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# TECHNICAL NOTES

## Gas Chromatographic Separation of Carbon Dioxide and Nitrous Oxide for Stable Isotopic Analysis of Carbon Dioxide

Kinga Revesz\* and Tyler B. Coplen

U.S. Geological Survey, 431 National Center, Reston, Virginia 22092

### INTRODUCTION

Analysis of atmospheric and unsaturated-zone  $\text{CO}_2$  for oxygen and carbon isotopic content is important for numerous environmental studies. Typically  $\text{CO}_2$  is separated from the atmospheric sample by trapping at  $-196^\circ\text{C}$ . The vapor pressure versus temperature characteristics of  $\text{N}_2\text{O}$  are very similar to those of  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  is collected along with the  $\text{CO}_2$ . Because the two gases have an identical molecular mass of 44, the presence of  $\text{N}_2\text{O}$  causes a discrepancy between the measured and true 45/44 and 46/44 ratios in the  $m/e$  spectrum of  $\text{CO}_2$ . Because direct analytical separation of  $\text{N}_2\text{O}$  from  $\text{CO}_2$  is very difficult, as  $\text{N}_2\text{O}$  is isosteric with  $\text{CO}_2$  and has almost identical physical properties, correction factors are commonly applied to neutralize the effects of  $\text{N}_2\text{O}$  contamination. Craig and Keeling (1) calculated correction factors as a function of the  $\text{N}_2\text{O}/\text{CO}_2$  concentration ratio assuming equal ionization efficiencies for  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . Mook and Hoek (2) observed that molecular ion production efficiency is 23% less for  $\text{N}_2\text{O}$  than for  $\text{CO}_2$  and modified the correction factors introduced by Craig and Keeling. Later their theoretical value was supported by an experimental separation (3) in which gas was passed through copper pellets at  $650^\circ\text{C}$ . In this procedure  $\text{N}_2\text{O}$  is reduced to nitrogen so  $\text{CO}_2$  can be trapped while the nitrogen is pumped away. However, the  $\delta^{18}\text{O}$  value of the  $\text{CO}_2$  is altered by this procedure. Additionally, the ion production efficiencies of ion sources may not be the same in every mass spectrometer so that correction factors for  $\text{N}_2\text{O}$  mixtures may vary for different mass spectrometers. In our laboratory, for example, a sample with  $\text{N}_2\text{O}$  concentration of 0.1% gave  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values differing by 0.2–0.4‰ in different mass spectrometers. Carbon and oxygen isotope results are expressed in per mill (‰) relative to VPDB and VSMOW, respectively (4). One sigma standard deviations are 0.09‰ and 0.05‰ for oxygen and carbon isotope ratio analysis, respectively.

The  $\text{N}_2\text{O}$  correction factor depends upon the  $\text{N}_2\text{O}/\text{CO}_2$  ratio. Tropospheric  $\text{N}_2\text{O}$  concentration is increasing at  $\sim 0.2\%$  per year (5, 6) and  $\text{N}_2\text{O}$  concentration is higher in the northern than in the southern hemisphere. Considering the fact that the  $\text{CO}_2$  concentration is also increasing due to anthropogenic activities, it is inappropriate to assume a constant  $\text{N}_2\text{O}/\text{CO}_2$  ratio in atmospheric  $\text{CO}_2$  samples. In unsaturated-zone gases,  $\text{CO}_2$  concentrations vary by nearly an order of magnitude from 0.037% to 0.300%; therefore, application of a constant correction factor could result in large errors in isotope ratio.

In summary, a unique factor to correct carbon and oxygen isotope ratios of  $\text{CO}_2$  for  $\text{N}_2\text{O}$  content is not acceptable for most geochemical samples. These observations led us to develop a method to separate  $\text{N}_2\text{O}$  from  $\text{CO}_2$  without altering the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the  $\text{CO}_2$ . We employ gas chromatographic (GC) separation on a high-vacuum preparation line.

### EXPERIMENTAL PROCEDURE

The gas chromatograph system used for removing  $\text{N}_2\text{O}$  from

Table I. Isotope Ratio of  $\text{CO}_2$  before and after Removal of the  $\text{N}_2\text{O}$ , in per Mill

concn of $\text{N}_2\text{O}$ in $\text{CO}_2$	before $\text{N}_2\text{O}$ removal		after $\text{N}_2\text{O}$ removal	
	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$
Experiment a				
0	-45.19	+11.84		
25%	-163.23	-148.00	-45.16	+11.74
Experiment b				
0	-44.95	+12.69		
0.1%	-45.17	+12.47	-44.95	+12.60

$\text{CO}_2$ - $\text{N}_2\text{O}$  mixtures is similar to that used by Hoering and Estep (7) to clean gas mixtures prior to isotope ratio measurement. It is shown schematically in Figure 1. It has three major parts: (1) the sample-injection loop, (2) the separation column and associated thermal conductivity detector, and (3) the sample-collection loop. Helium carrier gas (25 mL/min flow rate) is employed. The sample-injection loop consists of a 30-cm length of 0.64 cm o.d. stainless steel tubing. The separation column is 0.32 cm o.d. stainless steel tubing, 4.9 m in length, filled with Chromosorb 100 80/100 mesh polymer filling. Column temperature is kept at  $40^\circ\text{C}$  throughout the entire procedure. The sample-collection loop consists of  $\sim 60$  cm of 0.64 cm o.d. stainless steel tubing. The tubing was made as a double-oval loop to avoid isotopic fractionation by aerosol formation of  $\text{CO}_2$ . By use of a carrier gas with high thermal conductivity (He), the gas temperature in the middle of the flow can reach the freezing point of the  $\text{CO}_2$ . The  $\text{CO}_2$  can solidify, not only on the wall of the tube but also at the middle of the flow, and can be carried away by the carrier gas causing isotopic fractionation. This problem can be eliminated by using either a double-oval collection loop where one part can be kept warm and the other cold so the  $\text{CO}_2$  has time to remelt and freeze back on the wall; alternatively, stainless steel wire can be put into the tube to create a large surface area.

The experimental procedure is as follows: (i) The sample-collection loop is evacuated, filled with helium, and immersed in liquid  $\text{N}_2$  until a stable base line is achieved on the gas chromatograph. During this time valve B is in such a position that He flows through the sample-collection loop before going to the waste. (ii) After a steady base line is achieved, valve B is switched so that He bypasses the sample-collection loop and goes directly to the waste. (iii) The sample-injection loop is evacuated and the sample (1 to 3  $\mu\text{mol}$ ) is frozen into the bottom of the loop. (iv) The bottom of the sample-injection loop is immersed in a preheated (to  $80^\circ\text{C}$ ) water bath and at the same time the He flow is directed through this loop by turning four-way valve A so that the  $\text{CO}_2$ - $\text{N}_2\text{O}$  sample is carried into the separation column. (v) The  $\text{CO}_2$  peak is trapped by operation of valve B. (vi) He is pumped out of the sample-collection loop while the  $\text{CO}_2$  is still frozen; the  $\text{CO}_2$  is then collected in a sample tube to be analyzed mass spectrometrically.

The apparatus and method described above are calibrated by using two mixtures of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  of known molecular and isotopic ratios. One mixture is identical with the 0.001  $\text{N}_2\text{O}/\text{CO}_2$  ratio characteristic of the earth's atmosphere. Another mixture contains  $\sim 25\%$   $\text{N}_2\text{O}$ . The gas mixture representing the atmospheric ratio is prepared with a method similar to that described by Weiss et al. (6). Two-milliliter and 2-L volumes are

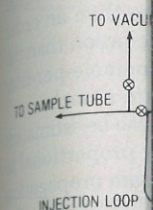


Figure 1. Gas chromatograph system. A and B are four-way valves closed during injection.

Figure 2. Gas chromatograph system. The separation column is 4.0 m, 0.32 cm o.d. at  $29^\circ\text{C}$ . Sample collection are indicated.

filled with  $\text{N}_2\text{O}$  and frozen together in liquid  $\text{N}_2$ . The sample is collected before a steady base line is achieved on the gas chromatograph by taking ten aliquots of the sample and analyzing them by mass spectrometry.

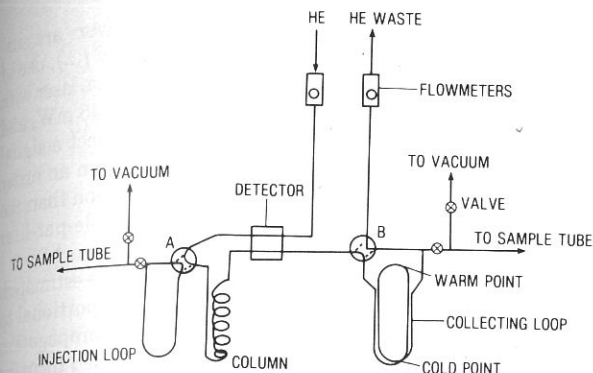
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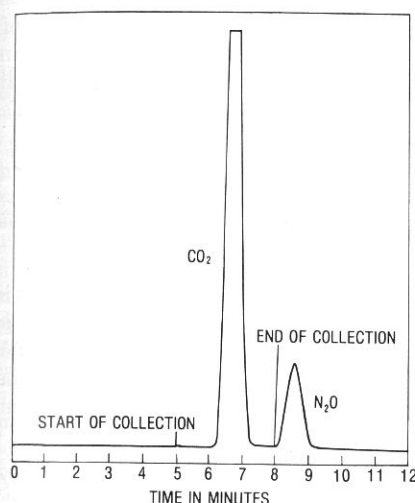
Two-photon  
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## Stable



**Figure 1.** Gas chromatograph system for CO<sub>2</sub> and N<sub>2</sub>O separation. A and B are four-way valves and ⊗ are Kontes stopcocks, which are closed during injection and collection.



**Figure 2.** Gas chromatogram of CO<sub>2</sub> and N<sub>2</sub>O mixture. Separation column is 4.0 m, 0.64 cm o.d., packed with Porapak PS and operated at 29 °C. Sample size is 15 μmol. The start and end of the CO<sub>2</sub> peak collection are indicated.

filled with  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , respectively, up to 1 atm pressure, and frozen together in the 2-L container. An aliquot of the  $\text{CO}_2$ , collected before adding  $\text{N}_2\text{O}$ , was used as a reference in the isotope-ratio measurements. The  $\text{CO}_2$ - $\text{N}_2\text{O}$  mixtures were analyzed by taking ten aliquots, five of which were introduced into the GC apparatus described above and five of which were analyzed directly by mass spectrometry. All the gases were analyzed with a Finnigan

lows: (i) The sample is placed in the sample chamber, the valve is closed, and the chamber is evacuated on the gas chromatograph pump. (ii) The sample is placed in such a position that it is directly above the loop before going to the detector. (iii) The valve is closed, valve B is switched to the sample position, the sample is moved into the loop and goes directly to the detector. (iv) The sample loop is evacuated and the valve is switched to the sample position. (v) The sample is immersed in a preheated liquid. (vi) The sample is in the same time the He flow is stopped. (vii) The four-way valve A is switched to the sample position. (viii) The sample is moved into the separation column. (ix) The valve is switched to valve B. (x) The sample is moved into the loop of valve B. (xi) The valve is switched to the sample position while the  $\text{CO}_2$  is still flowing. (xii) The sample tube to be analyzed is placed in the sample chamber.

above are calibrated by known molecular weights with the 0.001 N<sub>2</sub>O/CO<sub>2</sub> mixture. Another mixture representing the atmosphere and similar to that described by 1-L and 2-L volumes are

251 mass spectrometer using its Micro Volume Inlet System.

The results are given in Table I. Experiments a and b refer to the mixtures containing 25% and 0.1% N<sub>2</sub>O, respectively. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values after N<sub>2</sub>O removal are identical within experimental error to those of the CO<sub>2</sub> prior to addition of N<sub>2</sub>O.

The technique discussed here is limited to a maximum sample size of 3  $\mu\text{mol}$  to achieve satisfactory separations. To process samples in the range of 10–15  $\mu\text{mol}$ , we raised the capacity of the column by using a 4 m long, 0.64 cm o.d. column. This time we chose Porapak PS as a packing material and used a He flow of 30 mL/min at ambient temperature (7). We achieved separations such that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values after  $\text{N}_2\text{O}$  removal were identical within experimental error to those of the  $\text{CO}_2$  prior to addition of  $\text{N}_2\text{O}$ . A typical chromatogram of the separation is shown in Figure 2. The time between peaks ( $\text{CO}_2$  and  $\text{N}_2\text{O}$ ) and the collection time of  $\text{CO}_2$  vary, depending on the column; in this case the collection time was 3 min.

In conclusion, the gas chromatograph separation technique described above gives accurate values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of atmospheric and unsaturated-zone  $\text{CO}_2$  samples without relying on correction factors for the  $\text{N}_2\text{O}$  content. The precision of the technique is 0.09‰ and 0.05‰ for oxygen and carbon isotope ratio analysis, respectively.

## ACKNOWLEDGMENT

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## LITERATURE CITED

- (1) Craig, H.; Keeling, C. D. *Geochim. Cosmochim. Acta* **1963**, *27*, 549-551.
- (2) Mook, W. G.; Hoek, D. *Isot. Geosci.* **1983**, *1*, 237-242.
- (3) Mook, W. G.; Jongsma, J. *Tellus* **1987**, *39B*, 96-99.
- (4) Coplen, T. B. *Chem. Geol.*, (Isotope Geoscience Section) **1988**, *72*, 293-297.
- (5) Weiss, R. I. *J. Geophys. Res.* **1981**, *86*, 7185-7195.
- (6) Weiss, R. I.; Keeling, C. D.; Craig, H. *J. Geophys. Res.* **1981**, *86*, 7197-7202.
- (7) Hoering, T. C.; Estep, M. L. F. Annual Report of the Director of Geophysical Laboratory; Carnegie Institution of Washington: Washington, DC, 1980; pp 410-414.

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### Very High Detectability in Two-Photon Spectroscopy

M. J. Wirth\* and H. O. Fatunmbi

*Department of Chemistry & Biochemistry, University of Delaware, Newark, Delaware 19716*

## INTRODUCTION

Two-photon spectroscopy has been used in analytical chemistry for probing optically dense media (1), chromatographic detection (2-4), and distinguishing solutes based on their symmetry parameters (5). Symmetry parameters can be measured with very high precision (6), potentially allowing fingerprinting of solutes based on the polarization dependence of their excitation spectra. A method for reliably obtaining corrected excitation spectra has been developed (7). Two-

photon spectroscopy is suited to small-volume measurements by virtue of the need to focus the excitation laser for the nonlinear process.

Two-photon spectroscopy has had limited use in analytical spectroscopy, in part, because it is perceived as having low sensitivity. This perception has been reinforced by the fact that typical applications have used sample concentrations on the sub-millimole-per-liter scale. Sub-micromole-per-liter detection limits have been demonstrated with the use of a