



**CERTIFICATE OF ANALYSIS  
FOR CERTIFIED REFERENCE MATERIAL**

**NMIA MX014**

**Trace Elements in Sea Water**

**Batch No. 2013.01**

**(i) Description**

Certified reference material NMIA MX014 is an acidified coastal sea water bottled in units of approximately 120 mL. Certified values are provided for the mass fractions and mass concentrations of twelve trace elements. The sea water is stabilized with 0.3 M HNO<sub>3</sub>.

**(ii) Certified values**

**Certified values for NMIA MX014.**  
Measurement uncertainty is reported as a 95% level of confidence.

|    | Mass fraction<br>µg/kg | Mass concentration <sup>†</sup><br>µg/L |
|----|------------------------|---|
| As | 2.96 ± 0.26            | 3.06 ± 0.26                             |
| Cd | 1.318 ± 0.034          | 1.363 ± 0.036                           |
| Co | 2.864 ± 0.068          | 2.961 ± 0.070                           |
| Cr | 2.613 ± 0.075          | 2.701 ± 0.077                           |
| Cu | 2.90 ± 0.25            | 2.99 ± 0.27                             |
| Fe | 21.70 ± 0.32           | 22.43 ± 0.34                            |
| Hg | 0.433 ± 0.010          | 0.448 ± 0.010                           |
| Mn | 1.48 ± 0.16            | 1.53 ± 0.16                             |
| Ni | 3.66 ± 0.10            | 3.78 ± 0.12                             |
| Pb | 2.467 ± 0.065          | 2.550 ± 0.067                           |
| Se | 3.06 ± 0.26            | 3.17 ± 0.28                             |
| V  | 4.76 ± 0.12            | 4.93 ± 0.14                             |

<sup>†</sup> Mass concentration reference values are valid for a working temperature range of 15-25 °C. The density of NMIA MX014 is 1.0339 ± 0.0016 kg/L.

**(iii) Expiry of certification**

Certified values for NMIA MX014 are valid until **6 March 2023** provided the material is stored and handled in accordance with the instructions given in this certificate. **After opening the original packaging, NMIA MX014 has a shelf life of 12 months.** NMIA MX014 may be reassessed prior to the certificate expiration date to investigate an extension of the certification period.

**(iv) Intended use**

Certified reference material NMIA MX014 is intended to be used to verify and/or validate analytical methods for elemental analysis in sea waters or similar sample matrices.

## (v) Instructions for use

**Storage**— NMIA MX014 is packaged in aluminised polyethylene terephthalate (PET) to minimise solvent transpiration. Do not open the packaging until the CRM is to be used. When the package is opened for the first time, write the opening date in the space provided on the bottle label. The expiration date is then 12 months from the opening date or the certificate expiry date (see section (iii) above), whichever is sooner. If possible, reseal the packaging with a heat sealer for ongoing storage. If this is not possible, ensure that NMIA MX014 is stored tightly capped in the original bottle. Validity of NMIA MX014 reference values for volumes less than 25 mL stored for longer than one month is not guaranteed. Storage must be between 4 °C and 25 °C. Do not store in a desiccator. NMIA MX014 should not be exposed to direct sunlight or sources of intense radiation.

**Subsampling**— Shortly before subsampling, the contents of the NMIA MX014 bottle should be mixed thoroughly by inverting several times. NMIA MX014 should only be opened in a clean environment such as a ULPA-filtered laminar flow hood. For trace element analysis, NMIA MX014 should be subsampled and handled in such a way as to avoid contamination of both the bulk material and the subsample. Only high-purity reagents should be used for sample processing.

## (vi) Details of NMIA MX014 Production

NMIA MX014 is a natural coastal sea water sample collected from the shore of Curl Curl beach in Sydney, Australia. The sea water was filtered through 0.45 µm and 0.20 µm filters then acidified with high purity HNO<sub>3</sub> to a final acid concentration of 0.3 M HNO<sub>3</sub>. All the analytes for which certified values are provided were fortified using Australian marine environment regulatory limits as a guide. The bulk sea water was mixed thoroughly by end-over-end tumbling for several hours. The reference material was then subsampled into 125 mL acid-cleaned LDPE bottles (360 units) in a trace metals clean laboratory using a pre-cleaned volumetric dispensing apparatus. Each bottle was labelled with a unique bottle number and sealed in an aluminised PET bag to minimise solvent transpiration from the CRM. Ongoing storage of the bottles is in a cool room at 4 °C.

## (vii) Analytical methods

Certified values for Cd, Cr, Cu, Fe, Hg, Ni, Pb and Se were determined by isotope dilution ICP-MS quantification. Certified values for As, Co, Mn and V were determined by standard addition ICP-MS quantification. Measurement details are given in the following table. Mass concentration reference values were calculated from the mass fraction and the density of NMIA MX014 at 20 °C. The measurement uncertainty of the density value was expanded to cover the temperature range 15-25 °C.

### Summary of Analytical Methods for NMIA MX014.

|           | Quantification Technique | Sample Preparation                               | Analytical Instrumentation               |
|-----------|--------------------------|--|--|
| <b>As</b> | Standard Addition        | 1. Undiluted<br>2. Undiluted                     | ICP-MS-MS<br>ICP-CC-QMS                  |
| <b>Cd</b> | Isotope Dilution         | 1. Co-precipitation<br>2. Undiluted              | ICP-SFMS (LR)<br>ICP-QMS                 |
| <b>Co</b> | Standard Addition        | 1. 1/10 dilution<br>2. Undiluted                 | ICP-SFMS (MR)<br>ICP-CC-QMS              |
| <b>Cr</b> | Isotope Dilution         | 1. Co-precipitation<br>2. Undiluted              | ICP-SFMS (MR)<br>ICP-CC-QMS              |
| <b>Cu</b> | Isotope Dilution         | 1. Co-precipitation<br>2. Undiluted              | ICP-SFMS (MR)<br>ICP-CC-QMS              |
| <b>Fe</b> | Isotope Dilution         | 1. Co-precipitation                              | ICP-SFMS (MR)                            |
| <b>Hg</b> | Isotope Dilution         | 1. 1/10 dilution<br>2. Undiluted                 | ICP-SFMS (LR)<br>ICP-QMS                 |
| <b>Mn</b> | Standard Addition        | 1. 1/10 dilution<br>2. Undiluted<br>3. Undiluted | ICP-SFMS (MR)<br>ICP-CC-QMS<br>ICP-MS-MS |
| <b>Ni</b> | Isotope Dilution         | 1. Undiluted                                     | ICP-CC-QMS                               |
| <b>Pb</b> | Isotope Dilution         | 1. Co-precipitation<br>2. Undiluted              | ICP-SFMS (LR)<br>ICP-QMS                 |
| <b>Se</b> | Isotope Dilution         | 1. Undiluted<br>2. Undiluted                     | ICP-RC-QMS<br>ICP-MS-MS                  |
| <b>V</b>  | Standard Addition        | 1. 1/10 dilution<br>2. Undiluted<br>3. Undiluted | ICP-SFMS (MR)<br>ICP-CC-QMS<br>ICP-MS-MS |

**Isotope Dilution**— Double isotope dilution quantification using a mixed isotopic spike solution. Ratio-matching was used to minimise systematic errors in isotope ratio measurements. Bracketing was used during instrumental measurement to account for instrument drift.

**Standard Addition**— Standard addition optimised for reference measurements using a mixed standard solution. An addition factor of 10 or greater was used to minimise error propagation from precision of isotope signal measurements. Bracketing was used during instrumental measurement to account for instrument drift.

**Undiluted**— Sea water samples were analysed undiluted where ICP-MS instrumentation has inline dilution for high matrix samples.

**1/10 dilution**— Sea water samples were diluted 1/10 before ICP-MS measurements.

**Co-precipitation**— 20 g sea water was prepared for isotope dilution analysis. Aqueous NH<sub>4</sub>OH (0.5 mL, 20% w/w) was added and mixed thoroughly then aqueous TMAH (1.8 mL, 25% w/w) was added and left to stand for 90 seconds as Mg(OH)<sub>2</sub> precipitated. The mixture was then shaken and left for another 3 min to aid further precipitate formation. The mixture was centrifuged at 3,000 rpm for 3 min. The supernatant (containing the major sea water matrix components) was decanted. The precipitate (containing Mg(OH)<sub>2</sub> and co-precipitated trace elements) was then redissolved in 0.8 M HNO<sub>3</sub> (5 mL) and analysed by ICP-MS. Co-precipitation was only used in conjunction with isotope dilution so method accuracy was unaffected by absolute recovery.

**ICP-SFMS**— Inductively coupled plasma sector field mass spectrometer operated with low mass resolution (LR), medium mass resolution (MR) or high mass resolution (HR).

**ICP-(C/RC)-QMS**— Inductively coupled plasma quadrupole mass spectrometer (with in-line dilution for high matrix samples). The collision/reaction cell (C/RC) was operated in collision mode (with He gas), reaction mode (with H<sub>2</sub> gas) or standard mode (no gas in the cell).

**ICP-MS-MS**— Inductively coupled plasma tandem mass spectrometer (with collision/reaction cell). The cell was operated in reaction mode pressurised with NH<sub>3</sub> (Mn, V) or O<sub>2</sub> (As, Se).

### (viii) Homogeneity assessment

The homogeneity of NMIA MX014 was assessed according to the procedure outlined in ISO Guide 35 *Reference materials – General and statistical principles for certification*. Twenty-four units of NMIA MX014 were randomly selected and analysed in duplicate, quantifying a representative set of trace elements. Isotope dilution was used for all homogeneity assessment measurements. Single factor analysis of variance was used to estimate the component of measurement uncertainty of certified values attributable to analyte inhomogeneity.

### (ix) Stability assessment

A short-term isochronous stability trial demonstrated stability of NMIA MX014 under extremes of conditions that may be encountered during transport and delivery. The stability of NMIA MX014 for the period of validity of the certificate was demonstrated in a long-term stability trial. Particular attention was paid to mercury which was shown to be stable in two similar acidified sea water samples for 54 months. The degree of water transpiration from the CRM under recommended storage conditions has been assessed and included in the measurement uncertainty of certified values.

### (x) Measurement uncertainty

Measurement uncertainty was calculated according to the equation

$$U = k\sqrt{u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{stab}}^2}$$

$U$  = expanded uncertainty of the certified value

$k$  = coverage factor for 95% level of confidence

$u_{\text{char}}$  = standard uncertainty associated with characterisation of the certified value

$u_{\text{hom}}$  = standard uncertainty associated with between bottle homogeneity

$u_{\text{stab}}$  = standard uncertainty associated with stability

All factors that could reasonably be expected to affect the measurement result were identified and the standard uncertainty of each was estimated from experimental data. The measurement uncertainty contributors examined were the calibration standards, gravimetric preparation, isotopic composition, isotope ratio measurement, method precision, method bias, between-bottle homogeneity, short-term stability and long-term stability. Standard uncertainty estimates were combined and expanded to a 95% level of confidence using coverage factors ( $k$ ) calculated from the effective degrees of freedom ( $\nu_{\text{eff}}$ ).

#### Coverage factors and effective degrees of freedom for NMIA MX014.

|           | Mass fraction |                    | Mass concentration |                    |
|-----------|---------------|--------------------|--------------------|--------------------|
|           | $k$           | $\nu_{\text{eff}}$ | $k$                | $\nu_{\text{eff}}$ |
| <b>As</b> | 2.04          | 33                 | 2.04               | 33                 |
| <b>Cd</b> | 2.00          | 61                 | 2.00               | 62                 |
| <b>Co</b> | 1.99          | 80                 | 1.99               | 81                 |
| <b>Cr</b> | 2.02          | 45                 | 2.01               | 45                 |
| <b>Cu</b> | 2.09          | 21                 | 2.09               | 21                 |
| <b>Fe</b> | 1.99          | 79                 | 1.99               | 81                 |
| <b>Hg</b> | 1.98          | 97                 | 1.98               | 98                 |
| <b>Mn</b> | 2.06          | 26                 | 2.06               | 26                 |
| <b>Ni</b> | 1.99          | 73                 | 1.99               | 74                 |
| <b>Pb</b> | 2.02          | 43                 | 2.02               | 44                 |
| <b>Se</b> | 2.02          | 41                 | 2.02               | 41                 |
| <b>V</b>  | 1.99          | 70                 | 1.99               | 70                 |

### **(xi) Metrological traceability**

NMIA MX014 certified values are metrologically traceable to the SI unit for mass (kilogram) through the Australian standards for mass. Gravimetric preparation is traceable to the SI kilogram through calibrated analytical balances. Elemental quantification was calibrated by isotope dilution mass spectrometry and standard addition mass spectrometry and is traceable to SI units through single element calibration solutions certified by the National Institute of Standards and Technology (USA). Density measurement was calibrated with ultra-high purity water and is traceable to published data for the density of water.

### **(xii) Legal notice**

Neither NMI nor any person acting on NMI's behalf assumes any liability with respect to the use of, or for damages resulting from the use of, this reference material or the information contained in this certificate.

Authorised by:



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Certified property values in this report supersede those in reports issued prior to 6 March 2018.