

The N₂O correction in mass-spectrometric analysis of CO₂

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Abstract During cryogenic separation of CO₂ from atmosphere and soil air for isotopic analyses, N₂O present in the air condenses together with CO₂. The N₂O, having the same molecular masses (44, 45 and 46) as CO₂, seriously affects the results of ¹³C and ¹⁸O isotope analyses of carbon dioxide, making it necessary to introduce appropriate corrections. A simple method of correcting the measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the analysed CO₂ was developed. It requires experimental determination of several parameters of the used mass spectrometer and changes in the computational algorithm. The performance of the method was tested using N₂O–CO₂ mixtures. The experiments showed that the proposed correction method removes the effect of presence of N₂O in the analysed CO₂ sample down to analytical uncertainty of the measurement. This method was adopted in routine analyses of stable isotope composition of carbon dioxide in atmospheric and soil air samples being performed in our laboratory.

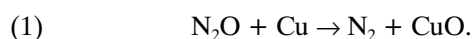
Key words carbon dioxide • isotopic composition • nitrous oxide • N₂O correction

Introduction

The most commonly used method for separating CO₂ from atmospheric air or soil gas samples is cryogenic extraction at the liquid nitrogen temperature [4]. The N₂O present in the atmosphere at typical concentrations of 300 ppb [17] and in soil air samples up to 1000 ppm [7], has almost the same physical properties as CO₂ and is frozen together with carbon dioxide. Since N₂O has the same molecular masses (44, 45 and 46) as CO₂, its presence in the analysed CO₂ sample seriously affects the isotope analyses of carbon dioxide, shifting $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the analysed CO₂ towards more negative values.

In order to obtain correct isotopic results for the CO₂, two types of procedures can be adopted: (i) N₂O can be removed from the N₂O–CO₂ mixture prior to mass spectrometric measurement, and (ii) an appropriate correction of the result of isotope analysis of the N₂O–CO₂ mixture can be elaborated and applied.

Removing of N₂O from an N₂O–CO₂ mixture can be achieved by passing the mixture over hot copper. Nitrous oxide begins to decompose at temperatures over 500°C, according to the following reaction:



During purification of carbon dioxide originating from atmospheric air samples this purification step can be achieved either by passing the gas several times through hot copper wires [14], or by circulating it in a closed vacuum line for several minutes, forcing the gas-flow by means of a small circulation pump installed in the line [13]. In the

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method developed by Dudziak and Halas [8], the gas circulates in the vacuum line due to thermogravitational effect.

It has been demonstrated that the purification step involving high-temperature reduction of N_2O over hot copper does not change $\delta^{13}C$ value [8, 14], while $\delta^{18}O$ can be affected seriously [14]. Moreover, the purification procedure requires additional equipment and increases the total time of sample preparation.

The results of mass-spectrometric analyses of CO_2 in presence of N_2O can be corrected by introducing appropriate correction factors. Craig and Keeling calculated necessary corrections for $\delta^{13}C$ and $\delta^{18}O$ values of atmospheric CO_2 , assuming constant concentration ratio N_2O/CO_2 and constant $^{15}N/^{14}N$ ratio in the sample [5]. However, the correction factors derived by these authors turned out to be too high due to a false assumption that ionisation efficiencies of N_2O and CO_2 are equal. Mook and Van der Hoek calculated the appropriate correction factors as a function of N_2O/CO_2 concentrations ratio, taking into account the ionisation efficiency ratio, which was significantly different from the unity for the mass spectrometer they have used [14]. The calculated correction factors equal to +0.22‰ for ^{13}C and +0.32‰ for ^{18}O were very close to those derived experimentally for atmospheric air samples [13, 14]. Friedli and Siegenthaler repeated the measurements of Mook and Van der Hoek by analysing pure N_2O and CO_2 gases as well as different N_2O-CO_2 mixtures and obtained very similar results (+0.22‰ and +0.30‰ for ^{13}C , ^{18}O , respectively) [9]. In addition, they proposed a simple method for determining mass-spectrometrically the concentration of N_2O in CO_2 , which turned out to be very useful for calculating the isotopic correction factors in cases when the N_2O/CO_2 concentrations ratio (ρ) in the analysed gas sample is not known.

In the method described in this study, the corrected isotopic results were obtained by modifying original computational algorithm used by the mass spectrometer in such a way that it takes into account the presence of N_2O in the CO_2 sample.

Determination of N_2O/CO_2 concentrations ratio in the sample by means of a mass spectrometer

Friedli and Siegenthaler developed a mass-spectrometric method for determining concentration of N_2O in the analysed CO_2 sample [9]. The method is less precise than the gas-chromatographic method, but is sufficient for calculating the necessary isotopic corrections in situations when the N_2O concentration in the measured CO_2 sample is unknown. The method can be very useful in cases when access to a gas chromatograph is restricted or when the sample is too small for two separate measurements.

Moore [15] noted that due to production of NO^+ fragments of mass 30 in the ion source, the mass spectrum of N_2O exhibits a relatively large mass 30 peak when compared to the CO_2 mass 30 peak, originating from $^{12}C^{18}O^+$ fragments. Due to this fact, the abundance of mass 30 can be used as a measure of the N_2O partial pressure [9, 13]. However, instead of measuring the mass ratio 30:44, Friedli and Siegenthaler [9] proposed to measure the ratio 30:28, because mass discrimination in the spectrometer affects the ratio of the neighbouring masses 30 and 28 to

a lesser extent than the mass ratio 30:44. The mass ratio 30:28 in the N_2O-CO_2 mixture can be substituted by a ratio of the corresponding voltages $^{30}U/^{28}U$, which can be expressed by the following formula [9]:

$$(2) \quad \frac{^{30}U}{^{28}U} = \frac{^{30}u_c p_c + ^{30}u_n p_n}{^{28}u_c p_c + ^{28}u_n p_n}$$

where: $^{30}U, ^{28}U$ – voltages measured for the N_2O-CO_2 mixture, corresponding to masses 30 and 28; p_c, p_n – partial pressures of CO_2 and N_2O in the sample; $^{30}u_c, ^{28}u_c$ – specific voltages (per unit pressure, e.g. $^{30}u_c = ^{30}U/p_c$) for pure CO_2 ; $^{30}u_n, ^{28}u_n$ – specific voltages (per unit pressure, e.g. $^{30}u_n = ^{30}U/p_n$) for pure N_2O .

If we define the N_2O/CO_2 partial pressures ratio as:

$$(3) \quad \rho = \frac{p_n}{p_c}$$

we can rewrite equation (2) in the following form:

$$(4) \quad \frac{^{30}U}{^{28}U} = \frac{^{30}u_c + ^{30}u_n \rho}{^{28}u_c + ^{28}u_n \rho} = \frac{^{30}u_c + \rho}{1 + B\rho}$$

$$\text{where: } A = \frac{^{28}u_c}{^{30}u_n}, B = \frac{^{28}u_n}{^{28}u_c}.$$

Assuming $\rho \ll 1$ and solving this equation for ρ yields:

$$(5) \quad \rho = A \left[\frac{^{30}U}{^{28}U} - \frac{^{30}u_c}{^{28}u_c} \right] = A \frac{^{30}U}{^{28}U} - C$$

$$\text{where: } C = A \frac{^{30}u_c}{^{28}u_c}.$$

We prepared different N_2O-CO_2 mixtures and analysed them using our mass spectrometer Delta S (Finnigan MAT), as well as pure CO_2 samples [2, 10]. Figure 1 shows

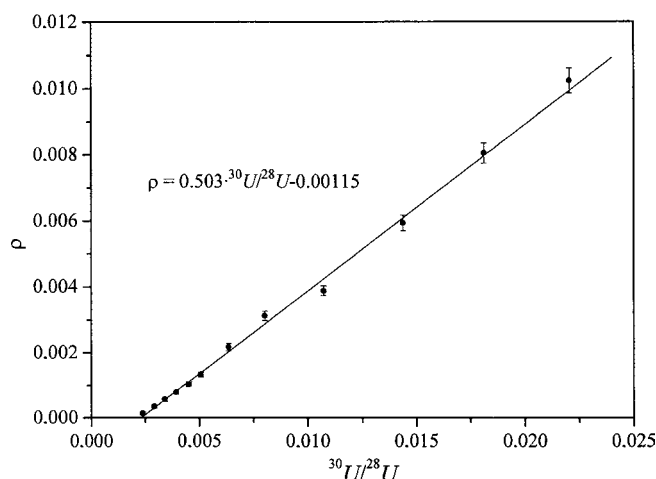


Fig. 1. The relation between the N_2O/CO_2 concentrations ratio (ρ) and the voltage ratio $^{30}U/^{28}U$.

the N₂O/CO₂ concentrations ratio (ρ) used in the experiment as a function of the resulting $^{30}U/^{28}U$ voltages ratio. The least-squares fit of the data leads to experimental values for A and C:

$$(6a) \quad A = 0.503 \pm 0.001$$

and

$$(6b) \quad C = -0.00115 \pm 0.00008.$$

These values are then used to calculate ρ values applied in the isotopic correction algorithm described in the next paragraphs.

The computational algorithm

The mass spectrometer used in our laboratory (Delta S, Finnigan MAT) calculates $\delta^{13}C$ and $\delta^{18}O$ values of the analysed CO₂ samples according to the algorithm proposed by Santrock *et al.* [11, 16]. This algorithm is briefly described below.

The measured ion currents ^{44}I , ^{45}I and ^{46}I , corresponding to masses 44, 45 and 46, are converted into voltages ^{44}U , ^{45}U and ^{46}U by preamplifiers connected to three ion collectors. Based on the measured values of voltages and considering different preamplifier resistors involved, the isotopic ratios ^{45}R and ^{46}R can be calculated:

$$(7a) \quad ^{45}R = \frac{^{45}I}{^{44}I} = \frac{\frac{^{45}U}{3 \cdot 10^{10} \Omega}}{\frac{^{44}U}{3 \cdot 10^8 \Omega}} = \frac{1}{100} \cdot \frac{^{45}U}{^{44}U}$$

$$(7b) \quad ^{46}R = \frac{^{46}I}{^{44}I} = \frac{\frac{^{46}U}{1 \cdot 10^{11} \Omega}}{\frac{^{44}U}{3 \cdot 10^8 \Omega}} = \frac{3}{1000} \cdot \frac{^{46}U}{^{44}U}.$$

On the other hand, the isotopic ratios ^{45}R and ^{46}R are defined as follows:

$$(8a) \quad ^{45}R = \frac{^{45}I}{^{44}I} = \frac{^{13}C^{16}O_2 + 2 \cdot ^{12}C^{17}O^{16}O}{^{12}C^{16}O_2} = ^{13}R + 2 \cdot ^{17}R$$

$$(8b) \quad ^{46}R = \frac{^{46}I}{^{44}I} = \frac{2 \cdot ^{12}C^{16}O^{18}O + 2 \cdot ^{13}C^{16}O^{17}O + ^{12}C^{17}O_2}{^{12}C^{16}O_2} \\ = 2 \cdot ^{13}R^{17}R + (^{17}R)^2 + ^{18}R.$$

The relationship between ^{17}R and ^{18}R adopted by Santrock *et al.* [16] is equal to:

$$(9) \quad ^{17}R = K(^{18}R)^a$$

where: $a = 0.516$ [11] and $K = 0.0099235$ [1].

Combining equations (8) and (9) yields the following equation:

$$(10) \quad 3K^2 \cdot (^{18}R)^{2a} - 2 \cdot ^{45}R \cdot K \cdot (^{18}R)^a - 2 \cdot ^{18}R + ^{46}R = 0.$$

Using values of ^{45}R and ^{46}R given both for standard and sample gases and solving this equation numerically for ^{18}R we can obtain ^{18}R and subsequently ^{17}R (eq. (9)) and ^{13}R (eq. (8a)) for working standard ($^{18}R_{ws}$, $^{17}R_{ws}$ and $^{13}R_{ws}$) and sample ($^{18}R_{sa}$, $^{17}R_{sa}$ and $^{13}R_{sa}$). Finally, we can calculate $\delta^{13}C$ and $\delta^{18}O$ values of measured sample *vs.* working standard [4]:

$$(11a) \quad \delta^{13}C_{ws} = \left(\frac{^{13}R_{sa}}{^{13}R_{ws}} - 1 \right) \cdot 1000\%$$

$$(11b) \quad \delta^{18}O_{ws} = \left(\frac{^{18}R_{sa}}{^{18}R_{ws}} - 1 \right) \cdot 1000\%.$$

This values can be expressed *vs.* Vienna-PDB standard according to the formulas:

$$(12a) \quad \delta^{13}C_{VPDB} = \delta^{13}C_{ws} + \delta^{13}C_{ws/VPDB} \\ + \frac{\delta^{13}C_{ws} \cdot \delta^{13}C_{ws/VPDB}}{1000}$$

$$(12b) \quad \delta^{18}O_{VPDB} = \delta^{18}O_{ws} + \delta^{18}O_{ws/VPDB} \\ + \frac{\delta^{18}O_{ws} \cdot \delta^{18}O_{ws/VPDB}}{1000}$$

where: $\delta^{13}C_{ws/VPDB}$, $\delta^{18}O_{ws/VPDB}$ – δ values of working standard *vs.* Vienna-PDB standard.

The N₂O correction

In the procedure described above, it is assumed that ion currents ^{44}I , ^{45}I and ^{46}I are generated by adequate ion beams of pure CO₂. However, in case of N₂O–CO₂ mixture ion beams of these two gases can interfere, as the different isotopic species of CO₂ and N₂O have the same molecular masses (Table 1), thus leading to false results. In order to obtain correct results, ^{45}R and ^{46}R isotopic ratios measured in the N₂O–CO₂ mixture and used subsequently in equations (8a),(8b) should be replaced with $^{45}R_C$ and $^{46}R_C$ values, calculated for pure CO₂ present in the sample.

Table 1. Molecular masses of different isotopic species of CO₂ and N₂O gases.

| Mass | CO ₂ | N ₂ O |
|------|----------------------|----------------------|
| 44 | $^{12}C^{16}O^{16}O$ | $^{14}N^{14}N^{16}O$ |
| 45 | $^{13}C^{16}O^{16}O$ | $^{14}N^{15}N^{16}O$ |
| | $^{12}C^{17}O^{16}O$ | $^{14}N^{14}N^{17}O$ |
| 46 | $^{12}C^{17}O^{17}O$ | $^{15}N^{15}N^{16}O$ |
| | $^{13}C^{16}O^{17}O$ | $^{14}N^{15}N^{17}O$ |
| | $^{12}C^{16}O^{18}O$ | $^{14}N^{14}N^{18}O$ |

First, one has to consider the fact that ionisation efficiency for CO₂ is different from that for N₂O. The ionisation efficiency ratio can be defined as follows [14].

$$(13) \quad E = \frac{{}^{44}I(\text{N}_2\text{O})}{{}^{44}I(\text{CO}_2)} \cdot \frac{p_c}{p_n} = \frac{{}^{44}I(\text{N}_2\text{O})}{{}^{44}I(\text{CO}_2)} \cdot \frac{1}{\rho}$$

where: ${}^{44}I$ stands for mass 44 ion current; p_c and p_n for the pressure of the respective gas in the analyser.

From measurements for pure N₂O and CO₂ we obtained $E = 0.75 \pm 0.01$ on our Delta S spectrometer. This is comparable with the values reported earlier for other types of mass spectrometers: 0.73 [13, 14] and 0.75 [9]. Since the total current measured in each of the three collectors is the sum of currents produced by the respective ion beams of CO₂ and N₂O, we can write:

$$(14) \quad {}^{44}I_{\text{total}} = {}^{44}I(\text{CO}_2) + {}^{44}I(\text{N}_2\text{O}) = {}^{44}I(\text{CO}_2) \cdot (1 + \rho E).$$

If we define isotopic ratios (eq. (7a), (7b)) R_C for pure CO₂ and R_N for pure N₂O as:

$$(15a) \quad {}^{45}R_C = \frac{{}^{45}I(\text{CO}_2)}{{}^{44}I(\text{CO}_2)}$$

$$(15b) \quad {}^{46}R_C = \frac{{}^{46}I(\text{CO}_2)}{{}^{44}I(\text{CO}_2)}$$

$$(16a) \quad {}^{45}R_N = \frac{{}^{45}I(\text{N}_2\text{O})}{{}^{44}I(\text{N}_2\text{O})}$$

$$(16b) \quad {}^{46}R_N = \frac{{}^{46}I(\text{N}_2\text{O})}{{}^{44}I(\text{N}_2\text{O})}$$

we can express total ion currents ${}^{45}I$ and ${}^{46}I$ produced in the N₂O–CO₂ mixture as:

$$(17a) \quad {}^{45}I_{\text{total}} = {}^{45}I(\text{CO}_2) + {}^{45}I(\text{N}_2\text{O}) = {}^{45}R_C \cdot {}^{44}I(\text{CO}_2) + {}^{45}R_N \cdot \rho E \cdot {}^{44}I(\text{CO}_2)$$

and similarly

$$(17b) \quad {}^{46}I_{\text{total}} = {}^{46}I(\text{CO}_2) + {}^{46}I(\text{N}_2\text{O}) = {}^{46}R_C \cdot {}^{44}I(\text{CO}_2) + {}^{46}R_N \cdot \rho E \cdot {}^{44}I(\text{CO}_2).$$

Considering equations (15), (16) and (17) we can define again ${}^{45}R_m$ and ${}^{46}R_m$ in the N₂O–CO₂ mixture (eqs. (8a), (8b)):

$$(18a) \quad {}^{45}R_m = \frac{{}^{45}I_{\text{total}}}{{}^{44}I_{\text{total}}} = \frac{{}^{45}R_C + {}^{45}R_N \cdot \rho E}{1 + \rho E}$$

$$(18b) \quad {}^{46}R_m = \frac{{}^{46}I_{\text{total}}}{{}^{44}I_{\text{total}}} = \frac{{}^{46}R_C + {}^{46}R_N \cdot \rho E}{1 + \rho E}.$$

Using these values we can express ${}^{45}\delta_m$ and ${}^{46}\delta_m$ values in the mixture in the following form:

$$(19a) \quad {}^{45}\delta_m = \left(\frac{{}^{45}R_m}{{}^{45}R_{ws}} - 1 \right) \cdot 1000 = {}^{45}\delta_C \frac{1}{1 + \rho E} + {}^{45}\delta_N \frac{\rho E}{1 + \rho E}$$

$$(19b) \quad {}^{46}\delta_m = \left(\frac{{}^{46}R_m}{{}^{46}R_{ws}} - 1 \right) \cdot 1000 = {}^{46}\delta_C \frac{1}{1 + \rho E} + {}^{46}\delta_N \frac{\rho E}{1 + \rho E}$$

where ${}^{45}\delta_C$ and ${}^{46}\delta_C$ values (for pure CO₂) are defined as:

$$(20a) \quad {}^{45}\delta_C = \left(\frac{{}^{45}R_C}{{}^{45}R_{ws}} - 1 \right) \cdot 1000$$

$$(20b) \quad {}^{46}\delta_C = \left(\frac{{}^{46}R_C}{{}^{46}R_{ws}} - 1 \right) \cdot 1000$$

and δ_N values (for pure N₂O) were determined experimentally by measuring pure N₂O used for preparing N₂O–CO₂ mixtures against CO₂ working standard (see below).

Finally, we can calculate the required ${}^{45}R_C$ and ${}^{46}R_C$ values for pure CO₂:

$$(21a) \quad {}^{45}R_C = {}^{45}R_{ws} \cdot \left(\frac{{}^{45}\delta_C}{1000} + 1 \right)$$

$$(21b) \quad {}^{46}R_C = {}^{46}R_{ws} \cdot \left(\frac{{}^{46}\delta_C}{1000} + 1 \right).$$

Substituting ${}^{45}R$ and ${}^{46}R$ (eqs. (8a), (8b)) with ${}^{45}R_C$ and ${}^{46}R_C$ we can repeat the calculations according to the computational algorithm resulting in the corrected final $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values (eqs. (12a), (12b)).

Results and discussion

In order to verify the correction procedure several measurements have been performed. First, the isotopic composition of pure CO₂ and N₂O used at the later stage for preparation of different N₂O–CO₂ mixtures was measured. For pure CO₂ the following results were obtained:

$$(22a) \quad \delta^{13}\text{C}_{\text{VPDB}} = -51.626 \pm 0.001\text{‰}$$

$$(22b) \quad \delta^{18}\text{O}_{\text{VPDB}} = -34.917 \pm 0.008\text{‰}.$$

By measuring pure N₂O against the CO₂ working standard we obtained ${}^{45}\delta_N$ and ${}^{46}\delta_N$ values (eqs. (19a), (19b)):

$$(23a) \quad {}^{45}\delta_N = -320.285 \pm 0.011\text{‰}$$

$$(23b) \quad {}^{46}\delta_N = -486.156 \pm 0.034\text{‰}.$$

A set of N₂O–CO₂ mixtures in the range of concentration ratio ρ (eq. (3)) from 0 to 0.01 was prepared (Fig. 1) and subsequently analysed by mass spectrometer. The influence of varying amounts of N₂O added to the CO₂ sample on the isotopic results is shown in Fig. 2a ($\delta^{13}\text{C}_{\text{VPDB}}$) and Fig. 2b ($\delta^{18}\text{O}_{\text{VPDB}}$). For all the measured mixtures the proposed correction procedure was applied. Results of this correction are plotted in Fig. 2 (filled circles). The mean values calculated for the corrected results of $\delta^{13}\text{C}_{\text{VPDB}}$ ($-51.628 \pm 0.003\text{‰}$) and $\delta^{18}\text{O}_{\text{VPDB}}$ ($-34.902 \pm 0.008\text{‰}$) agree within the range of quoted uncertainty with the values measured in pure CO₂. The calculated standard deviations of the mean values are comparable with that specified by the mass spectrometer manufacturer as an internal precision of the instrument (0.006‰ for C and 0.012‰ for O) [6].

In the time period from January 1998 to December 2002 *ca.* 820 CO₂ samples extracted from soil (*ca.* 750) and atmospheric air (*ca.* 70) were analysed mass-spectrometrically and results were corrected for N₂O presence [10]. In case when the calculated concentration ratio ρ (eq. (5)) was close to that assumed for atmospheric air (*ca.* 0.88×10^{-3}) [9, 14], the values of corrections (calculated differences between corrected and measured values of δ) were $+0.225\text{‰}$ for $\delta^{13}\text{C}$ and $+0.325\text{‰}$ for $\delta^{18}\text{O}$, very close to that reported by others [9, 13, 14].

The source of largest uncertainty in the correction procedure described above is the unknown isotopic composition of N₂O present in the CO₂ sample. In equation (19) the values of $^{45}\delta_{\text{N}}$ and $^{46}\delta_{\text{N}}$ from eq. (23) were applied both for the N₂O–CO₂ mixtures and for all environmental samples. Such approach is correct in the first case, whereas for the environmental samples it can introduce additional uncertainty. The influence of the deviation of the assumed $^{45}\delta_{\text{N}}$ and $^{46}\delta_{\text{N}}$ values from the real ones on the result of correction depends on the actual value of ρ (eqs. (19a), (19b)). Calculations show that for atmospheric N₂O ($\rho < 0.001$) $^{45}\delta_{\text{N}}$ and $^{46}\delta_{\text{N}}$ values can change within a range $\pm 5\text{‰}$ [3, 12] introducing the uncertainty of corrected results in the order of $\pm 0.005\text{‰}$. The isotopic composition of soil nitrous

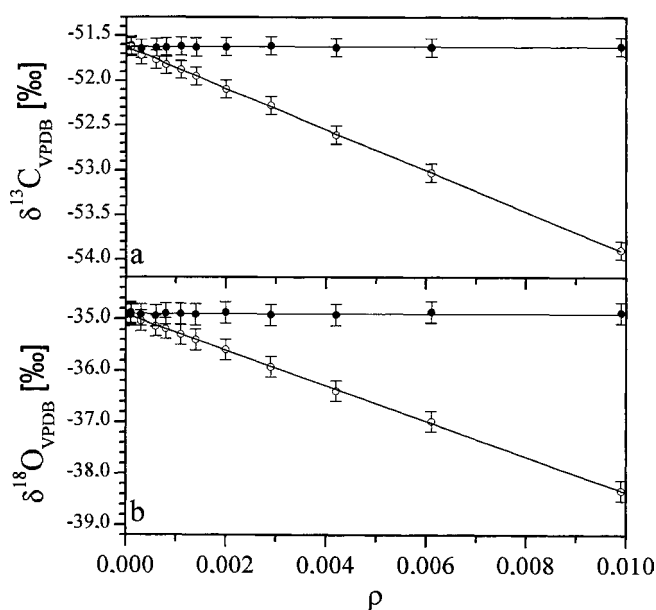


Fig. 2. Relationship between the measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the CO₂ and the N₂O/CO₂ concentrations ratio ρ in the sample (open circles). The corrected values are shown as heavy dots.

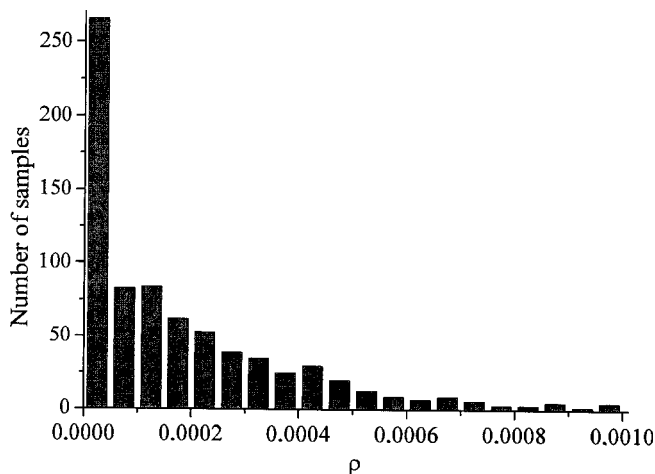


Fig. 3. The distribution of a number of soil and atmospheric CO₂ samples measured during the period January 1998 – December 2002 as a function of the N₂O/CO₂ concentrations ratio (ρ).

oxide can vary in a broader range [3], in the order of $\pm 20\text{‰}$. The resulting uncertainty of $^{45}\delta_{\text{N}}$ and $^{46}\delta_{\text{N}}$ values are around $\pm 0.02\text{‰}$ for $\rho = 0.001$, still comparable with the precision of single measurement (0.02‰ for C and 0.04‰ for O) [6]. Therefore the proposed correction method is sufficient for the measured environmental samples (95% of those samples were characterised by $\rho < 0.001$ (cf. Fig. 3)). Such small ρ values in the soil air samples can be explained by elevated CO₂ concentration due to the production of this gas by organic matter decomposition and root respiration.

Conclusions

The presented method allows to correct the results of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of CO₂ in the presence of N₂O. This is a typical situation when CO₂ is extracted from samples of atmospheric air or soil gas. The procedure is easy to apply and does not require any special equipment nor additional measurement to be carried out. It was demonstrated that it can produce satisfactory results for both C and O isotopes of CO₂. For atmospheric carbon dioxide samples the calculated values of the corrections are comparable to those obtained in previous studies [9, 13, 14]. In case of the soil CO₂ samples, the results of correction are less certain but still precise enough to be used in environmental studies.

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