National Institute of Standards & Technology

Report of Investigation

Reference Materials 8549, 8558, 8568 and 8569

Nitrogen and Oxygen Isotopes in Nitrate

These Reference Materials (RMs) are intended for use in developing and validating methods for measuring relative differences in nitrogen (N) and oxygen (O) isotope-amount ratios in nitrate. While the values for these RMs are not certified, their widespread use permits comparability of data from different laboratories. Equivalent names used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS) for these RMs are listed in column 2 of Table 1. RM 8549 is supplied in plastic vials containing approximately 0.4 g of KNO_3 salt. RMs 8558 and 8568 are supplied in glass bottles containing approximately 0.9 g of KNO_3 while RM 8569 is supplied in glass bottles containing approximately 0.9 g of $NaNO_3$.

Table 1. Reference values for the relative N and O isotope-amount ratios of the nitrate RMs

RM Number	Name	$\delta^{15}N_{AIR} \times 10^3$	$U^{(b)} \times 10^3$	$\delta^{18}O_{VSMOW} \times 10^3$	$U^{(c)} \times 10^3$	$\Delta^{17}O_{VSMOW} \times 10^3$	$U^{(d)} \times 10^3$	Data Sources
RM 8549	IAEA-NO-3[(a)]	+4.7	± 0.3	+25.6	± 0.4	–0.2	± 0.2	[1–3]
RM 8558	USGS32	+180	Exact	+25.7	± 0.4	n.d.[e]	n.d.[(e)]	[1,2,4]
RM 8568	USGS34	–1.8	± 0.2	–27.9	± 0.6	–0.1	± 0.2	[2]
RM 8569	USGS35	+2.7	± 0.2	+57.5	± 0.4	+21.6	± 0.2	[2,3]

(a) IAEA-NO-3 is also known as IAEA-N3.
(b) Uncertainties for $\delta^{15}N$ are two times the standard uncertainty of reported values from an inter-laboratory comparison test [1], or reported values from a single study [2], after normalization to +0.43 ‰ for RM 8547 (IAEA-N1) and +180 ‰ for RM 8558.
(c) Uncertainties for $\delta^{18}O$ are two times the standard uncertainty of reported values from a single study [2], after normalization to 0 ‰ for VSMOW and –55.5 ‰ for SLAP.
(d) Uncertainties for $\Delta^{17}O$ are two times the standard uncertainty of reported values from a single study [2].
(e) n.d. no data.

Expiration Date of Reference Materials: The nitrate isotopic RMs are stable and can be used indefinitely if handled properly and not contaminated (see "Instructions for Use"). The recommended relative isotope-amount ratios given in this Report may change after further evaluation. Users should contact NIST or IAEA for updates to this report.

Maintenance of this Report: NIST will monitor these RMs. If substantive technical changes occur that affect the value assignments, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

This Report of Investigation was prepared by J.K. Böhlke, T.B. Coplen and R.D. Vocke, Jr.

Technical aspects of the preparation, analysis, and distribution of these RMs were coordinated through the USGS National Research Program in Water Resources by J.K. Böhlke and T.B. Coplen and through the NIST Analytical Chemistry Division by R.D. Vocke, Jr.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

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See Report Revision History on Last Page

Recommended values are given in Table 1 for relative N and O isotope-amount ratios. Nitrogen isotope-amount ratios [$n(^{15}N)/n(^{14}N)$] are reported as $\delta^{15}N$ values:

$$\delta^{15}N = ([n_{sample}(^{15}N)/n_{sample}(^{14}N)] - [n_{AIR}(^{15}N)/n_{AIR}(^{14}N)])/[n_{AIR}(^{15}N)/n_{AIR}(^{14}N)]$$

where AIR refers to tropospheric N_2, for which $n_{AIR}(^{15}N)/n_{AIR}(^{14}N) = 0.003677$ [5–7].

The reported $\delta^{15}N$ results for nitrate samples have been normalized to yield a value of +180 ‰ for RM 8558 [1]. Oxygen isotope-amount ratios [$n(^{18}O)/n(^{16}O)$] are reported as $\delta^{18}O$ values:

$$\delta^{18}O = ([n_{sample}(^{18}O)/n_{sample}(^{16}O)]/[n_{VSMOW}(^{18}O)/n_{VSMOW}(^{16}O)]) - 1$$

where VSMOW refers to Vienna Standard Mean Ocean Water (RM 8535), for which $n_{VSMOW}(^{18}O)/n_{VSMOW}(^{16}O) = 0.0020052$ [8].

Similarly, oxygen isotope-amount ratios [$n(^{17}O)/n(^{16}O)$] are reported as $\delta^{17}O$ values:

$$\delta^{17}O = ([n_{sample}(^{17}O)/n_{sample}(^{16}O)] - [n_{VSMOW}(^{17}O)/n_{VSMOW}(^{16}O)])/ [n_{VSMOW}(^{17}O)/n_{VSMOW}(^{16}O)]$$

where $n_{VSMOW}(^{17}O)/n_{VSMOW}(^{16}O) = 0.0003799$ [9].

By convention, the $\delta^{18}O$ scale is normalized to yield a value of –55.5 ‰ for Standard Light Antarctic Precipitation (SLAP, RM 8537) [10,11]. For RM 8549, RM 8558, RM 8568, and most other terrestrial nitrate samples, major variations in $\delta^{18}O$ and $\delta^{17}O$ values may be expected to be related by:

$$(1 + \delta^{17}O) = (1 + \delta^{18}O)^{\lambda}$$

where λ is an isotopic-mass-dependent coefficient having a value between 0.51 and 0.53.

For atmospherically derived nitrate samples (including RM 8569), $\delta^{18}O$ and $\delta^{17}O$ values deviate markedly from this relation. Deviations from mass dependent O isotope-amount-ratio variations have been described in different ways, depending on the variability and use of the data [3,12,13]. Approximate values of $\delta^{17}O$ for the RMs can be calculated from the independent measurements of $\delta^{18}O$ [2] and $\Delta^{17}O$ [3] given in Table 1, with the following equation [3]:

$$\Delta^{17}O = [\delta^{17}O - 0.52 \times \delta^{18}O]$$

The recommended values and uncertainties given in Table 1 are subject to revision as unknown sources of error may result in revised values that are not included within the stated uncertainties

INSTRUCTIONS FOR USE

Storage and Handling: Nitrate salts should be kept in a dry environment, as they will attract water when exposed to air. These RMs should be dried in a low-temperature oven or under vacuum before being weighed for analysis. There is no exchange of oxygen in nitrate with oxygen in water except in strong acid conditions, so wetting and drying these RMs should not affect their isotopic compositions unless other contaminants are present. The Material Safety Data Sheets (MSDS) that accompany these RMs provide additional information about handling nitrate salts.

Use: Because the supplies of these RMs are limited, it is recommended that they be used to calibrate or check working laboratory standards that are used routinely. Working laboratory standards with a range of N and O isotope-ratios can be produced by the methods described by J.K. Böhlke, C. Gwinn, and T.B. Coplen [14] and J.K. Böhlke, S.J. Mroczkowski, and T.B. Coplen [2].

Normalization of Data: $\delta^{15}N$, $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ results for nitrate samples can be normalized by analyzing reference materials with $\delta^{15}N$, $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ values that bracket those of the samples. Generalized equations for normalization are given in several publications [10,15] and a database program for assisting with normalization is available [16]. ***Because the values for these reference materials are subject to change, users are advised to report measured or assumed values for the normalizing reference materials when reporting isotope data for samples.***

PREPARATION AND ANALYSIS OF REFERENCE MATERIALS

Preparation: RM 8549 was prepared by A. Mariotti from KNO_3 having normal terrestrial isotope-amount ratios [17]. RM 8558 was prepared by J.K. Böhlke, C. Gwinn, and T.B. Coplen by dissolving and recrystallizing a mixture of normal and ^{15}N-enriched KNO_3 [14]. RM 8568 and RM 8569 were prepared by J.K. Böhlke, S.J. Mroczkowski, and T.B. Coplen [2]. RM 8568 was prepared by equilibrating nitric acid with ^{18}O-depleted meteoric water, and neutralizing the mixture with KOH. RM 8569 was purified from the natural nitrate ore deposits of the Atacama Desert in Chile.

Analytical Methods: $\boldsymbol{\delta^{15}}$**N -** The reference values for δ^{15}N of RM 8549 and RM 8558 were derived from results of an interlaboratory comparison test after elimination of outliers [1]. The δ^{15}N values were measured by mass spectrometry on N_2 gas that was produced from the nitrate by a variety of methods in the different laboratories. The assigned reference value of +180 ‰ for RM 8558 was selected from a slightly skewed distribution of data around a mean value of +179.2 ‰ with a standard deviation of 1.3 ‰ (n = 11), based on the assumption that relatively low values were caused by lack of correction for contamination by air or other contaminants [1]. The reference value is supported by subsequent measurements in two laboratories using both continuous flow and dual-inlet mass spectrometry on N_2 produced by high-temperature reduction of nitrate with Cu [4], yielding a mean value of +180.1 ‰ with a standard deviation of 0.3 ‰ (n = 5). It is also supported by an earlier measurement of +180.0 ‰ with a standard deviation of 0.2 ‰ (n = 6) [14]. These supporting values were calculated by assuming a value of +0.43 ‰ for RM 8547.

The reference values for δ^{15}N of RM 8568 and RM 8569 were determined by dual-inlet mass spectrometry on N_2 gas that was produced from nitrate by off-line reduction with Cu at 850 °C [2]. These measurements were normalized to the recommended values of RM 8549 and RM 8558, which were analyzed by the same technique.

$\boldsymbol{\delta^{18}}$**O,** $\boldsymbol{\Delta^{17}}$**O** - The reference values for δ^{18}O of the nitrate RMs were determined by continuous flow mass spectrometry on CO gas that was produced from nitrate by on-line reaction with carbon at 1325 °C [2]. These measurements were normalized to the VSMOW-SLAP δ^{18}O scale by analyzing water samples with $\delta^{18}O_{VSMOW}$ values of -1.5 ‰ and -51.3 ‰ with the nitrate RMs by the same technique. The Δ^{17}O values were determined by dual-inlet mass spectrometry on O_2 gas that was produced by off-line decomposition of nitrate at 520 °C [3]. Thermal decomposition of nitrate produces NO_2 in addition to O_2. Because of isotopic fractionation between NO_2 and O_2, the measured δ^{18}O values of the O_2 are not equal to the nitrate δ^{18}O values; however, the Δ^{17}O values of the O_2 were assumed to be unaffected by mass-dependent fractionation and thus equal to the nitrate values. Users are advised that the definition of Δ^{17}O may differ among laboratories [3,12,13].

Isotopic Homogeneity: There is no documented evidence for isotopic heterogeneity in the distributed supplies of these reference materials. Aliquots of RM 8558 containing 20 micromole of nitrate were reported to yield reproducible δ^{15}N results with a standard deviation of 0.16 ‰ (n = 15) [14]. Aliquots of RM 8568 and RM 8569 containing 2.5 micromole of nitrate were reported to yield reproducible δ^{18}O results with a standard deviation of 0.11 ‰ (n = 25) and 0.14 ‰ (n = 24, 1 outlier), respectively [2].

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Users of these RMs should ensure that the Report in their possession is current. This can be accomplished by contacting the SRM Program at telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.