

Rapid Analysis of Radium-226 in Water Samples by ICP-QQQ

Application Note

Nuclear, environmental

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Introduction

Radium-226 is a radionuclide that occurs naturally as part of the uranium-238 decay series. ²²⁶Ra decays with a half-life of 1,600 years to radon-222 with the emission of alpha and gamma radiation. The element is known for its historical use in the luminescent paint used in clocks, watches, and other instruments. These uses led to severe health problems for the so-called Radium Girls who painted the watch and clock dials. ²²⁶Ra has a long half-life compared to the other Ra isotopes, and is considered a significant contributor to occupational radiological dose with regards to industrial sources of naturally occurring radioactive materials (NORM).

²²⁶Ra occurs naturally in waters through interaction with uranium-bearing minerals [1]. It is also present as a result of waste from the industrial exploitation of mineral resources (including uranium mining and processing sites, and produced waters following hydraulic fracturing). Radium waste producers are required to comply with stringent limits when discharging to watercourses. Analytical methods must therefore be capable of detecting ²²⁶Ra at values ranging from 0.01 Bq/L to 1 Bq/L (equivalent to 0.3 – 30 pg/L (ppq) or 0.0003 – 0.03 ppt) [2,3,4].



^{226}Ra analysis is typically performed by alpha spectrometry, which requires time-consuming and labor-intensive separation before measurement, followed by count times of several days per sample to reach the target detection limits.

This study outlines a new method developed by the National Physical Laboratory (NPL) Nuclear Metrology Group for the rapid analysis of ^{226}Ra in water samples. The new method uses a preconcentration step prior to measurement of ^{226}Ra using triple quadrupole ICP-MS (ICP-QQQ)[5]. The procedural time is significantly reduced compared to decay counting techniques, and ^{226}Ra is measurable at concentrations required to meet the regulatory detection limits.

Experimental

Sample preparation

Radium-226 calibration standards were prepared from an in-house standard solution in a dedicated facility used for the preparation of aqueous radioactive sources for decay counting or mass spectrometry measurement. The calibration standards were diluted in 2% (v/v) HNO_3 .

Groundwater samples were also investigated to assess the impact of a more complex sample matrix. Samples were evaporated to dryness and redissolved in 2% (v/v) HNO_3 . The solutions were then spiked with ^{226}Ra over a concentration range of 0.03 – 30 ppt to represent the concentrations expected following preconcentration.

High volume water samples (1 L) were spiked over the same concentration range as the groundwater samples to represent samples close to, and higher than, the regulatory discharge limits. Samples were acidified to pH 2 and passed through a chromatographic column to trap ^{226}Ra [6]. The ^{226}Ra was then eluted, evaporated to incipient dryness and then made up in 5 mL 2% HNO_3 , representing a concentration factor of ~200. Unspiked water samples were run through the same preconcentration procedure, and then measured to establish the elemental composition and confirm no contribution of polyatomic interferences to the background at $m/z = 226$. Matrix matched calibration standards were prepared by spiking water samples following preconcentration, which also enabled the recovery to be calculated ($\geq 70\%$ over the concentration range studied).

Instrumentation

An Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was used throughout. The standard sample introduction system was used, comprising a quartz torch with 2.5 mm i.d. injector, a quartz spray chamber, glass concentric nebulizer, and nickel-tipped interface cones. The instrument operating conditions are summarized in Table 1.

Table 1. ICP-QQQ operating conditions; low matrix tuning is appropriate for samples where most of the matrix has been removed during analyte preconcentration.

| Parameter | Setting | |
|----------------------|---|-----------|
| Scan mode | Single Quad | |
| Plasma conditions | Low matrix (optimized for high sensitivity) | HMI |
| RF power (W) | 1550 | |
| Carrier gas (L/min) | 1.07 | 0.60 |
| Dilution gas (L/min) | 0 | 0.35 |
| Extract 1 | 0.0 | |
| Extract 2 | -200.0 | |
| Omega Bias (V) | -100.0 | |
| Omega lens (V) | 13.6 | |
| Octopole bias (V) | -8.0 | |
| He cell gas (mL/min) | 0 – 1.0 | 0.5 – 1.0 |

Results and Discussion

Sensitivity of ICP-QQQ for ^{226}Ra

The half-life of ^{226}Ra is relatively short with regards to ICP-MS measurements (1 Bq/kg is equivalent to 27.3 ppq, compared to long-lived ^{238}U (half-life 4.5×10^9 years), where 1 Bq/kg is equivalent to 8.0×10^7 ppq). In practice, this means that calibration should be performed using standards prepared for the radioisotope of interest, rather than calibrating using a long-lived or stable isotope as an analog. The instrument detection limits (IDLs) for several operating conditions (Q1 modes and cell gas flows), were calculated from a calibration curve prepared by spiking 2% (v/v) HNO_3 with ^{226}Ra at concentrations of 0.01–30 ppt (Table 2) .

Table 2. Limit of detection for different instrument conditions and cell gas flow rates.

| Instrument mode | Single Quad | | | MS/MS | | |
|--------------------------|-------------|------|------|-------|------|------|
| He flow rate (mL/min) | 0.0 | 0.5 | 1.0 | 0.0 | 0.5 | 1.0 |
| Limit of detection (ppt) | 0.08 | 0.10 | 0.02 | 0.04 | 0.04 | 0.07 |

The IDLs in Table 2 are close to the higher end of the regulatory limits quoted (0.03 ppt), and orders of magnitude higher than the lowest values (0.3 ppq). Measurement of ^{226}Ra at environmentally relevant levels therefore requires an effective preconcentration step prior to ICP-QQQ analysis, to rival the detection limits of traditional alpha spectrometry measurement.

Interference removal by ICP-QQQ

Multiple potential interferences from polyatomic ions including $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{87}\text{Sr}^{139}\text{La}^+$, $^{86}\text{Sr}^{140}\text{Ce}^+$, $^{208}\text{Pb}^{18}\text{O}^+$, $^{186}\text{W}^{40}\text{Ar}^+$, and $^{97}\text{Mo}^{129}\text{Xe}^+$ can potentially affect ICP-MS measurement of ^{226}Ra . Multiple separation stages prior to sample introduction are often required to remove the interferences. As an alternative approach, helium (He) collision mode was investigated for the removal of polyatomic interferences, initially by introducing up to 100 ppm Sr + Ba, Sr + La, Ce, W, and Pb standards. The background at $m/z = 226$ was 0 cps in single quad mode when using 0.5–1.0 mL/min He cell gas, confirming the ability of He mode to attenuate all the polyatomic ions. Given that the on-mass polyatomic interferences are formed during sample introduction and not in the collision/reaction cell (CRC), MS/MS was not required, so the instrument was operated in single quad mode throughout.

Groundwater samples from different locations in North West England were then analyzed to determine the impact of a more complex sample matrix on instrument performance. The samples were spiked with ^{226}Ra , and measured at varying He gas flow rates together with unspiked samples and blank solutions. Bismuth-209 was used as an internal standard. The impact of matrix suppression was overcome using robust plasma conditions and aerosol dilution with the High Matrix Introduction (HMI) system of the 8800. HMI allows higher matrix levels to be analyzed directly without requiring chemical separation prior to measurement, further reducing the total procedural time. The reduction in sensitivity when operating with 0.5 mL/min He cell gas was offset by the lower background, giving comparable or improved background equivalent concentrations (BECs) at $m/z = 226$ compared to no gas mode (Table 3). The sensitivity at 0.5 mL/min He cell gas is illustrated in the calibration plot shown in Figure 1.

Table 3. BECs of ^{226}Ra using no gas and He gas mode

| He flow rate (mL/min) | BEC (ppt) | | |
|-----------------------|-----------|----------|----------|
| | Sample 1 | Sample 2 | Sample 3 |
| 0 | 0.015 | 0.017 | 0.0085 |
| 0.5 | 0.0083 | 0.0089 | 0.0092 |
| 1.0 | 0.011 | 0.0092 | 0.013 |

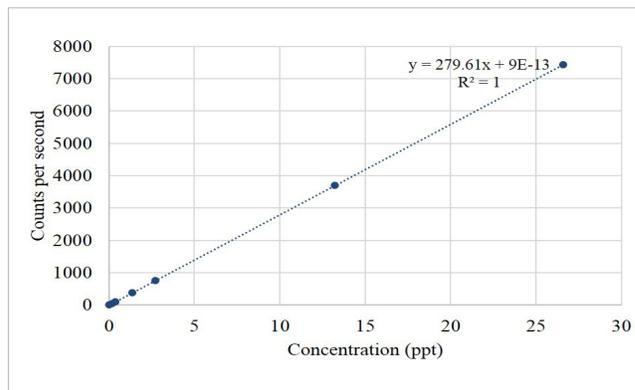


Figure 1. Calibration plot for ^{226}Ra standards in single quad mode with 0.5 mL/min He.

Measurement of high volume water samples

In water samples, ^{226}Ra was detected down to 0.03 ppt (1 Bq/L), which is equivalent to 5 mBq/L in the original sample, assuming a preconcentration factor of 200. The RSD was <10% at concentrations above 1.4 ppt (50 Bq/L), equivalent to 250 mBq/L in the original sample. The results demonstrate that ICP-QQQ combined with preconcentration from high volume water samples is capable of measuring ^{226}Ra at concentrations relevant to regulatory discharge limits. Improved accuracy at the lower limits is potentially achievable through higher preconcentration factors.

Conclusions.

A method is presented that demonstrates the capabilities of ICP-QQQ for the measurement of the naturally occurring radionuclide ^{226}Ra . The use of He collision gas effectively removes potential polyatomic interferences, while operating with HMI reduces the impact of matrix suppression. When combined with preconcentration using chromatographic separation techniques, the detection limits achievable are applicable to the regulatory limits for water. The measurement time of several minutes per sample represents a significant improvement compared to several days using traditional alpha spectrometry. The increase in sample throughput is potentially beneficial for routine monitoring of water supplies, as well as routine environmental monitoring at nuclear and industrial sites.

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