N$_2$O influence on isotopic measurements of atmospheric CO$_2$

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In spite of extensive efforts, even the most experienced laboratories dealing with isotopic measurements of atmospheric CO$_2$ still suffer from poor inter-laboratory consistency. One of the complicating factors of these isotope measurements is the presence of N$_2$O, giving rise to mass overlap in the isotope ratio mass spectrometer (IRMS). The aim of the experiment reported here has been twofold: first, the re-establishment of the correction for ‘mechanical’ interference of N$_2$O in the IRMS, along with its variability and drift, and the best way to quantitatively determine the correction factors. Second, an investigation into secondary effects, i.e. the influence of N$_2$O admitted with the CO$_2$ sample on the “cross contamination”$^1$ between sample and (pure CO$_2$) working gas. To make the suspected effects better detectable, isotopically enriched CO$_2$ gas with different concentrations of N$_2$O has been measured for the first time. No evidence of secondary effects was observed, from which we conclude that N$_2$O is not a major player in the inter-laboratory consistency problems. Still, we also found that the determination of the ‘mechanical’ N$_2$O correction needs to be very carefully determined for each individual IRMS, and should be periodically re-determined. We show that the determination of the correction should be performed using CO$_2$/N$_2$O mixtures with concentration ratios around that of the atmosphere, as the extrapolation from pure gas end member behaviour will give erroneous results due to non-linearities. For our IRMS, a VG SIRA series II, we find a correction of 0.23‰ for $\delta^{15}$CO$_2$ and 0.30‰ for $\delta^{16}$CO$_2$ of atmospheric samples, (with 0.85% mixing ratio). This implies that the relative ionisation efficiency (E) value associated with this machine is 0.75. Copyright © 2004 John Wiley & Sons, Ltd.

The spatial and temporal variations of the sources and sinks of atmospheric CO$_2$ can be distinguished and quantified applying measurements of stable isotopic ratios of atmospheric CO$_2$,$^2$–$^7$ especially the ratio of the stable carbon isotopes $^{12}$C and $^{13}$C. Since the trends in this ratio caused by anthropogenic emissions are small compared with the natural variations, very high precision and accuracy are needed in these measurements, as well as long-time stability and traceability. For $\delta^{13}$C an inter-comparability of 0.01‰ between different laboratories or measurement networks is demanded, to permit the integration of data from all collection sites into one global dataset as input for global carbon cycle models.$^8$ Slightly relaxed requirements apply to $\delta^{18}$O, $\delta^{13}$C and $\delta^{15}$O are defined in the usual way and given on the VPDB-CO$_2$ scale,$^9$ where not stated otherwise.

Sources of uncertainty can be found throughout the process from sampling to data processing. Air samples from remote places are normally filled into glass flasks for laboratory analysis manually or applying dedicated devices.$^5$,$^{10}$–$^{12}$ Concentrations and isotopic compositions of the sampled gases might be changed during storage and travel times by effects such as water interaction$^1$ or leakage and permeation through the flask valves.$^{14}$ In the laboratories, different extraction devices are used to quantitatively freeze out the CO$_2$ for mass spectrometric isotope analysis.$^{15}$ Finally, the calibration of reference gases (derived from calcium carbonate material), IRMS effects, like reservoir bleed effect and cross-contamination,$^1$ and the ion correction algorithms employed$^9$ may vary between laboratories or between mass spectrometer types. Corrections have to be applied due to:

(i) conversion of the measured $\delta^{15}$CO$_2$ to $\delta^{13}$C, correcting for the $^{12}$C$^{17}$O$^{16}$O contribution to $m/z$ 45;
(ii) conversion of the measured $\delta^{16}$CO$_2$ to $\delta^{18}$O, correcting for the $^{13}$C$^{17}$O$^{16}$O and $^{13}$C$^{17}$O$_2$ contributions to $m/z$ 46; and
(iii) cryogenic co-extraction of N$_2$O with CO$_2$ (both have isotopomers with $m/z$ 44, 45, 46).

Although all steps have been studied quite extensively, doubts arise every time an inter-comparison exercise is conducted, often resulting in a consistency among different laboratories that is poor compared not only with the precision requirements, but also the respective laboratories’ internal precision.

At present, the majority of the groups that perform high accuracy isotopic measurements on atmospheric CO$_2$ rely on their suite of “whole air standards”, from which they extract CO$_2$ in the same way they extract CO$_2$ from their samples. Variability or drifts between the “whole air CO$_2$” and pure
CO₂ reference materials is quite commonly observed. Whereas this complicates the calibration of the isotopic measurement, and — thus — the comparability of one’s program with that of other groups, it is generally agreed upon to be the best way of keeping one’s own measurement series internally consistent.

Differential drift, i.e. the difference between isotopic measurements of whole air CO₂ and pure CO₂, is commonly attributed to variability in the cryogenic extraction process. Variability in completeness of extraction, wall exchange effects, etc., are the type of effects that are usually referred to. Other possible sources of differential drift, such as N₂O effects, are generally thought to be less of a problem.

The N₂O experiments we report on here result from the unique situation that emerged connected to the isotopic analysis of atmospheric CO₂ from the sampling network of the Carbon Dioxide Research Group of the Scripps Institution for Oceanography of the University of California, San Diego (SIO). Our group had started these isotopic analyses on CO₂ already in 1977. From 1993 onwards, the measurements were carried out at SIO itself, with a full year of overlap between the two laboratories, as well as intensive exchange of whole air standards and pure CO₂ gases. The unique fact is that from 1977 onwards, until the present day, the CO₂ extraction has been performed at the SIO laboratory with the same cryogenic device and procedure. The extracted CO₂ samples were transferred, first to CIO, and later ‘in-house’, in so-called flame-off tubes (Pyrex tubes that were closed by melting the glass together).

The results of the detailed CIO-SIO inter-comparison showed a systematic offset in the δ¹³C values of whole air samples measured at the CIO of (−0.102 ± 0.005)%o compared with those measured at SIO (i.e. the CIO values being more negative), while the offset in pure CO₂ was found to be significantly smaller at (−0.049 ± 0.005)%o (determined using the GS-19 and GS-20 reference materials, which are pure CO₂ gases close to atmospheric isotopic CO₂ composition; H. A. J. Meijer et al., in preparation). Obviously, in this case, the cryogenic extraction procedure cannot be blamed for this difference.

Therefore, an alternative explanation has been sought. As the only difference between the two classes of samples is the presence of N₂O, we decided to study the effects of N₂O in detail. Our idea was that there might be an N₂O influence beyond the ‘mechanical’ addition of isotopomers with significantly smaller at (−0.21 ± 0.01)%o and (0.30 ± 0.01)%o, respectively.

Until now any alternative procedure of removing the N₂O fraction proved to be inadequate because of insufficient precision (e.g. separation by gas chromatography) or because it destroys the oxygen isotope ratio (reducing N₂O in a copper oven). A correction for the N₂O contribution after measurements of its fragments in the same time (following Friedli and Siegenthaler or Mook and Jongsmā), or after N₂O concentration measurements, is still the most common practice. This, however, depends strongly on the mass spectrometer type and even on the actual operating conditions.

As reported by Friedli and Siegenthaler, the observed isotopic ratios R₄₅ for masses 45:44 and R₆₆ for 46:44 of the CO₂ and N₂O mixtures can be expressed as:

\[ R_{45}^* = R_{45} + \rho R_{44}^* \]

(1)

Here \( \rho = [N_2O]/[CO_2] \) is the concentration ratio of the two species, which can also be expressed as the ratio of the respective partial pressures \( \rho = P_{N_2O}/P_{CO_2} \), further on reported as mol N₂O/mol CO₂ (sometimes omitted) or in % units. E, termed ‘ionisation efficiency ratio’, is the ratio of the ionisation yields of N₂O and CO₂. With ionisation yield we mean the ion current of m/z = 44 (I₄₄) produced by the CO₂ or N₂O gas, with a certain partial pressure p.

\[ E = \frac{I_{44}(N_2O)}{I_{44}(CO_2)} \]

(2)

where the subscripts c, n and m refer to CO₂, N₂O and measured, respectively, and the symbol * stands for either 45 or 46.

The observed raw delta value measured on a mass spectrometer when a CO₂/N₂O mixture has been admitted can be expressed as:

\[ \delta_{45}^m = \frac{R_{45}^*}{R_{reference}^*} - 1 = \frac{\rho E}{1 + \rho E} \left( \frac{R_{45}^* - R_{reference}^*}{R_{reference}^*} \right) + \frac{1}{1 + \rho E} \left( \frac{R_{44}^* - R_{reference}^*}{R_{reference}^*} \right) \]

(3)

Writing the delta values that one would obtain measuring N₂O as if it were CO₂, i.e. versus a CO₂ standard, as:

\[ \delta_{45}^m = \frac{R_{45}^*}{R_{Reference}^*} - 1 \]

(4)

THEORETICAL BACKGROUND

For mass spectrometric stable isotope analysis of carbon dioxide from atmospheric samples, CO₂ has to be separated from the other air constituents. The most widely used procedure for extracting CO₂ is by quantitatively freezing out the CO₂ fraction in a cold trap at liquid nitrogen temperature (−196 °C), combined with a separation step from water vapour, kept at −80 °C. Unfortunately, nitrous oxide (N₂O) an atmospheric greenhouse gas with concentrations around 320 ppb) has very similar physical properties and thus cannot be separated cryogenically from CO₂. Moreover, the masses of the N₂O isotopomers equal those of CO₂ with the main mass numbers 44, 45 and 46 amu. Thus atmospheric N₂O interferes with the mass spectrometric isotope analysis of CO₂, turning the apparent δ¹³C and δ¹⁸O values of CO₂ too negative by (0.21 ± 0.01)%o and (0.30 ± 0.01)%o, respectively.

CO₂ or N₂O gas, with a certain partial pressure p.

\[ \delta_{45}^m = \frac{R_{45}^*}{R_{Reference}^*} - 1 \]

(4)

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and substituting in Eqn. (3), the relation between the measured and the corrected delta values can be given as:

$$\delta^13C_{cation} = \frac{\rho E}{1 + \rho E} \delta^13C_{cation} + \frac{1}{1 + \rho E} \delta^13C_{cation}$$

(5)

Finally, from the last equation the corrected value for CO2 samples, contaminated by co-extracted N2O, can be derived:

$$\delta^13C_{cation} = \delta^13C_{cation} + E(\delta^13C_{cation} - \delta^13C_{cation})$$

(6)

This equation shows that the deviation introduced by the N2O contribution is with a good approximation linearly dependent on the mixing and ionisation efficiency ratios, the variation introduced into the brackets by \( \delta_{cation} \) being negligible as compared with \( \delta_{cation} \) and the measurement uncertainties. Craig and Keeling[22] were in 1963 the first to correct for the mixing ratios of the artificial mixtures used and the series BE using CO2 enriched both in 13C and in 18O. Series AN and series BN/BE were prepared and measured in different time periods with an 18 month time lag. Table 1 gives a summary of the sample descriptions. Doubly labelled CO2 was used in order to highlight possible secondary N2O effects, such as an enhanced cross contamination of the machine working standard due to N2O admitted to the source with the sample. The enriched gas was prepared at the CIO. For the oxygen signature, enriched water, usually employed as tracer in biological applications, was brought into isotopic equilibrium with the CO2 sample. For the carbon signature, CO2 was developed from highly enriched sodium carbonate (98% Na13CO3). The CO2 gas, enriched or not, was transferred into 250 mL stainless steel cylinders, and sealed with two manually operated Nupro valves series H (Nupro Company-Willoughby, OH, USA). The same cylinders were used later also to contain the final samples. After their filling with CO2, the cylinders of each series were connected to a common manifold (pumped to vacuum beforehand) and left open and connected for about a week to allow the gas to be isotopically the same in all the cylinders of a certain batch. This appeared to be sufficient for the natural series only. Repeated measurements of all four cylinders of series BN showed a standard deviation of 0.015% for delta 45 and 0.011% for delta 46 as measured with respect to the machine reference gas. No differences in the composition of the gas could be found in the different containers. Therefore, just one cylinder was used as a test cylinder to directly compare the pure CO2 gas with the N2O-spiked ones. The enriched samples, however, stayed significantly different from each other even after 1 week of diffusive exchange. Thus they had to be characterised individually by repeated independent measurements before the addition of N2O. Furthermore, the oxygen measurements of the enriched samples in particular were influenced by daily variations in the machine behaviour. This could be confirmed by the variations in the measurements of an independent enriched CO2 gas standard (GS-45), routinely measured in three flasks at the end of every measurement day. This part of the test was conducted in early summer, when, according to our experience, the increase in temperature and thus the variability of the laboratory

**EXPERIMENTAL**

Three series of four different artificial mixtures each, i.e. CO2 with N2O traces, were prepared. Series AN and BN were prepared using CO2 with a natural isotopic composition and the series BE using CO2 enriched both in 13C and in 18O. Series AN and series BN/BE were prepared and measured in different time periods with an 18 month time lag. Table 1 gives a summary of the sample descriptions. Doubly labelled CO2 was used in order to highlight possible secondary N2O effects, such as an enhanced cross contamination of the machine working standard due to N2O admitted to the source with the sample. The enriched gas was prepared at the CIO. For the oxygen signature, enriched water, usually employed as tracer in biological applications, was brought into isotopic equilibrium with the CO2 sample. For the carbon signature, CO2 was developed from highly enriched sodium carbonate (98% Na13CO3). The CO2 gas, enriched or not, was transferred into 250 mL stainless steel cylinders, and sealed with two manually operated Nupro valves series H (Nupro Company-Willoughby, OH, USA). The same cylinders were used later also to contain the final samples. After their filling with CO2, the cylinders of each series were connected to a common manifold (pumped to vacuum beforehand) and left open and connected for about a week to allow the gas to be isotopically the same in all the cylinders of a certain batch. This appeared to be sufficient for the natural series only. Repeated measurements of all four cylinders of series BN showed a standard deviation of 0.015% for delta 45 and 0.011% for delta 46 as measured with respect to the machine reference gas. No differences in the composition of the gas could be found in the different containers. Therefore, just one cylinder was used as a test cylinder to directly compare the pure CO2 gas with the N2O-spiked ones. The enriched samples, however, stayed significantly different from each other even after 1 week of diffusive exchange. Thus they had to be characterised individually by repeated independent measurements before the addition of N2O. Furthermore, the oxygen measurements of the enriched samples in particular were influenced by daily variations in the machine behaviour. This could be confirmed by the variations in the measurements of an independent enriched CO2 gas standard (GS-45), routinely measured in three flasks at the end of every measurement day. This part of the test was conducted in early summer, when, according to our experience, the increase in temperature and thus the variability of the laboratory

**Table 1.** The isotopic characteristics of the pure gases (all values are given in % with respect to our machine reference gas) and mixing ratios of the artificial mixtures used

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( \rho ) assigned (mol N2O/mol CO2)</th>
<th>( \rho ) calculated (mol N2O/mol CO2)</th>
<th>( \delta^{13}C_{CO2} ) raw (w.r.t. mach. Ref.) pure gases</th>
<th>SD</th>
<th>( \delta^{18}O_{CO2} ) raw (w.r.t. mach. Ref.) pure gases</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 Series AN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>AN0</td>
<td>0</td>
<td>0</td>
<td>7.11</td>
<td>0.02</td>
<td>-4.22</td>
<td>0.02</td>
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<tr>
<td>AN1</td>
<td>(4.21 ± 0.04)10^-4</td>
<td>4.38 10^-4</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>AN2</td>
<td>(8.39 ± 0.09)10^-4</td>
<td>9.17 10^-4</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>AN3</td>
<td>(1.68 ± 0.02)10^-3</td>
<td>1.82 10^-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN0</td>
<td>0</td>
<td>0</td>
<td>-349.16</td>
<td>0.35</td>
<td>-491.60</td>
<td>0.30</td>
</tr>
<tr>
<td>BN1</td>
<td>(3.59 ± 0.04)10^-4</td>
<td>3.08 10^-4</td>
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<tr>
<td>BN2</td>
<td>(7.25 ± 0.07)10^-4</td>
<td>6.70 10^-4</td>
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<tr>
<td>BN3</td>
<td>(1.45 ± 0.01)10^-3</td>
<td>1.37 10^-3</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CO2 Series BN</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BE0</td>
<td>0</td>
<td>0</td>
<td>446.09</td>
<td>0.02</td>
<td>510.77</td>
<td>0.08</td>
</tr>
<tr>
<td>BE1</td>
<td>(3.61 ± 0.04)10^-4</td>
<td>3.38 10^-4</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BE2</td>
<td>(7.23 ± 0.07)10^-4</td>
<td>6.58 10^-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE3</td>
<td>(1.44 ± 0.01)10^-4</td>
<td>1.35 10^-3</td>
<td></td>
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<tr>
<td>CO2 Series BE</td>
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*Calculated from the ion beam of \( m/z \) 30, according to Eqn. (9).*

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conditions influence the measurement performance. We suspect that traces of water vapour, entering the inlet system with every sample change, affect the cross contamination of the mass spectrometer. Enriched samples with high precision demands are the most susceptible to this.

The addition of N₂O was done by freezing N₂O gas, kept at a known pressure in a calibrated volume, into the sample cylinders cooled down to liquid nitrogen temperature. The mixing ratios assigned volumetrically are accurate to ±1%, taking into account the errors in the pressure, temperature and volume determinations.

The N₂O/CO₂ mixing ratios (see Table 1) vary largely around the atmospheric mixing ratio. We roughly aimed at one ‘blank’ sample, containing pure CO₂, one sample at half of the present atmospheric mixing ratio (0.4%), one sample at the present atmospheric mixing ratio (0.8%), and one sample with double the present atmospheric mixing ratio (1.6%).

The assigned mixing ratios were checked by inference based on the mass spectrometric determination of the ion current of m/z = 30 (NO⁻) and after subtraction of the background signal representing fragments, mainly ¹²C¹⁸O, produced from CO₂ ([(13)CO₂]¹⁹) divided by that of CO₂ of natural isotopic composition.

\[
\frac{[N_2O]}{[CO_2]}_{SAMPLE} = \frac{(130)_{SAMPLE} - (130)_{SAMPLE}}{(130)_{STANDARD} - (130)_{STANDARD}} \times \frac{[N_2O]}{[CO_2]}_{STANDARD}
\]

The standard for this ‘mass 30’ N₂O determination was produced volumetrically, in a similar way as described above for the mixtures; it had a N₂O/CO₂ ratio of 0.0089, prepared volumetrically, in a similar way as described above.

The mass spectrometric response to different inlet pressures of the pure gases used for the mixtures is shown in Fig. 1(a). These results show a clear picture of the non-linear response of the ionisation yield at different inlet pressures of a gas. The assumption that the relative yield of the two species is independent of the gas pressure in the ion source, commonly adopted to estimate E for a given mass spectrometer, is clearly not even applicable in the case of pure gases. Considering a pressure domain between 15 and 32 hPa, E is estimated to vary from 0.80 to 0.87, for the N₂O yield compared with that of enriched CO₂, and from 0.78 to 0.83, when the N₂O yield is compared with that of natural CO₂. Approximately at the centre of this range, 24 hPa for enriched CO₂ and 23 hPa for natural CO₂, are the inlet pressures that give a m/z = 44 current of about 4 nA, on which reference and sample beam are normally adjusted for the measurement. At these inlet pressures N₂O produces signals of 3.4 and 3.2 nA, that give E values of 0.85 and 0.80, respectively, with a difference too large to be explained simply by isotope mass balance considerations. Besides this, both these estimations differ from the best guess of E (0.75) obtained from measurements on the artificial mixtures as described below.

The plot in Fig. 1(c) compares the behaviour of pure enriched CO₂, the same as used for the mixture, pure N₂O and a mixture of the two in equal parts. The behaviour of the mixture does not follow quantitatively the expected response estimated from the behaviour of the pure gases (solid line in the plot).

A summary of the measurements on the artificial mixtures is given in the plots in Figs. 2–4. The averages of the measurements (5 and 10 repetitions, respectively, on AN and BN) on the ‘natural CO₂’/N₂O mixtures have been reported as completely raw data in terms of delta 45 and delta 46 on the machine working gas scale. The linear relationship expressed by Eqn. (6) is completely fulfilled. Regression analysis between the isotopic results and the assigned mixing ratios shows values comparable to each other and to those reported in the previous paragraph.
in the literature: for the coefficients we find $E_{\Delta_{45}^{14}}$ of $-(268 \pm 10)\%$ and $-(267.7 \pm 6.0)\%$, and $E_{\Delta_{46}^{14}}$ of $-(378 \pm 19)\%$ and $-(320 \pm 20)\%$, for the AN and BN series, respectively. If we assume an atmospheric N$_2$O/CO$_2$ mixing ratio of 0.85\% computed from the most recent concentrations and trends given for both species by Houghton et al.,$^{24}$ then the corrections to be applied would be 0.23 and 0.30\% for $\delta^{13}$CO$_2$ and $\delta^{18}$CO$_2$, respectively. Some $\delta^{13}$CO$_2$ values of the BN series have suffered from the consequences of traces of water in the mass spectrometer inlet. This is even more so for the values of the enriched series (BE), measured during the same period. For obvious reasons the samples of the BE series could not be measured with the same accuracy as the natural series. However, the isotope ratios show a linear dependence of the mixing ratio (\(\rho\)) as described in Eqn. (6), with a coefficient $E(\delta^{13}_{\Delta_{45}^{14}} - \delta^{13}_{\Delta_{45}^{14}})$ estimated from a least-squares fit to be $(583 \pm 33)\%$ for $E_{\Delta_{45}^{14}}$ and $(910 \pm 90)\%$ for $E_{\Delta_{46}^{14}}$. These coefficients depend on $\delta^{13}_{\Delta_{45}^{14}}$, so they increase as the CO$_2$ gas gets enriched. As mentioned above, in this case, the deviation from the CO$_2$ gas present in each cylinder before the addition of N$_2$O had to be regarded, instead of the absolute \(\delta\)-value. Comparing the theoretical corrections with those measured, no peculiar effects or evident deviations from the expectations can be shown, indicating that no evident secondary effects due to N$_2$O 'contamination' can be proven.

As the conclusive step of this experiment, we assigned the best estimate for the ionisation efficiency ratio $E$ according to

Figure 1. Mass spectrometric response to different inlet pressures of the pure gases used for the mixtures. (a) $m/z = 44$ currents versus the pressure registered by the inlet transducer of the VG SIRA series II mass spectrometer. (b) Relative ionisation efficiency ($E$) of N$_2$O compared with CO$_2$ natural and enriched, calculated from pure gases. Symbols represent $E$ values computed as the ratio of the N$_2$O and CO$_2$ $m/z = 44$ at the same inlet pressure. The lines are computed from the cubic spline fits in (a). (c) Representation of the behaviour of a 1:1 mixture compared with that of its pure gas constituents. The solid line in the plot is the calculated mean response of those of the pure gases.
the measurements conducted on the mixtures belonging to the AN, BN and BE series. $\delta^{46}$CO$_2$ values have been excluded from the best estimation of the E parameter, because some of them, belonging to the BN and BE series, suffered from the consequences of traces of water in the inlet of the mass spectrometer.

The deviation of the true $\Delta^{45}$CO$_2$ values from those computed applying Eqn. (6) is:

$$\Delta^{45}$CO$_2 = \delta^{45}_m - \left[ \left( \delta^{45}_c - \delta^{45}_m \right) E \right]$$

$\Delta^{45}$CO$_2$ must be equal to zero when the correct parameters are applied. As ‘true value’ for ($\delta^{45}_c$) we took the original CO$_2$ composition of the samples before the N$_2$O spiking. This is a single value per series for the natural mixtures AN and BN, as measured on the pure CO$_2$ samples along with the mixtures. For the enriched series individual ‘true values’ were assigned to each different mixture, according to the initial isotopic composition of the pure CO$_2$ gas. The results of this exercise are reported in Figs. 5(a) (series AN), 5(b) (series BN), and 5(c) (series BE), respectively, in which we plotted the results for E values from 0.6 to 0.9, in steps of 0.02. The closer the arbitrary E values get to the best E value, the more the corrected values approach the true pure CO$_2$ value and the deviations $\Delta^{45}$CO$_2$ tend to be constant at 0. A summary of this simulation can be obtained by plotting versus E the slope or the correlation coefficient of the regression line through the different data sets obtained by each value of E (shown in Fig. 6). The definition of the best E value to be assigned to the VG SIRA series II instrument is given by the intercept of the slope or the correlation coefficient functions with the x-axis, associated to a horizontal line (slope $= 0$) fitting perfectly uncorrelated values.

As shown in Fig. 6, the best value for E is 0.749 $\pm$ 0.003, showing no correlation at all between the final CO$_2$ isotopic values with changing CO$_2$/N$_2$O ratios. The estimation derived from the analysis of the mixtures containing enriched CO$_2$ is just slightly higher (0.750) than the estimations based

Figure 2. Isotope measurements on series AN N$_2$O/CO$_2$ mixtures. Mass ratios 45/44 (left axis) and 46/44 (right axis) are expressed as $\delta^{45}$CO$_2$ and $\delta^{46}$CO$_2$, respectively. [N$_2$O]/[CO$_2$] is the partial pressure ratio of N$_2$O to CO$_2$. The symbols represent the average of repeated measurements, their standard error is given as error bars ($\pm$1$\sigma$/n). Least-squares regression leads to: $\delta^{45}_{m}$CO$_2$ = (7.11 $\pm$ 0.01) – (268 $\pm$ 10)[N$_2$O]/[CO$_2$]; $\delta^{46}_{m}$CO$_2$ = (– 4.22 $\pm$ 0.01) – (378 $\pm$ 19)[N$_2$O]/[CO$_2$]. The present [N$_2$O]/[CO$_2$] mixing ratio is indicated in the figure as a vertical line; it is computed from the most recent (2001) concentrations and trends given for both species by Houghton et al.$^{24}$

Figure 3. Isotope measurements on series BN N$_2$O/CO$_2$ mixtures. Least-squares regression leads to: $\delta^{45}_{m}$CO$_2$ = (6.79 $\pm$ 0.01) – (267.7 $\pm$ 6.0)[N$_2$O]/[CO$_2$]; $\delta^{46}_{m}$CO$_2$ = (– 0.36 $\pm$ 0.01) – (320 $\pm$ 16)[N$_2$O]/[CO$_2$]. For further description, see Fig. 2.

Figure 4. Isotope measurements on series BE N$_2$O/CO$_2$ mixtures. The apparent change in isotopic composition ($\delta^{45}$CO$_2$, left axis, and $\delta^{46}$CO$_2$, right axis) is shown as the deviation from the individual CO$_2$ gas composition present in each cylinder before the addition of N$_2$O. The error bars give the standard errors of repeated measurements after N$_2$O spiking. Least-squares regression leads to: ($\delta^{45}_{c}$CO$_2$ – $\delta^{45}_{m}$CO$_2$) = (583 $\pm$ 33)[N$_2$O]/[CO$_2$]; ($\delta^{46}_{c}$CO$_2$ – $\delta^{46}_{m}$CO$_2$) = (910 $\pm$ 90)[N$_2$O]/[CO$_2$].
on natural mixtures, as is expected from mass balance considerations. This testifies to the absence of any provable secondary effect due to the N₂O admitted to the source of a mass spectrometer together with the sample.

CONCLUSIONS

In order to achieve very accurate atmospheric CO₂ isotopic determinations, a very accurate N₂O correction has to be applied. We did not find any secondary effects produced by N₂O different from the barometric additions on \( m/z = 44, \ m/z = 45, \ m/z = 46 \), as shown by the behaviour of enriched CO₂ samples spiked with N₂O. However, evidence of non-linear response to the inlet pressure of the pure gases and a different behaviour of these compared with mixtures of CO₂ with traces of N₂O suggest a careful determination of the relative ionisation efficiency used as parameter in the N₂O correction algorithm. In particular it is recommended to estimate the N₂O correction to be applied for each machine from mixtures of well-known mixing ratios in the range of the measured samples, and using the same settings of the IRMS source as for the actual measurements. This procedure is preferable over the application of the theoretical algorithms with the E parameter being derived from pure gas measurements. For our VG SIRA series II, we find as best value for the ionisation efficiency ratio \( E = 0.75 \). This results in a correction of 0.23% for \( \delta^{45} \)CO₂ and of 0.30% for \( \delta^{46} \)CO₂, for atmospheric samples with 0.85% N₂O/CO₂ mixing ratio. Regarding our results, we conclude that it is unlikely that N₂O effects cause the difference between pure gas and whole air CO₂ results between CIO and SIO. The N₂O corrections made for \( \delta^{45} \)CO₂ were almost the same (0.217 and 0.210% for CIO and SIO, respectively, for 1992–1994 air with mixing ratios around 0.87%\(^{15} \)). To explain the difference of over 0.05% in \( \delta^{45} \)CO₂ we would have to assume drastic errors in these values, and thus in the E determination of the IRMS systems involved. Furthermore, as our results show that secondary effects of N₂O are absent, the differential drifts between pure CO₂ and atmospheric CO₂ that many groups observe cannot be blamed on N₂O either. However, the CIO-SIO comparison shows that, besides the cryogenic extraction, there must be other sources of error and deviation, yet to be identified.
REFERENCES