuclide measurements include cosmogenic ^{41}Ca in meteorites using tandem accelerator mass spectrometry (Kubik, 1986), measurement of isotopic ratios of U alongside Pb, Os, and B standards (Russ and Bazan, 1987), and measurement of U concentrations in various environmental samples (Boomer and Powell, 1987).

Early mass spectrometric measurement of long-lived transuranics and fission products such as ^{99}Tc was favoured due to the rapid measurement and improved sensitivity compared with conventional event counting techniques. A further advantage of mass spectrometry is the possibility of rapid and simultaneous multi-nuclide analysis. This compares to some decay counting techniques that must separate the individual radionuclides of interest prior to measurement through complex multi-stage sample preparation, or only report the total activity present. This is especially true for samples that may have low levels of activity of the radionuclides to be measured in complex sample matrices. As mass spectrometric techniques have improved, the number of measurable radionuclides has increased.

By the beginning of the 21st century, there was widening interest in both analytical and academic laboratories to leverage the specific advantages of mass spectrometry in the analysis of radionuclides. Although metrology, per se, was often a secondary consideration for these applications, there is a current and growing need for validated reference materials for instrument calibration, and for metrological traceability for decision making and to meet regulatory requirements. National Measurement Institutes (NMIs) have begun to expand their use of mass spectrometry for the measurement of radionuclides to better meet stakeholder needs in the application areas described below.

Applications

Today, mass spectrometry deployed in radionuclide metrology laboratories at NMIs continues to increase. Often used in parallel with more conventional decay counting techniques, mass spectrometry is providing services for stakeholders in a wide range of radioactivity-relevant applications, including:

- Decommissioning and decontamination of nuclear/radiological sites- range of fission and activation products across complex materials (Seo, et al., 2020).
- Environmental pollution monitoring and control- trace level monitoring of radionuclides in environmental materials including soil, air and water, contributing to a clean environment and public safety.
- Nuclear safeguards and nuclear forensics- including isotopic ratio measurements to determine the origin of nuclear materials.
- Geo- and Cosmochronology- dating of events on geological timescales and origins of the solar system.

- Impurity and interference evaluation- especially in materials such as environmental samples and nuclear medicine therapeutic agents (Klika et al. 2024).
- Nuclear decay data- half-life, branching ratios, and other evaluation parameters for extremely long-lived radioisotopes.

Presently, there are approximately 30 radionuclides (^{14}C, ^{32}Si, ^{36}Cl, ^{41}Ca, ^{59,63}Ni, ^{79}Se, ^{90}Sr, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135,137}Cs, ^{151}Sm, ^{210}Pb, ^{226}Ra, ^{229,230,232}Th, ^{232,233,234,235,236,238}U, ^{239,240,242}Pu, ^{241,243}Am) that have been measured by mass spectrometric techniques. There are a range of instrument designs, each with its relative advantages and limitations depending on the radionuclide and sample matrix of interest.

The increasing application of mass spectrometry for radionuclide measurement must be supported through the underlying provision of traceable methods, standards, and reference materials. Specifically, for reference materials, these must be characterised for radionuclides and activity levels relevant to mass spectrometry. This will likely involve recharacterization of existing materials that were initially developed for decay counting applications, or development of new materials. There is also growing discussion on the approach taken for production and certification of mass-spectrometry relevant reference materials. Various national and international user groups and consortia are responding to this, such as the Euramet 'Metrology for the harmonisation of measurements of environmental pollutants in Europe' (MetroPOEM) project or the Mass Spectrometry Subgroup of the International Committee on Radionuclide Metrology (ICRM).

Objectives of the task group

With the expanding use of mass spectrometry for radionuclide analysis, it is timely to establish this technology as a metrological tool for radionuclide measurements. The Consultative Committee on Ionizing Radiation Section II on the Measurement of

Radionuclides [CCRI(II)] recognizes the potential of mass spectrometry and has been investigating how mass spectrometry can fill the metrological gaps in a variety of applications.

To begin meeting this need—following discussions with colleagues from the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) with the relevant expertise—the CCRI(II) established a Task Group, the CCRI(II)-MS-TG, to further the goal of expanding the traceable use of mass spectrometry in radionuclide metrology. The CCRI(II)-MS-TG is made up of members from both the CCRI and the CCQM communities and represents expertise in stable and radioactive isotope measurements. Launched in early 2024, the Task Group established Terms of References (including a review of current and planned activities in using mass spectrometry to support radionuclide metrology; liaising with experts to improve understanding of the need of the metrology community, including relevant radionuclides and reference materials, the sharing of information on the latest relevant programs in the metrology community; and proposing future activities to enhance CCRI(II)'s understanding of the field). In addition to organizing webinars and workshops, it will provide written reports for future CCRI(II) meetings, including possible future activities related to mass spectrometry measurement of radionuclides. The Task Group meets monthly to ensure progress is being made in relation to its Terms of Reference.

Activities and Successes

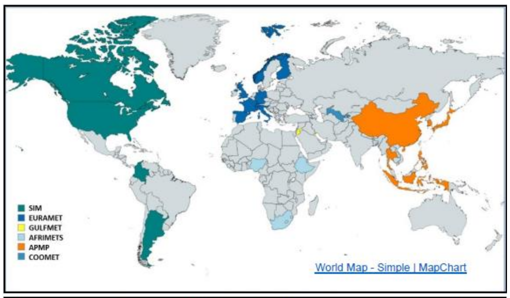
<u>Online workshops</u>

An early achievement of the Task Group was the organization of a CCRI-CCQM workshop on the use of mass spectrometry for radionuclide metrology. This was a follow-up to a webinar held in February 2022, which introduced the topic to the CCRI(II) community. There are 29 recorded presentations on various aspects of mass spectrometry for radionuclide metrology available online, including supporting tutorials. These tutorials, ranging from the basics of radionuclide metrology to fundamentals of mass spectrometry, provided an opportunity for participants (and others) to gain a basic understanding of interrelated technical fields. This workshop welcomed experts and stakeholders from both the radionuclide metrology and inorganic chemical analysis communities with experience or interest in using mass spectrometry to support metrological analysis of radioactive elements for many applications captured above.

A range of invited talks were given from different stakeholders (including NPL, NIST, PTB, the International Atomic Energy Agency (IAEA), US Centre for Disease Control and Prevention (CDC) and the US Nuclear Regulatory Commission (NRC)). Half-life measurements, isotope dilution analysis, isotopic ratio measurements, synergies between radiometric and mass spectrometric techniques, and examples of current activities at different laboratories were discussed. Sessions were also held on mass spectrometry and radionuclide metrology, how to best enable mass spectrometry in this field, and on the needs of stakeholders. The workshop was well attended, with 137 attendees and an appetite for future in-person or hybrid opportunities for further discussions and development.

Survey

To assess the current and planned future activities in the use of mass spectrometry for radionuclide measurement, the Task Group distributed a survey to more than 250 NMIs, Designated Institutes (DI's), and relevant stakeholders. The aim was to inform the content of future CCRI(II) activities in mass spectrometry including webinars and workshops, as well as continuing to build mass spectrometry networks.



SIM: Sistema Interamericano de Metrología, **EURAMET:** European Association of National Metrology Institutes, **GULFMET:** Gulf Association for Metrology, **AFRIMETS:** Intra-Africa Metrology System/Système Intra-Africain de Métrologie, **APMP:** Asia Pacific Metrology Programme, **COOMET:** Euro-Asian Cooperation of National Metrological Institutions

Figure 1, distribution of respondents to mass spectrometry survey (from the document "Mass Spectrometry for Radionuclide Measurements Survey Results", 2024).

Fifty four responses (20 % response rate) were received from laboratories around the world (Figure 1- Canada, United States, Colombia, Argentina, Spain, Norway, Finland, Italy, Switzerland, Germany, France, United Kingdom, Slovenia, Ethiopia, Nigeria, South Africa, Jordan, Kuwait, Uzbekistan, Indonesia, South Korea, Thailand, Philippines, Japan, Peoples Republic of China), who are actively using mass spectrometry for radionuclide measurement, giving a wide breadth of activities, perspectives and evidence of the growing prevalence of these techniques in the field.

A summary of the principal findings, 'Mass Spectrometry for Radionuclide Measurements Survey Results', is available online and briefly noted here. The survey reflected that most laboratories were working with a single instrument (most commonly a quadrupole inductively coupled plasma mass spectrometer ICP-QMS) with up to three staff members involved. There was a range of areas of interest, including geosciences, nuclear safeguards, and emergency response, with the most popular being environmental science. Stable isotopes were the most frequent nuclides measured, but radionuclides linked to the nuclear fuel cycle and fission/activation were nearly as frequent and were expected to increase. Medical isotopes were the most popular area that organizations were interested in developing, while less than a quarter of the responding laboratories had no plans to expand their applications further.

Mass spectrometry was seen as particularly beneficial for measurements at low activities. For the same activity concentration, the use of mass spectrometry for accurate low-level measurement is sensitive for longer-lived radionuclides, as this corresponds to a higher number of atoms, contrary to decay counting which favours a higher decay rate. Evaluation of interferences (impurities) and determination of half life and other nuclear data were also identified as key areas where mass spectrometry is beneficial. Despite the potential utility in these areas, however, they were also recognized as being more globally underrepresented, so they should be considered as focus areas. The primary challenges faced by organizations using mass spectrometry were the lack of calibration and quality control standards, maintenance costs, the absence of relevant Certified Reference Materials (CRMs), and the cost of instrumentation.

Publications and Presentations

In addition to the workshops and surveys, the Task Group has been working towards peer-reviewed publications to further understand the current and future use of mass spectrometry in radionuclide metrology.

The first is a comprehensive review on 'The Role of Mass Spectrometry in Radionuclide Metrology' and geared for the radionuclide metrologist, to be published later in 2025. There have been extensive reviews on the role of mass spectrometry for radionuclide measurements for applications including decommissioning, environmental monitoring, and nuclear medicine (Hou, 2008; Croudace, 2017; Klika, 2024). However, there has not been a review covering the status of mass spectrometry as a metrological tool. The Task Group review will address this, covering the role of mass spectrometry relative to decay counting techniques, the range of instruments available, measurement techniques (e.g., isotope dilution), application areas, and limitations (such as instrument availability, measurement interferences, and limited reference material availability). The goal is to have a compilation of information that can serve the radionuclide metrologist as mass spectrometry continues to become more common in the toolbox of radionuclide metrology.

The second paper (also expected to be published later in 2025) is a detailed review of the role of mass spectrometry in the half-life measurement of radionuclides. Specifically, mass spectrometers excel in estimating the number of atoms in a sample, a crucial variable in the decay equation used to determine the half life. In recent years, there has been a steady increase in the number of publications where mass spectrometry has been used to contribute to half-life measurements. There is an ever-greater number of publications for radionuclides that have not been measured for a long time, have discrepancies between currently published results, and/or have high measurement uncertainties. This review paper will cover case studies of all radionuclides that have used mass spectrometry to contribute to the measurement of half-life, considering the methods used (including uncertainty budgets, isotope dilution approach, and starting sample materials and reference materials) to assess if there is the potential for a more harmonized approach to future half-life measurements.

As the use of mass spectrometry in radionuclide metrology (i.e., beyond using mass spectrometry to measure radioactive materials), in which activity is the key measurand, is relatively new in the radionuclide metrology community (although it has been used in characterizing "radioactive" reference materials by mass concentration), it has been key to increase the visibility of the technique to a wide audience. An update at the ICRM 2023 meeting during the Low-Level Measurement Techniques working group session described the activities in CCRI(II), in cooperative efforts (such as the joint workshop in February 2023) with colleagues in CCQM, to widen exploration in the possible applications of these technologies. Following this update and further discussions, which led to the formation of the CCRI(II) Task Group on mass spectrometry, several presentations and outreach efforts have been spreading and gathering information among various groups and organizations that have a vested interest in measurement precision for radioactivity. These include presentations to instrument manufacturers (such as the Agilent User Group meetings for UK and Norwegian users), for national labs (such as the Korean Atomic Energy Research Institute (KAERI)) and NMIs who are looking to develop mass spectrometric capabilities for radionuclide measurement (such as the Korean Research Institute on Standards and Science (KRISS)).

Conclusions and future plans

Participants of the survey had also been asked about future activities they would like to see the Task Group take on; the vast majority (92 %) wanted to have a workshop or similar information-sharing opportunity focused on radionuclide metrology by mass spectrometry, especially concerning certified reference materials, measurement traceability, databases, and methods development. There are many factors to consider when commingling metrological measurements of the mole and that of the becquerel. For example, a decision as simple as the composition and concentration of a carrier solution has profound effects on how and if mass spectrometric measurement of a source is possible. Therefore, the Task Group will have held a follow-up workshop ("Current and Future Applications of Mass Spectrometry in Radionuclide Metrology") at the NPL in May 2025. This is being combined with a stakeholder workshop for the EURAMET MetroPOEM project, which is hoped to further improve collaboration among mass spectrometry users.

A written report of potential metrology activities for distribution to CCRI(II) members will be completed in September 2025 and will be discussed at the biennial CCRI(II) meeting in November 2025. The inputs from the workshops, surveys, and publications will provide valuable input for the update of the CCRI long-term strategy.

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