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# Influence of $N_2O$ on isotope analyses in $CO_2$ and mass-spectrometric determination of $N_2O$ in air samples

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ABSTRACT

If $CO_2$ is cryogenically separated from atmospheric air for mass-spectrometric isotope analysis, the presence of $N_2O$ simultaneously condensed makes it necessary to correct the isotope results. The corrections were experimentally determined by analyzing $N_2O$–$CO_2$ gas mixtures. The results are in good agreement with those of Mook and van der Hoek. A mass-spectrometric method for determining $N_2O/CO_2$ partial pressure ratios is discussed. During our experiments, we found that $N_2O$ can be produced in a Penning cold cathode manometer.

## 1. Introduction

For the determination of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric carbon dioxide, the $CO_2$ is usually frozen out from the air sample at liquid nitrogen temperature. As pointed out originally by Craig and Keeling (1963), the mass-spectrometric results for the isotope ratios are then affected by the presence of $N_2O$ which condenses simultaneously with $CO_2$, since $N_2O$ has the same isotopic masses, 44, 45 and 46, as $CO_2$. Therefore, the mass-spectrometric results have to be corrected in order to obtain the true carbon and oxygen isotope ratios. Mook and van der Hoek (1983) determined experimentally the necessary corrections. We have repeated their measurements on an isotope mass spectrometer MAT 250 by analyzing pure $N_2O$ and $CO_2$ as well as different $N_2O$–$CO_2$ mixtures. In addition, we have developed a method for determining mass-spectrometrically the concentration of $N_2O$ in $CO_2$, which is less precise than the gas-chromatographic method used by trace gas chemists, but good enough for calculating the isotopic corrections in case the $N_2O$ concentration of a gas sample is not known. The method is based on the fact that in the ion source of a mass spectrometer, $NO^+$ fragments of mass 30 are produced, so that the abundance of mass 30 can be used as a measure of the $N_2O$ partial pressure. $N_2O$ measurements based on the same principle were carried out also by Moore (1974) and by Mook and Jongsma (1987).

## 2. Isotope measurements of $N_2O$

For determining $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in $CO_2$, the mass ratios 45/44 and 46/44 are measured. The same masses also occur for $N_2O$, namely 44: $^{14}N_2{}^{16}O$, 45: $^{15}N^{14}N^{16}O$ and $^{14}N_2{}^{17}O$, 46: $^{15}N_2{}^{16}O$, $^{14}N^{15}N^{17}O$ and $^{14}N_2{}^{18}O$. It is practical to define apparent $\delta^{45}$ and $\delta^{46}$ values of $N_2O$, referring to standard $CO_2$. These can be measured for instance by introducing pure $N_2O$ at the sample side and standard $CO_2$ at the standard side of the double inlet system of the mass spectrometer. We can then define

$$^{45}\delta_n \equiv {}^{45}\delta(N_2O \text{ against } CO_2) = \frac{{}^{45}R_n - {}^{45}R_c}{{}^{45}R_c} = \frac{{}^{45}R_n}{{}^{45}R_c} - 1, \quad (1)$$

where $^{45}R$, $^{46}R$ = mass ratios 45/44 and 46/44 in $N_2O$ (index n) and $CO_2$ (index c).

If $N_2O$ and $CO_2$ are measured *with equal mass 44 voltage*, we can write:

$$^{45}\delta_n = \frac{2\,^{15}R_n + {}^{17}R_n}{{}^{13}R_c + 2\,^{17}R_c} - 1 = -337‰, \quad (2a)$$

$$^{46}\delta_n = \frac{(^{15}R_n)^2 + 2\,^{15}R_n\,{}^{17}R_n + {}^{18}R_n}{2\,^{13}R_c\,{}^{17}R_c + 2\,^{18}R_c + (^{17}R_c)^2} - 1$$

$$= -483‰, \quad (2b)$$

where $^{13}R$, $^{15}R$, $^{17}R$, $^{18}R$ = isotope ratios $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{17}O/^{16}O$, $^{18}O/^{16}O$ in $N_2O$ or $CO_2$. The numerical values have been obtained using the isotope ratios given by Mook and Grootes (1973), $^{15}R_n = 0.003663$, $^{17}R_n = 0.000387$ and $^{18}R_n = 0.002079$ for $N_2O$, and $^{13}R_c = 0.010868$, $^{17}R_c = 0.000382$ and $^{18}R_c = 0.002021$ for our standard $CO_2$, using the appropriate $\delta$ values versus PDB. Because the actual isotopic composition of $N_2O$ is not known, the numerical values in eq. (2) are uncertain to a few percent. By measuring pure $N_2O$ against pure $CO_2$, we have obtained experimentally $^{45}\delta_n = -349‰$ and $^{46}\delta_n = -487‰$, which agrees well with the above values derived theoretically for some average elemental isotope ratios.

The ratio of mass 44 ion yields of $N_2O$ and $CO_2$ at equal pressures in the analyzer, $E$ (termed "ionization efficiency ratio" by Mook and van der Hoek (1983)), is given by:

$$E = \frac{^{44}I(N_2O)}{^{44}I(CO_2)} \cdot \frac{p_c}{p_n}, \quad (3)$$

where $I$ stands for ion current, $p_c$ and $p_n$ for the pressure of the respective gas in the analyzer. From measurements with pure gases, we obtained $E = 0.75$ on our MAT 250 machine. (For these measurements, the ratio of the two currents is simply equal to the ratio of the voltages, since the same pre-amplifier is used.) This is comparable with the value of 0.73 reported by Mook and van der Hoek (1983) and Mook and Jongsma (1987) for a VG Micromass 903 and a VG SIRA 9 spectrometer, while Francey and Goodman (1986) found a slightly lower value of 0.68 for a Micromass 603 D.

The fact that the mass 44 ion yields are not equal for the two gases, i.e., that $E < 1$, can be understood by looking at the fragmentation pattern of the two molecules in the ion source. Table 1 shows typical fragmentation patterns (main isotopic peaks only). Mass 44 makes 59.0% of the sum of all peaks in Table 1 for $N_2O$ and 78.5% for $CO_2$. If we make the simplifying assumption that the ratio of total ion current to partial pressure in the analyzer, i.e., the overall ionization efficiency, is the same for both gases, then $E$ is given by the ratio of these two figures, or $E = 0.752$; this agrees with the experimental values. Thus the different mass 44 ion yields of $N_2O$ and $CO_2$ can be explained essentially by the fact that more molecule fragments are formed in the ion source for $N_2O$ than for $CO_2$.

## 3. Analysis of $N_2O$–$CO_2$ mixtures

The $\delta$ values of a mixture will be shifted by an amount depending on the concentration ratio of the two gases, $\rho = p_n/p_c$. From the above discussion, we can calculate the expected $\delta$ shift due to the presence of $N_2O$ as follows. Putting the ion current of mass 44 due to $CO_2$ equal to 1, the total mass 44 intensity for the mixture will be $1 + \rho E$, and the mass 45 (or 46) intensity $R_c + \rho E R_n$, so that the 45/44 (or 46/44) ratio of the mixture is given by

$$R_m = \frac{R_c + \rho E R_n}{1 + \rho E}.$$

The corresponding delta value is then given by

$$\delta_m \equiv \frac{R_m - R_{st}}{R_{st}} = \delta_c + \frac{\rho E}{1 + \rho E}(\delta_n - \delta_c), \quad (4)$$

Table 1. *Typical mass spectra of $CO_2$ and $N_2O$, normalized to mass 44 intensity = 1*

| Mass (M) | $CO_2$ Ion | $CO_2$ Peak height | $N_2O$ Ion | $N_2O$ Peak height |
|---|---|---|---|---|
| 12 | $^{12}C^+$ | 0.067 | | |
| 14 | | | $^{14}N^+$ | 0.129 |
| 16 | $^{16}O^+$ | 0.094 | $^{16}O^+$ | 0.050 |
| 28 | $^{12}C^{16}O^+$ | 0.113 | $^{14}N_2^+$ | 0.156 |
| 30 | $^{12}C^{18}O^+$ | $2.6 \cdot 10^{-4}$ | $^{14}N^{16}O^+$ | 0.36 |
| 44 | $^{12}C^{16}O_2^+$ | 1 | $^{14}N_2{}^{16}O^+$ | 1 |
| Sum | | 1.274 | | 1.695 |

Masses 28, 30 and 44 measured with our MAT 250 machine, electron energy 100 eV; masses 12, 14, 16: from Hall (1981), electron energy 70 eV. (Masses <27 cannot be measured with the MAT 250.)

where $R_{st}$ is the 45/44 or 46/44 ratio of standard $CO_2$. Thus the delta difference between pure $CO_2$ and a $CO_2$–$N_2O$ mixture is given by:

$$\Delta\delta \equiv \delta_c - \delta_m = \frac{\rho E}{1 + \rho E}(\delta_c - \delta_n). \quad (5)$$

This is the correction to be added to the measured $\delta^{45}$ and $\delta^{46}$ values of a mixture to obtain the values of the pure $CO_2$. For atmospheric air, $\rho \ll 1$, and (5) reduces to

$$\Delta\delta = \rho E(\delta_c - \delta_n). \quad (6)$$

Eq. (6) can now be evaluated using the experimental values of the different quantities.

On the other hand, we determined this correction by measuring different $N_2O$–$CO_2$ mixtures that we had prepared by determining the amount of each gas volumetrically. The concentration ratio $\rho = p_n/p_c$ varied for these mixtures between 0 and 0.04. As working standard for the mass-spectrometric measurements, we took the same $CO_2$ as was used for preparing the gas mixtures, so that $\delta_c = 0$ and the measured $\delta$ values were equal to $-\Delta\delta$ of eq. (5). Fig. 1 shows

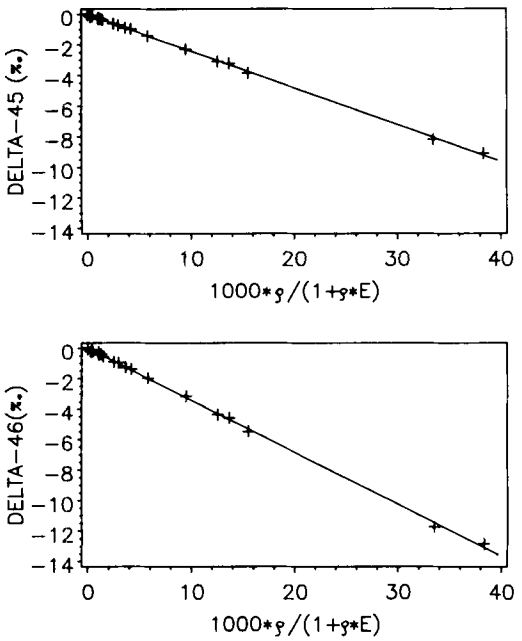


*Fig. 1.* Mass ratios 45/44 and 46/44, expressed as $\delta^{45}$ (top) and $\delta^{46}$ (bottom), measured for $N_2O$–$CO_2$ mixtures. $\rho$ = partial pressure ratio of $N_2O$ to $CO_2$. $\delta^{45}$ and $\delta^{46}$ were measured against the pure $CO_2$.

the $\Delta\delta^{45}$ and $\Delta\delta^{46}$ values as a function of $\rho/(1 + \rho E)$ for these mixtures. The linear relationship expected from eq. (5) is obviously fulfilled for the two series shown. Regression analysis yields

$$\Delta\delta^{45} = (244 \pm 2)\,\rho/(1 + \rho E), \quad (7a)$$

$$\Delta\delta^{46} = (347 \pm 2)\,\rho/(1 + \rho E). \quad (7b)$$

This can be compared with the values expected from eq. (5) when inserting the values for $E$ and $\delta_n$ obtained from the measurements of pure $N_2O$, which yields 262 and 365 for the factors in eqs. (7a, b). These values are less accurate than those of eqs. (7), since the mass 44 yield ratio $E$ has not been determined very precisely. In view of this, the agreement between the two methods is satisfactory. Also by measuring gas mixtures, Mook and van der Hoek (1983) found values of $277 \pm 12$ and $380 \pm 12$ for the coefficients in eqs. (7). Possible causes for the deviation from our results may be a different isotopic composition of the $N_2O$ used and a different mass 44 yield ratio, $E$.

For the final corrections, $\delta^{45}$ and $\delta^{46}$ values have to be translated into $\delta^{13}C$ and $\delta^{18}O$ values (Mook and Grootes, 1973).

Using the results of eqs. (7), this yields:

$$\delta^{13}C_{corr} = \delta^{13}C_{meas} + \rho\,250‰, \quad (8a)$$

$$\delta^{18}O_{corr} = \delta^{18}O_{meas} + \rho\,347‰. \quad (8b)$$

Mook and van der Hoek (1983) calculated, by inserting elemental isotope ratios and the experimental value of $E$, 250‰ and 362‰ for the constants on the right-hand side, in good agreement with our results.

For 1986, with the atmospheric concentrations 348 ppm $CO_2$ and 304 ppb $N_2O$, $\rho = 0.874 \cdot 10^{-3}$, so that the correction to be applied to the apparent $\delta^{13}C$ and $\delta^{18}O$ values is:

$$\delta^{13}C_{corr} = \delta^{13}C_{meas} + 0.22‰, \quad (9a)$$

$$\delta^{18}O_{corr} = \delta^{18}O_{meas} + 0.30‰. \quad (9b)$$

## 4. Mass-spectrometric determination of the $N_2O$ concentration

Precise measurements of the concentration of $N_2O$ are usually performed by means of gas chromatography. Lacking an appropriate gas

chromatograph, we developed a mass-spectrometric method that is less precise but suffices for calculating the necessary isotopic corrections. It is based on the fact that due to the production of the fragment $NO^+$ in the ion source, the mass spectrum of $N_2O$ exhibits a relatively large mass 30 peak (cf. Table 1), while mass 30 is a minor isotopic peak (stemming from $^{12}C^{18}O^+$) for $CO_2$. The possibility of using this fact was noted by Moore (1974).

Instead of measuring the mass ratio 30:44, we measure 30:28, because mass discrimination in the spectrometer affects the ratio between the neighboured masses 30 and 28 less than the mass ratio 30:44. We consider the (background-corrected) voltages measured, e.g., $^{28}U_c$ = mass 28 voltage for pure $CO_2$, and the specific voltages, i.e., the voltage per unit pressure of the respective gas, e.g., $^{28}u_c = {}^{28}U_c/p_c$, where $p_c$ is the partial pressure of $CO_2$ in the mass spectrometer. (With this notation the ionization efficiency ratio defined by eq. (3) is $E = {}^{44}u_n/{}^{44}u_c$.) The contributions from the two gases to the signals 28 and 30 then are

| | $CO_2$ | $N_2O$ |
|---|---|---|
| mass 28 | $^{28}u_c\,p_c$ | $^{28}u_n\,p_n$ |
| mass 30 | $^{30}u_c\,p_c$ | $^{30}u_n\,p_n$ |

and the voltage ratio $^{30}U/^{28}U$ for a sample consisting of a mixture of $CO_2$ and $N_2O$ is given by

$$\frac{^{30}U}{^{28}U} = \frac{^{30}u_c\,p_c + {}^{30}u_n\,p_n}{^{28}u_c\,p_c + {}^{28}u_n\,p_n} = \frac{^{30}u_c + {}^{30}u_n\rho}{^{28}u_c + {}^{28}u_n\rho} = \frac{^{30}u_c/{}^{28}u_c + \rho/A}{1 + B\rho}, \tag{10}$$

where $\rho = p_n/p_c$ is the $N_2O/CO_2$ concentration ratio, $A = {}^{28}u_c/{}^{30}u_n$ and $B = {}^{28}u_n/{}^{28}u_c$. Solving for $\rho$ yields

$$\rho = A\,\frac{^{30}U/^{28}U - {}^{30}u_c/{}^{28}u_c}{1 - AB(^{30}U/^{28}U)}. \tag{11}$$

For $\rho \ll 1$, for example, for atmospheric samples with $\rho \approx 0.001$, this can be simplified to

$$\rho = A[^{30}U/^{28}U - {}^{30}u_c/{}^{28}u_c]. \tag{12}$$

We have determined $A$ and $^{30}u_c/^{28}u_c$ for our MAT 250 by analyzing different $N_2O$–$CO_2$ mixtures and pure $CO_2$, respectively; the numerical values, besides depending on the isotope ratios, also depend on the ratio of the two preamplifier resistors involved.

We have used this method to estimate the $N_2O$ concentration in small air samples, collected in 75 ml glass flasks on the institute roof in the center of the city of Bern. The $CO_2$ concentration was determined volumetrically, $\rho$ from eq. (12). The mean $N_2O$ concentration from 14 samples was $308 \pm 5$ ppb, which agrees well with the value of 304 ppb expected from the results of Weiss (1981).

## 5. $N_2O$ concentrations in polar ice

In the same way, we estimated the average $N_2O$ concentration of air samples trapped in polar ice from Siple Station, Antarctica, stemming from the last two centuries, that we analyzed for $CO_2$ concentration and $\delta^{13}C$ (Friedli et al., 1986). The results are shown in Fig. 2. The larger scatter, compared to the modern air samples, may be due to production of $N_2O$ by the cold cathode manometer in the extraction systems (see below), which we could not correct for very precisely. Average values are ($\pm 1$ standard deviation) $276 \pm 15$ ppb for the period 1744–1850, $299 \pm 25$ ppb for 1850–1900 and $293 \pm 21$ ppb for 1900 to 1953. The first number can be compared with a mean of $289 \pm 10$ ppb for the time 1600–1800, determined by gas chromatography on air from another Antarctic ice core by Pearman et al. (1986). Also shown in

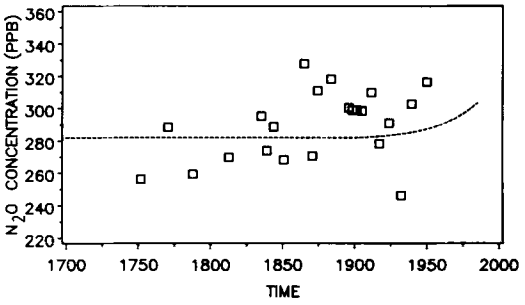


*Fig. 2.* $N_2O$ concentrations determined mass-spectrometrically on samples of air trapped in the ice core from Siple Station, Antarctica. Horizontal axis: estimated time of gas inclusion (Schwander and Stauffer, 1984). Dashed line: model estimate of anthropogenic $N_2O$ increase due to fossil fuel use (Weiss, 1981).

Fig. 2 (dashed line) is a model estimate of the past $N_2O$ increase by Weiss (1981), based on the assumption that $N_2O$ is produced by the combustion of fossil fuels. Our measurements cannot compete in precision with gas chromatography, but the agreement of mean values is satisfactory, and the method would clearly be sufficient to detect major deviations from the present $N_2O$ level, for instance in air samples from ice from the last glaciation. The results also demonstrate that the technique for extracting air from ice is suited for determining $N_2O$ concentrations.

## 6. $N_2O$ production in a cold cathode manometer

We extracted the $CO_2$ from air samples in a metal vacuum line equipped with a cold cathode manometer (Penning tube). First we observed bad reproducibility of the $\delta^{13}C$ and $\delta^{18}O$ values and at the same time noticed enhanced values of the $N_2O/CO_2$ ratio. Obviously, the extracted $CO_2$ samples were contaminated with some spurious $N_2O$ which, as we later found out, must have been produced in the cold cathode manometer. The reproducibility became better and the $N_2O/CO_2$ ratios normal when the cold cathode tube was disconnected from the voltage supply; consequently, we also removed a similar Penning manometer tube from the ice extraction system. Apparently, some $N_2O$ must be formed from $N_2$ and $O_2$ in the high voltage (3 kV) discharge in the tube. The amount thus produced was about 0.6 nmol in a normal sample extraction, which increased the $N_2O/CO_2$ concentration ratio by roughly $5 \cdot 10^{-4}$, i.e., by about half the atmospheric value.

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