

# Automated methods for analysis of $\Delta^{17}\text{O}$ of nitrate and sulfate at $\mu\text{mole}$ and sub- $\mu\text{mole}$ levels

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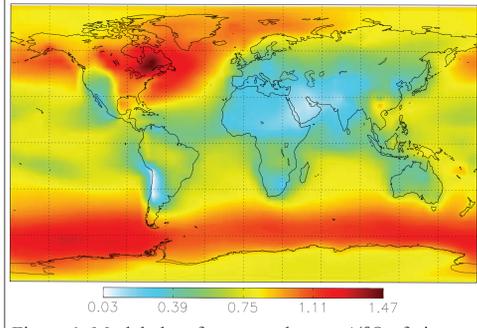
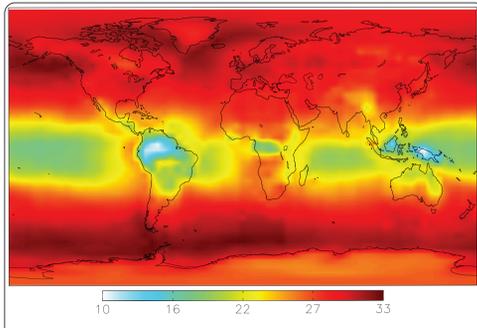


Figure 1. Modeled surface annual mean  $\Delta^{17}\text{O}$  of nitrate (top panel) and sulfate (bottom panel).

## Flow chart of method

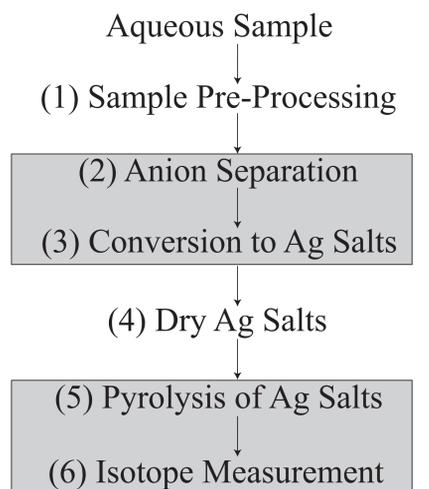


Figure 2. (1) Aqueous samples may need to have organic contaminants removed (Table 1). (2) Nitrate and sulfate are separated with an ion chromatograph. (3) Silver nitrate and sulfate are created with a cation exchange column. A fraction collector places the silver salts in respective vessels. (4) Silver sulfate salts are loaded into quartz and silver nitrate samples in silver capsules, freeze-dried, and (5) placed into an autosampler for pyrolysis. (6) Purified oxygen is carried through a gas chromatography column and an interface to an isotope ratio mass spectrometer. The automated steps are shaded.

## Acknowledgements

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## Abstract

The measurement of the triple oxygen isotope composition ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ , where  $\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of nitrate and sulfate in aerosol, rain, and snow samples provides a new means of elucidating the importance of various oxidation pathways in atmospheric nitrate and sulfate formation. We describe the development of automated methods for the analysis of  $\Delta^{17}\text{O}$  of nitrate and sulfate at  $\mu\text{mole}$  and sub- $\mu\text{mole}$  levels, using pyrolysis of silver salts ( $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$ ) in a continuous flow isotope ratio mass spectrometer system. We also present quantitative results of several methods for removal of sample organics, which can otherwise interfere with liberation of  $\text{O}_2$  by pyrolysis. Separation of aqueous sample anions and conversion to  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  are automated using an ion chromatograph interfaced with a cation exchange column and fraction collector. Pyrolysis of  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  and isotopic analysis of the evolved  $\text{O}_2$  are automated using a temperature conversion / elemental analyzer (TCEA), 5A molecular sieve packed gas chromatography column, a Conflo open-split interface, and an isotope ratio mass spectrometer (MAT253) with helium as the carrier gas. For  $\mu\text{mole}$  sample sizes, this method provides precision (1 $\sigma$ ) better than  $\pm 0.4\%$  for nitrate and  $\pm 0.3\%$  for sulfate, based on repeated analyses of the international reference standard USGS-35 ( $\text{NaNO}_3$ ,  $\Delta^{17}\text{O} = 21.6\%$ ) and inter-lab calibration standards (UCSD Standard #8, #9,  $\text{Na}_2\text{SO}_4$ ,  $\Delta^{17}\text{O} = 1.3\%$ ,  $2.4\%$ , respectively). For sub- $\mu\text{mole}$  sample sizes (50 nmol – 1  $\mu\text{mol}$ ), we use the TCEA coupled to a Gas Bench with 5A molecular sieve cryofocusing traps followed by a 5A molecular sieve capillary column. Samples smaller than 1  $\mu\text{mole}$  are influenced by (1) non-sample  $\text{O}_2$ , with  $\Delta^{17}\text{O} = 0\%$ , generated from  $\text{Ag}_2\text{O}$  produced during drying of  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  salts and (2) absorption of as much as 15 nmoles of  $\text{O}_2$  by Ag in the TCEA. Both of these processes affecting sub- $\mu\text{mole}$  samples necessitate further characterization. Automation of methods for analysis of  $\Delta^{17}\text{O}$  of nitrate and sulfate and reduction of sample sizes will enable critical improvements in atmospheric and ice core sampling.

## Ion chromatography system

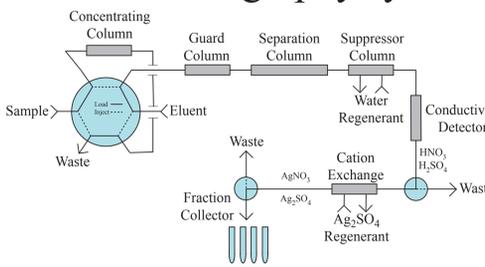


Figure 3. Silver nitrate and sulfate salts are created from aqueous samples using an ion chromatograph, cation exchange, fraction collector system. We use a Dionex ion chromatograph with an IonPac® AG15 column (4 x 50 mm) for anion preconcentration, IonPac® AG19 guard column (4 x 50 mm), IonPac® AS19 separation column (4 x 250 mm), ASRS-Ultra II suppressor (4 mm), and Dionex conductivity detector. The aqueous sample (<50 mL) is pumped through a six-way valve, retaining and concentrating sample anions on the Concentrating Column. Anions are then eluted and pass through guard and separation columns, the suppressor, and the conductivity detector. Anions elute from the suppressor in acid form, with chloride eluting first, followed by nitrate, then sulfate. The first anions to elute (organic compounds and chloride) flow to waste. Detection of the chloride peak end then triggers a pneumatic three-way valve to switch the eluent flow in-line with a Dionex AMMS 300 (4 mm) cation exchange column and Teledyne ISCO Foxy Jr. fraction collector. The remaining acidified nitrate ( $\text{HNO}_3$ ) and sulfate ( $\text{H}_2\text{SO}_4$ ) fractions are converted to  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  by cation exchange with  $\text{Ag}_2\text{SO}_4$  regenerant. The fraction collector begins collection of  $\text{AgNO}_3$  or  $\text{Ag}_2\text{SO}_4$  when the conductivity detector triggers a peak start and ends collection one minute after peak end detection. Samples containing 1  $\mu\text{mol}$  each of nitrate and sulfate generally yield 5-10 ml for each anion fraction, which is collected in 13 x 100 mm test tubes.

## Large Sample Results

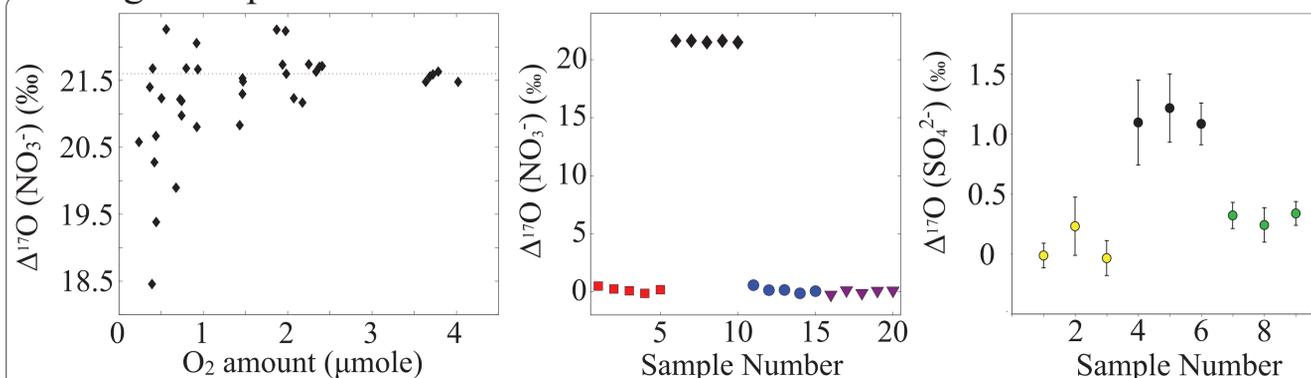


Figure 6. The left panel is  $\Delta^{17}\text{O}$  of USGS35 nitrate versus amount of  $\text{O}_2$ . The accepted  $\Delta^{17}\text{O}$  value of USGS35 is shown as a dotted line. The middle panel is  $\Delta^{17}\text{O}$  of nitrate (5  $\mu\text{mole}$   $\text{O}_2$ ) from an in house nitrate standard (■), USGS35 (◆), IAEA-N3 (●), and USGS34 (▼). The right panel is the  $\Delta^{17}\text{O}$  of sulfate (mean of a 3  $\mu\text{mole}$  run and 5  $\mu\text{mole}$  run) from an in house sulfate standard (○), UCSD Std#8 (●), and another in house sulfate standard (●). Samples presented in the bottom two panels were analyzed in the order presented, showing no memory effect. Data from all panels were generated using flow path (A) (Figure 4).

## Continuous flow system

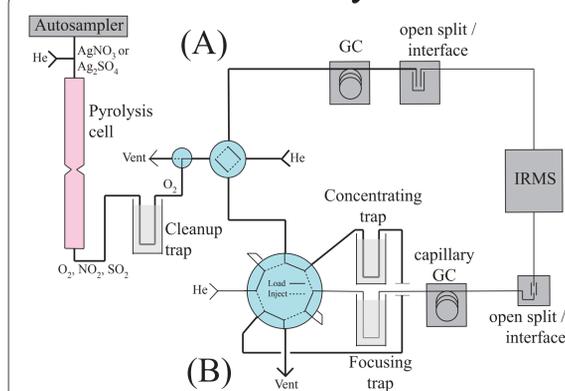


Figure 4. Two distinct flow paths are used to allow for larger (A) (1-10  $\mu\text{mole}$   $\text{O}_2$ ) and smaller (B) (0.01-1  $\mu\text{mole}$ ) samples. For all sample sizes, the Finnigan Temperature Conversion Elemental Analyzer (TCEA) autosampler (Costech Zero blank) introduces sample capsules into an empty modified quartz pyrolysis tube heated to 550°C for nitrate or 1100°C for sulfate. A 1/16" OD stainless steel tube immersed in liquid nitrogen (Cleanup Trap) removes pyrolysis byproducts other than  $\text{O}_2$  (e.g.  $\text{NO}_2$ ,  $\text{SO}_2$ ).

For large samples,  $\text{O}_2$  is carried to a packed 5A molecular sieve gas chromatography column (GC) at 90°C, through the open split of a Finnigan Conflo III interface, and into a MAT 253 Isotope Ratio Mass Spectrometer (IRMS) for isotope analysis (masses (m/z) 32, 33, and 34 and employ resistors of  $10^9$ ,  $10^{12}$ , and  $10^{11}$   $\Omega$ ). The sample oxygen peak is detected 100 seconds after sample pyrolysis (Figure 5).

For small samples,  $\text{O}_2$  is concentrated with a Gas Bench II by freezing on 5A molecular sieve in 1/16" OD tubing immersed in liquid nitrogen (Concentrating Trap).  $\text{O}_2$  is then transferred to a capillary molecular sieve-filled trap that has been lowered into liquid nitrogen (Cryofocusing Trap) prior to thawing the Concentrating Trap. The Cryofocusing Trap is thawed and the released  $\text{O}_2$  continues to a capillary GC at 90°C, then through the open split, and to the IRMS for isotope analysis. The sample oxygen peak is detected 800 seconds after sample pyrolysis (Figure 5).

## Organic removal

Table 1. Resulting percent reduction in the measured total organic carbon (TOC) of a rainwater sample using four different materials. IC-RP is a polystyrene matrix cartridge; PVP is Polyvinylpyrrolidone; C-18 is a carbon coated silicate commonly used in purification;  $\text{H}_2\text{O}_2$  has to potential to oxidize any organic compound to  $\text{CO}_2$ . For details see Allman (2009).

Method Tested	TOC Reduction (%)
IC-RP	18
PVP	23
C-18	35
PVP / C-18	48
$\text{H}_2\text{O}_2$	72

## IRMS chromatograms

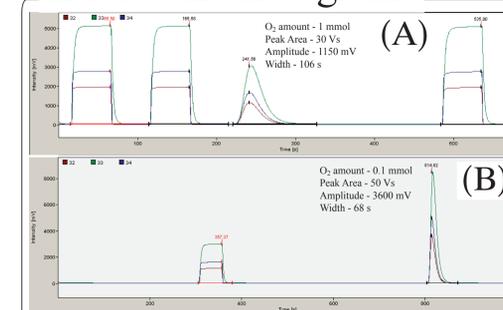


Figure 5. A 1  $\mu\text{mole}$   $\text{O}_2$  sample via the large sample flow path (top panel) and a 0.1  $\mu\text{mole}$   $\text{O}_2$  sample via the small sample flow path (bottom panel) (see Figure 4 for flow paths). Note the 0.1  $\mu\text{mole}$  sample has almost twice the peak area and half the peak width relative to the 1  $\mu\text{mole}$  sample.



Figure 7. Measurements of  $\Delta^{17}\text{O}$  in nitrate and sulfate of polar ice cores provide historical estimates of atmospheric oxidant concentrations.

## Summary

The recent development of techniques to measure the triple isotope composition of oxygen ( $\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) in nitrate and sulfate has provided a new tool for investigating atmospheric oxidation chemistry and global geochemical cycling of nitrogen and sulfur (Michalski, 2002; Savarino, 2001). Measurements of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in atmospheric aerosol and precipitation samples have been employed to investigate the role of different oxidants during modern atmospheric processes, such as polar  $\text{O}_3$  depletion events, as well as during paleoclimate changes, such as glacial-interglacial changes recorded in polar ice cores (Figures 1 and 7). Automating methods and reducing sample size requirements is critical for streamlining time-consuming sample processing and enabling improved temporal resolution for ice core measurements.

We present an automated method for the analysis of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  by pyrolysis of silver salts ( $\text{AgNO}_3$  or  $\text{Ag}_2\text{SO}_4$ ). We use an automated ion chromatography system (Figure 3) for preparation of  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  with greater than 90% yields, and an automated continuous flow TCEA-IRMS system to pyrolyze silver nitrate and sulfate salts and subsequent  $\text{O}_2$  isotope analysis (Figure 4). Our measurements of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of the international standard USGS35 using the large sample TCEA-IRMS method agree well (within 0.1‰) with accepted values (Bohlke et al., 2003; Michalski, 2002) for sample sizes as little as 1  $\mu\text{mol}$   $\text{O}_2$  (Figure 6). Our  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  measurements with an inter-laboratory calibration standard, UCSD Std#8, agree well with those made using other published methods (Savarino et al., 2001) for sample sizes as little as 1  $\mu\text{mol}$   $\text{O}_2$  (Figure 6). We find a precision (1  $\sigma$ ) of  $\pm 0.4\%$  for  $\Delta^{17}\text{O}(\text{NO}_3^-)$  analysis and  $\pm 0.3\%$  for  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  analysis using the TCEA-IRMS method for  $\mu\text{mole}$ -level samples. Memory effects of the TCEA-IRMS system are expected to be within analytical uncertainty for most measurement campaigns.

We have been developing an automated method for analysis of small samples (0.01 to 1  $\mu\text{mol}$   $\text{O}_2$ ) of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  using the TCEA-IRMS with a cryofocusing interface. This development has proven difficult due to the presence of (1) non-sample  $\text{O}_2$  leaking into the carrier or originating from  $\text{Ag}_2\text{O}$  generated during freeze-drying, (2) loss of as much as 0.015  $\mu\text{mole}$   $\text{O}_2$  by Ag absorption immediately downstream of the pyrolysis hot zone, and perhaps (3) a memory effect. The TCEA is not designed to be cryofocused on, and thus we have made progress by adding a 5A molecular sieve liquid nitrogen trap immediately upstream of the pyrolysis column, using thicker o-rings within the autosampler, and using a teflon ferrule set to seal the base of the pyrolysis column. We are currently testing alternative freeze-drying methods to prevent the formation of  $\text{Ag}_2\text{O}$ .

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