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A method to induce and assess isotopic equilibrium of oxygen

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Abstract

As part of the preparation of a primary isotopic gas standard (PIGS) for oxygen, a study was carried out to assess the feasibility of developing a method for the preparation of a gravimetrically prepared isotope mixture of oxygen. Enriched $^{18}O_2$ and O_2 of natural isotopic composition were mixed gravimetrically. Several procedures were investigated to attain isotopic equilibrium of this mixture, i.e., the isotopic species distribution obeying the statistical probability. Pt and Ag powder were used as catalysts. Mass spectrometric measurements were carried out on the mixture before and after isotopic equilibration. The observed values for the isotope ratios $J^0_{17/16}$ and $J^0_{18/16}$ were compared to computed values, using standard equations, for non-equilibrated mixing and for isotopic equilibrium. As a result, isotopic equilibration of the oxygen mixture was achieved. A method is proposed to assess isotopic equilibrium via a ratio consistency factor $\chi(^{i}O)$, which is a measure of the closeness of the observed ion current ratios for the prepared mixture to the computed ion current ratios for ideal isotopic equilibrium. In this study, the value of $\chi(^{18}O) = 0.0006\ (21)$ for the prepared mixture, with combined uncertainty u_c given in parentheses applying to the last two digits ($\chi = 0$ for complete equilibration). Preliminary conversion factors for oxygen ratio measurements $K_{\text{conv}} = 0.997\ (54)$ for $n(^{18}O)/n(^{16}O)$ and $K_{\text{conv}} = 0.990\ (28)$ for $n(^{17}O)/n(^{16}O)$ were derived from the comparison of the observed ion current ratios with the gravimetrically prepared isotope amount ratios. As a result of this study, the main areas of improvement in view of the preparation of a final gravimetric oxygen isotope mixture were exposed and discussed thoroughly. (Int J Mass Spectrom 214 (2002) 233–246) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Isotopic equilibrium of oxygen; Gas isotope mass spectrometry; Synthetic isotope mixtures; Isotope amount ratio; Oxygen; Traceability

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1. Introduction

Mass spectrometric measurements of the isotopic composition of oxygen have been performed for decades due to their major impact in various scientific fields such as geochemistry, environmental sciences and climate studies. For most of these applications precise measurements of differences in the isotopic composition of an unknown sample to a reference were carried out. The results of these so-called "δ-measurements" for oxygen are expressed on the δ^{18}O-scale, expressed in ‰, with Vienna Standard Mean Ocean Water (V-SMOW) adopted as zero point of this internationally recognised scale.

$$\delta^{18}O_{(\text{sample}/\text{V-SMOW})} = \left[\frac{R_{18/16\,(\text{sample})} - R_{18/16\,(\text{V-SMOW})}}{R_{18/16\,(\text{V-SMOW})}}\right] \times 1000$$

In general, the isotopic composition of oxygen in geological samples is measured by conversion to

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CO_2. Water samples are equilibrated with CO_2 for indirect $^{18}O_2$-analysis, carbonates are digested with phosphoric acid to produce CO_2, organic matter is combusted to give CO_2, minerals are reduced with graphite for subsequent conversion to CO_2 for direct $^{18}O_2$-analysis. Taking into account, correction for isobaric ions ($^{13}C^{16}O^{17}O^{+}$), the $n(^{18}O)/n(^{16}O)$ amount ratio can be determined via measurements of the main ion species $^{12}C^{16}O^{18}O^{+}$ at $m/z = 46$. CO_2 is not a suitable gas for determining $n(^{17}O)/n(^{16}O)$ because of the minor abundance of $^{12}C^{16}O^{17}O^{+}$ ions and due to interference of isobaric ions of $^{13}C^{16}O_2{}^{+}$ at $m/z = 45$. In isotope geochemistry, $n(^{17}O)/n(^{16}O)$ is derived from the $n(^{18}O)/n(^{16}O)$ measurements by a linear relation factor $\delta^{17}O = a\delta^{18}O$ where a is an average correlation factor observed in terrestrial samples [1,2].

If there is mass dependent fractionation for oxygen isotopes, then it follows this relationship. There are some application fields that are focusing on isotopic anomalies of oxygen, where significant deviations from this relationship have been observed. In this case, direct measurement of the isotopes on O_2 gas becomes indispensable. Mass-independent isotopic fractionation of oxygen in carbonaceus chondritic meteorites were reported [3]. Similar effects were observed measuring ozone isotopic composition in the stratosphere [4]. Particularly the investigation of photochemical processes occurring in the earth's upper atmosphere resulting in isotopically characteristic processes which are mass independent, is one field of research, where methods of oxygen separation from air and direct measurements of oxygen abundances play a key role [5,6]. Therefore, methods have been developed to transform water [7] or CO_2 into O_2 gas to enable the direct measurement of $n(^{17}O)/n(^{16}O)$, expressed as $\delta^{17}O$ values [8].

In the 1950s, one of the pioneers of mass spectrometry, Nier, published his famous series of highly reliable isotopic measurements on several gases, amongst them also oxygen. In his work, volumetrically prepared argon isotope mixtures were employed to correct for isotopic fractionation effects occurring during the measurement. At that stage Nier's measured isotope amount ratios for oxygen were the closest realisation of "accurate ratio" measurements of oxygen [9]. In 1961, "absolute" values of the isotope amount ratios in V-SMOW were calculated and reported based on Nier's results obtained by calibration with synthetic argon mixtures [10]. Some 25 years ago, direct abundance measurements of $^{18}O_2$ in V-SMOW have been performed [11]. In 1988, the abundance of $^{17}O_2$ was directly measured in V-SMOW [12]. Those values were adopted as "Best measurements from a single terrestrial source" from the International Union of Pure and Applied Chemistry, IUPAC [13]. For these measurements, gravimetrically prepared oxygen isotope mixtures were not used for calibration purposes, nor was it documented that the measurement results were directly linked to fundamental constants of the SI, by using special equipment.

As in all sectors, also in stable-isotope hydrology and geochemistry the comparison of results obtained by different laboratories is essential. Measurements on the $\delta^{18}O$ scale are without any doubt a very useful tool, but they refer to a prepared artefact (V-SMOW). So far this, $\delta^{18}O$ scale is not anchored via values, gained through accurate measurements of oxygen isotopes, to fundamental inalterable constants in nature. Traceability to SI by means of accurate isotope measurements is an indispensable link to an "absolute" measurement scale as soon as reliability and comparability of results over an extended period of time are required. Having reliability of measurement results and the need for direct measurements of oxygen gas for specific applications in mind, the purpose of this feasibility study was to assess the potential of preparing a synthetic isotope mixture for the envisaged preparation of a primary isotopic gas standard (PIGS) for oxygen, with certified SI-traceable values. The challenge in preparing a synthetic mixture of isotopically enriched oxygen "parent gases" is to develop a suitable catalytic procedure in order to establish isotopic equilibrium of the mixture, taking into account the physical properties of oxygen and of a suitable metal catalyst enabling the equilibration process. No publicly accessible study on oxygen isotopic equilibration could be found. In previous studies on fragmentation analysis of nitrous oxide, the conversion of N_2O into $N_2 + O_2$ with a gold catalyst at 700 °C was reported [14,15]. To apply a mathematical model describing gas adsorption effects in mass spectrometric measurements, a synthetic isotope mixture prepared of enriched carbon-dioxide isotopes was investigated for isotopic equilibrium. In this study, equilibrium of the mixture was achieved using a Pt catalyst at 500 °C [16].

In our work, a similar approach based on the experience of the two studies mentioned above was used to prove the feasibility of assessing isotopic equilibrium of oxygen. The intention is to communicate our promising assessment study to scientists working in fields where direct measurement of O_2 is mandatory and to create awareness of the need of anchoring δ-scales in “absolute” measurement scales. The final objective of preparing a PIGS for oxygen still requires more theoretical and experimental work.

2. A mathematical procedure to assess the extent of equilibration for oxygen isotopic species

Provided that the ion source parameters of the mass spectrometer are optimised, oxygen molecules are ionised with the highest ionisation probability to ${O_2}^+$. This enables the most abundant oxygen ion current intensities to be observed at $m/z = 32$–36. Assuming that all the isotopic species follow the most probable distribution, the relative abundance of the major isotopic oxygen species is proportional to the probability of their occurrence (Table 1). For oxygen gas of highest purity, the oxygen abundances can be derived from measurements at $m/z = 32$–34 [16–19].

Table 1
Most abundant isotopic species of oxygen

m/z	Species	Fractional abundance
32	$^{16}O_2$	$(f_{16})^2$
33	$^{16}O^{17}O$	$2f_{16}f_{17}$
34	$^{16}O^{18}O, {}^{17}O_2$	$2f_{16}f_{18}$, $(f_{17})^2$
35	$^{17}O^{18}O$	$2f_{17}f_{18}$
36	$^{18}O_2$	$(f_{18})^2$

$$R_{33/32} = \frac{2f_{17}}{f_{16}} \quad \text{and} \quad R_{34/32} = \frac{2f_{18}}{f_{16}} + \frac{(f_{17})^2}{(f_{16})^2}. \qquad (1)$$

$R_{k/l}$ is the ratio of the numbers of molecules of the major abundant isotopic oxygen species with mass number $k = 33$–36 to the numbers of molecules with mass number $l = 32$.

For isotopic disequilibrium, the isotopic species distribution does not obey the statistical probability. The oxygen abundances then cannot even be derived from measurements at $m/z = 32$–36, because the relative proportion of the isobaric molecules $^{16}O^{18}O$, and $^{17}O_2$ is unknown (Table 1). The equation system cannot be solved. Therefore, it is mandatory to verify and, if needed, to induce isotopic equilibrium in the gas. Only for oxygen in isotopic equilibrium, accurate values of the oxygen isotope abundances can be derived from measurements of the most abundant ion currents, applying Eq. (1).

2.1. Ratio consistency factor $\chi(^iO)$

A ratio consistency factor $\chi(^iO)$ can be introduced, which is a measure of the degree of equilibration of the mixture. $R_{i/j} = n(^iO)/n(^jO)$, $i = 17$ or 18, $j = 16$:

$$\chi(^iO) = \left\| 1 - \frac{R_{i/j}}{R_{(i/j)\text{cons}}} \right\|. \qquad (2)$$

The degree of isotopic equilibration can be expressed by means of the ratio consistency factor, assuming an isotopically completely equilibrated oxygen mixture was prepared by mixing fully enriched $^{16}O_2$, $^{17}O_2$, $^{18}O_2$.

$$R_{17/16} = \frac{R_{33/32}}{2} \quad \text{or} \quad R_{17/16\,\text{cons}} = \frac{R_{35/32}}{2\sqrt{R_{36/32}}} \quad \text{and}$$

$$R_{18/16} = \frac{4R_{34/32} - (R_{33/32})^2}{8} \quad \text{or}$$

$$R_{18/16\,\text{cons}} = \sqrt{R_{36/32}}.$$

For an equilibrated oxygen sample with isotopic species distributed according to statistical probability, all the ratios are perfectly consistent. This reflects the ideal case of $\chi(^i\mathrm{O}) = 0$ for a gas in isotopic equilibrium.

3. Experimental

3.1. Preparation of the oxygen isotope mixture

Oxygen of natural isotopic composition and oxygen 95% enriched in ^{18}O were used as “parent gases”. In view of investigating isotope exchange reactions due to mixing, an oxygen test mixture was prepared with an isotopic composition deviating by about one order of magnitude from the natural isotopic composition of oxygen. In such a mixture, all the isotopic species would be sufficiently abundant to yield statistical acceptable signal levels of the created ion currents, so that the ratio consistency of the mixture could be verified experimentally.

3.2. The mixing equipment and the mixing routine

The mixing of the two components was directly monitored on the “Avogadro II amount comparator”, an IRMM-modified Finnigan MAT-271 mass spectrometer [20]. Fig. 1 shows a scheme of the upgraded inlet system for isotope mixing of oxygen.

The empty 50 mL mixing cylinder was weighed and subsequently filled with 70 mg catalyst powder. Then the same cylinder was attached to the upgraded gas inlet system, evacuated with the fore-pump and heated to 200 °C to remove impurities. The mixing cylinder was evacuated to approximately 10^{-6} Pa. Accurate weighing before and after this “hot-evacuation” confirmed that there was no significant loss of catalyst volatiles during this procedure.

The enriched “parent gas”, sample B, was transferred from the supplier bottle via the “transfer finger” into the mixing cylinder (Fig. 1). After the evacuated mixing cylinder had been weighed, the supplier bottle with oxygen of natural isotopic composition, sample A, was attached and the gas inlet system evacuated. Sample B was transferred into the mixing cylinder. Subsequently, the cylinder containing the prepared test mixture was again accurately weighed.

3.3. Improved cooling gas transfer

In general, the main concern during the preparation of a gaseous isotope mixture is to avoid isotope effects, losses of precious material and to minimise the

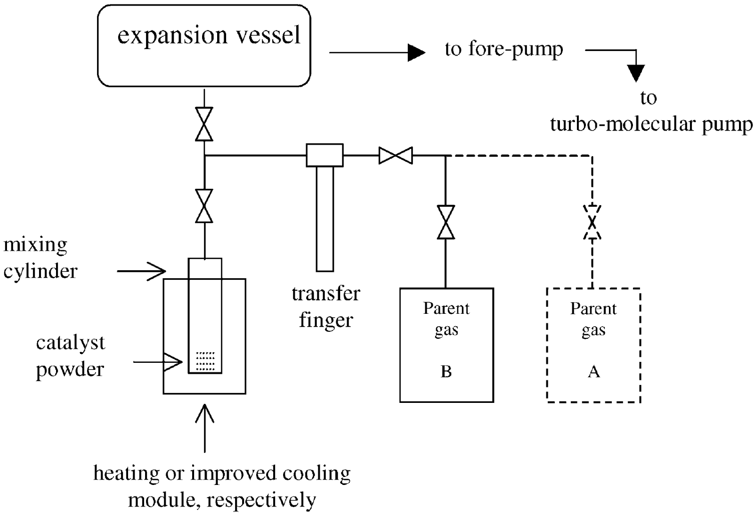

Fig. 1. Upgraded gas inlet system for isotope mixing of oxygen.

risk of introducing impurities. Therefore, low temperature gas transfer is often applied for preparing gaseous synthetic isotope mixtures [16,21]. In case of transferring oxygen gas, the regular cooling with liquid nitrogen is not applicable because of the physical properties of oxygen (b.p. $O_2 = -183\,^{\circ}C$ at atmospheric pressure). The saturated vapour pressure of oxygen is about 2×10^4 Pa at liquid nitrogen temperature [22]. Hence, an "improved cooling module" had to be developed to achieve complete gas transfer for the mixing of the two oxygen components.

Improved cooling gas transfer enables more nitrogen molecules into the gas phase, by creating a vacuum in the closed dewar. During this process, the temperature of the remaining liquid nitrogen phase decreases. To transfer the oxygen mixture components from the supplier bottles into the mixing cylinder the special "cooling module" had the following features: a tightly close dewar with a teflon lid with an opening in the centre, fitting exactly the dimensions of the mixing cylinder. There are two apertures, one for low temperature monitoring, and another one to avoid uncontrolled pressure rise. The whole system is placed on a magnetic rotator and connected to a mechanical pump for evacuation.

By means of "improved cooling" the temperature of the liquid nitrogen, the mixing cylinder was placed into, could be decreased to $-208\,^{\circ}C$, which is suitable for oxygen condensation (O_2: at $T = -210\,^{\circ}C$, vapour pressure $\approx 25 \times 10^2$ Pa).

3.4. The gravimetric mixing process

The accurate weighings were performed on a METTLER (69) Type B5C 1000 balance. The mass of the mixture components was calculated from the difference in weight of the mixing cylinder before and after each transfer, taking into account the required waiting time for the gas in the cylinder to equilibrate at ambient conditions. The atmospheric pressure, the relative humidity and the temperature were recorded during the weighing, in order to correct the weighing results for buoyancy. Moreover, also corrections originating from the presence of impurities in the "parent gases" were made, i.e., a complete uncertainty budget of the weighing was established. Finally, an oxygen test mixture was prepared with a gravimetric mixing ratio of sample A ($^{18}O_2$) to sample B ($^{nat}O_2$) of 57:1 (Table 2). The relative uncertainty of the weighing was higher compared to accurate weighings performed on krypton and xenon isotopes in the past, due to constraints of the equipment [23]. The weighing result within its uncertainty was considered acceptable in order to prepare a preliminary oxygen isotope mixture investigating isotopic equilibration behaviour. Already at this stage, it was obvious that the uncertainty of the weighing would have a major impact on the overall uncertainty of the prepared oxygen ratios.

Table 2
Gravimetrically prepared oxygen mixture components with combined uncertainties u_c (applying to the last two digits)

	Mass/10^{-3} kg
Sample A: ($^{18}O_2$)	0.0158 (10)
Sample B: ($^{nat}O_2$)	0.9031 (10)

4. Direct isotope amount ratios measurements of oxygen using the Avogadro procedure

All the measurements of samples A and B as well as of the prepared mixture were carried out on the "Avogadro II Amount Comparator", an IRMM-modified Finnigan MAT-271 mass spectrometer, applying the thoroughly documented "Avogadro II amount comparator method" [24]. This measurement procedure was developed for high accuracy measurements of the molar mass of silicon in the framework of the redetermination of the Avogadro constant, enabling isotope amount ratio measurements to a relative (combined) uncertainty on $[n(^{i}Si)/n(^{28}Si)]$ of 1×10^{-5} [25].

Sample A, oxygen of natural isotopic composition, was measured in symmetrical sequences from $m/z = 32$ to 34. Sample B, oxygen enriched in ^{18}O, and the prepared oxygen mixture were measured from $m/z = 32$ to 36 and back. The light oxygen isotopic species effuse from the expansion vessel into the ion source of the mass spectrometer at a higher rate than the heavy isotopic species, following a well-known first-order reaction [26].

$$\ln\left[\frac{I(^{i}\mathrm{O}_2)}{I_0(^{i}\mathrm{O}_2)}\right] = -k_{^{i}\mathrm{O}_2}t$$

with $I(^{i}\mathrm{O}_2)$ the observed current transported by ions of the oxygen molecule with mass $M(^{i}\mathrm{O}_2)$ and $I_0(^{i}\mathrm{O}_2)$ the same current extrapolated to time $t = t_0$ where

$$\frac{k_{^{i}\mathrm{O}_2}}{k_{^{j}\mathrm{O}_2}} = \left[\frac{M(^{i}\mathrm{O}_2)}{M(^{j}\mathrm{O}_2)}\right]^{-\phi} = \frac{K_{\mathrm{mad}}(^{i}\mathrm{O}_2)}{K_{\mathrm{mad}}(^{j}\mathrm{O}_2)}$$

is the effusion fractionation factor (*j*: most abundant isotopic species). For ideal gas behaviour, $K_{\mathrm{mad}}(^{i}\mathrm{O}_2)/K_{\mathrm{mad}}(^{j}\mathrm{O}_2)$ is inversely proportional to the square root of masses of the measured isotopes ($\phi = 1/2$). During the measurement, the gas remaining in the inlet system becomes progressively enriched in the heavy isotopic species. Hence, the initial isotope amount ratio is obtained by extrapolation of the oxygen ion currents to time $t = t_0$, the instant when effusion started.

The routine procedure for oxygen measurements is to measure the background signal on $m/z = 32$–36 in the mass spectrometer prior to the isotope ratio measurements of an oxygen sample. These background readings were subtracted from the ion current readings when an oxygen gas sample was introduced into the mass spectrometer. Subsequently, the ion current ratios of the oxygen molecule species ($\ln J_{k/l}$) only originating from the sample were calculated by extrapolation of

$$\ln J^0_{k/l} = \ln\left[\frac{I(^{i}\mathrm{O}_2)_{\mathrm{sample}} - I(^{i}\mathrm{O}_2)_{\mathrm{backgr}}}{I(^{j}\mathrm{O}_2)_{\mathrm{sample}} - I(^{j}\mathrm{O}_2)_{\mathrm{backgr}}}\right]$$

to $t = t_0$.

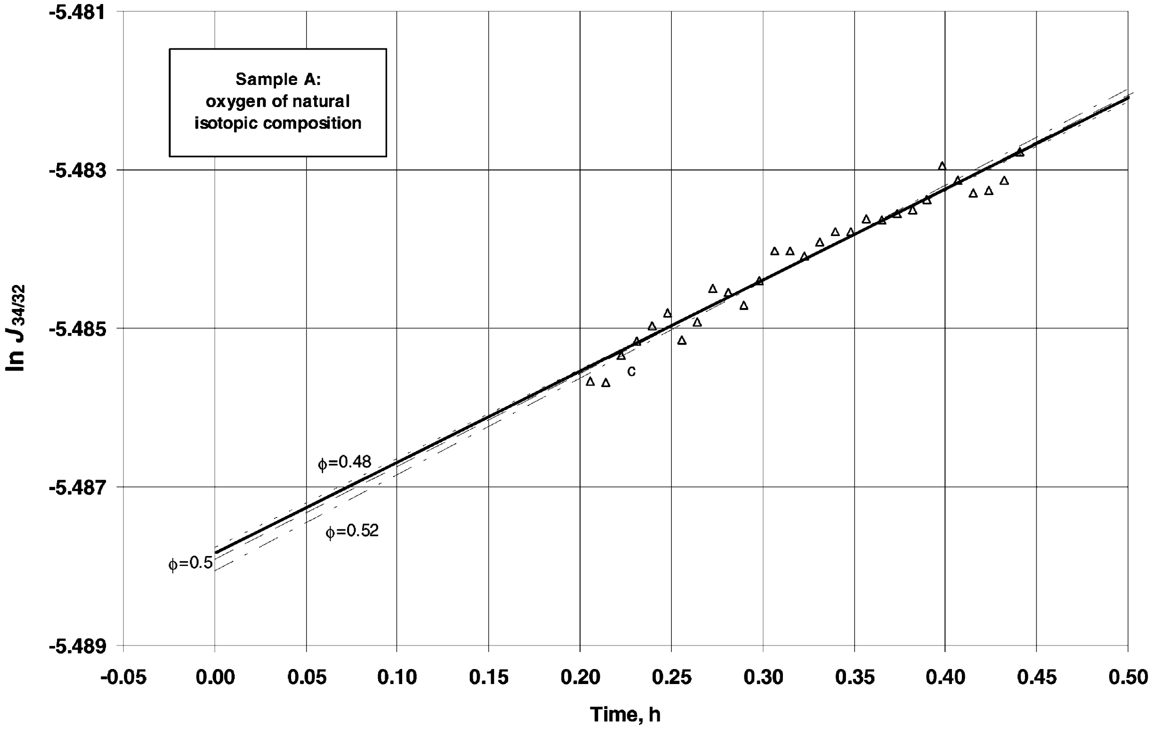

Fig. 2. Fitting of the ion current ratio $\ln J_{34/32}$ for $\phi + \Delta\phi$ ($\phi = 0.5$, $\Delta\phi = \pm 0.02$). The solid line, representing the linear fit of the measurement data, is next to the dashed line, the fit for ideal gas behaviour ($\phi = 0.5$), and within the two other lines representing the fit for $\phi = 0.48$ (dotted line) and $\phi = 0.52$ (dashed–dotted line).

Applying the "Avogadro amount comparator method" the values of the measured ion current ratios can be evaluated for their closeness to values as obtained for ideal gas behaviour of the oxygen in the mass spectrometer. Fig. 2 demonstrates the closeness to ideal gas behaviour of the extrapolated $\ln J^0_{34/32}$ for a single measurement run of sample A.

4.1. Background stability and isobaric interference

A challenge of this study was to measure the small ion currents for less abundant isotopic species. Emphasis was particularly put on measurements of nitrogen, indicating possible contamination in the mass spectrometer and/or in the "parent gases".

Additionally to instrumental background measurements from $m/z = 32$ to 36, measurements on $m/z = 28$ (nitrogen peak) were carried out, without an oxygen sample being introduced, over a period of four months in order to investigate the background stability in the mass spectrometer. As expected, the main instrumental background ion current readings were at $m/z = 28$ and $m/z = 32$. The ion current readings for the other isotopic oxygen species were close or beyond signal detection limit. The observed average isotope ratio for ion current readings of the isotopic species $^{16}O_2/^{14}N_2$ was 0.343 (30), which did not correspond to the ratio (natural $^{16}O_2/^{14}N_2$ is about 0.234) as expected for air contamination either occurring during the mixing or the measurements. During one measurement run significant instability was observed for a 10 hour instrumental background measurement. An increasing ion current signal at $m/z = 28$ was correlated to a decreasing signal at $m/z = 32$, but this effect was not reproducible for an instrumental background measurement performed 3 months later. More measurements will have to be made in the future in view of instrumental background stability. It has to be further investigated whether instability could result from compounds created during the measurement itself, interfering with the signals on $m/z = 28$ and $m/z = 32$ or/and from significant adsorption–desorption effects, acting like a virtual leak [27]. In general, it has to be said that due to poor statistics of ion current readings for instrumental background measurements, conclusions for the origin of instabilities have to be drawn very carefully.

4.2. Purity of oxygen samples

Chemical purity scans were also performed on the "parent gases" during this feasibility study. The results of the major abundant impurities are listed in Table 3. It can be seen that the chemical purity of sample A was acceptable for isotope mixing purposes, whereas in sample B increased impurity levels were observed, indicating air contamination, maybe due to handling of this sample in the past. For the preparation of a final synthetic isotope mixture of highest metrological quality a nitrogen impurity level of 3.3 vol.% would not have been acceptable. In the scope of this study, the preparation of a test mixture to assess isotopic equilibrium, sample B was nevertheless used for mixing. Corrections for weighing results and uncertainty propagation were applied, respectively.

Additionally, an impurity scan was performed on another oxygen sample enriched in ^{18}O, taken from the same supplier batch as sample B, which was not used for mixing. The results in Table 3 show that the chemical purity of this sample was far better at 0.9995 (33) mol(O_2)/mol(gas).

Table 3
Chemical purity of oxygen samples

Determined impurities	Amount in 10^2 times mol(impurity)/mol(O_2)		
	Sample A	Sample B	$^{\text{enr}\,18}O_2$ not used for mixing
N_2	<0.003	3.303	<0.03
Ar	<0.001	0.161	<0.01
CO_2	<0.001	<0.05	<0.01
Chemical purity in mol(O_2)/mol(gas)	≥0.99995 (33)	≥0.968 (61)	≥0.9995 (33)

4.3. Isobaric interference due to carbonmonoxide formation

Measurement results of $J_{k/32}$ for sample B were strongly biased. Because of the high nitrogen impurity level of sample B, which could have been caused by a contamination of air, a correction was applied to the measured isotope ratios as follows:

$$\ln J^{0}_{k/l} = \ln\left[\frac{I\,({}^{i}\mathrm{O}_2)_{\mathrm{sample}} - I\,({}^{i}\mathrm{O}_2)_{\mathrm{backgr}} - [((I^{14}\mathrm{N}_2)_{\mathrm{sample}} - I\,({}^{14}\mathrm{N}_2)_{\mathrm{backgr}}]/3.731)\,f_k}{I\,({}^{j}\mathrm{O}_2)_{\mathrm{sample}} - I\,({}^{j}\mathrm{O}_2)_{\mathrm{backgr}} - [((I^{14}\mathrm{N}_2)_{\mathrm{sample}} - I\,({}^{14}\mathrm{N}_2)_{\mathrm{backgr}}]/3.731)\,f_l}\right]$$

This correction was not successful. Instead, it was highly probable that the isobaric effect at $m/z = 32$ in the measurements of sample B originated from reactions of the tungsten filament with oxygen. Particularly formation of $^{12}C^{16}O$ during the measurement should lead to an interference at $m/z = 28$ and would therefore, significantly bias the measurements of the ion currents of oxygen. This assumption was confirmed by measurements of the unequilibrated mixture which showed significant ion currents not only at $m/z = 28$ and 29, as expected for nitrogen impurity, but also at $m/z = 30$ which strongly indicated $^{12}C^{18}O$ formation. Moreover, there was also a significant ion current observed at $m/z = 44$ (CO_2 peak) that was three times the signal as observed at $m/z = 40$ (Ar peak). For normal elemental composition of air, CO_2 is more than one order of magnitude less abundant than argon. This was also in contradiction to the assumption of air contamination, indicating isobaric interference of $^{12}C^{16}O_2$ at $m/z = 44$, instead.

After instrumental background subtraction, further investigations of the remaining ion current at $m/z = 28$ of sample A and the prepared oxygen mixture, revealed that the linear fit vs. time for the extrapolation of $\ln I_{28}$ had a positive slope. The major abundant isotopic species in both samples was $^{16}O_2$, thus, $^{12}C^{16}O$ would be the main isobaric species formed, increasing with time the ion current rate at $m/z = 28$. For sample B, where $^{12}C^{18}O$ would be the main isobaric species, the $\ln I_{28}$ ion current readings at $m/z = 28$ decreased (negative slope) vs. time as expected, assuming the signal at $m/z = 28$ originated mainly from nitrogen impurities. These observations underpinned the prior assumption that the main contribution of the interference at $m/z = 32$ did not originate from air contamination, but from the formation of CO and CO_2 during the measurement. There was no significant signal at $m/z = 37$ to be observed for the equilibrated mixture, thus, $^{18}O_2H$ formation was assumed to be less dominant (if not negligible) compared to carbon-oxides formation.

Due to the high ion currents at $m/z = 32$ for sample A of natural isotopic composition, even possible isobaric and/or background effects, which occurred mainly at $m/z = 32$, were obviously not significant. Significant bias of the measurement result would have led to a significant deviation from the “ideal gas behaviour” of the sample during the measurement. As Fig. 2 demonstrates this was not observed for measurements of sample A. Summarising it can be said that for samples highly enriched in ^{16}O, isobaric interferences occurring are not significant within the measurement uncertainty. It is a problem to find a method to perform good isotopic measurements at $m/z = 32$ for oxygen mixtures/samples enriched in ^{17}O or ^{18}O.

5. Equilibration and ratio consistency

Because of the high enrichment in ^{16}O of sample A, no ratio consistency check could be performed on this “parent gas”. The signals at $m/z = 35$ and 36 were beyond detection limit.

For sample B, a consistency check was performed, applying Eq. (2). As a result, the measured isotope ratios were not consistent, which indicates typically a lack of isotopic equilibrium in the gas. Due to the fact that sample B was a purchased gas and that possible isobaric interference would result in a significant effect at $m/z = 32$, it was very improbable to assume that lack of isotopic equilibrium was the reason for the biased measurement results.

5.1. Ratio consistency factor for oxygen enriched in ^{18}O

For that reason the ion current readings at $m/z = 32$ were excluded to calculate the oxygen isotope abundances of sample B. Measurements of $J_{k/36}$ were used instead, which is also straightforward as $^{18}O_2$ is the major abundant isotopic species in sample B. The oxygen isotope amount ratios were calculated from measurements at $m/z = 33$–36 only. The consistency of the obtained results was investigated by solving the following equations:

$$R_{17/18} = \frac{R_{35/36}}{2} \quad \text{and} \quad R_{16/18} = \frac{R_{33/36}}{R_{35/36}} \quad \text{or}$$

$$R_{16/18\,\text{cons}} = \frac{R_{34/36} - (R_{35/36/2})^2}{2}.$$

Using this approach for the calculation of the oxygen isotope amount ratios, consistency was proved for sample B prior to mixing ($\chi(^{18}O) = 0.0011$ (41)). To underpin this result, another sample from the same batch of oxygen enriched in ^{18}O was measured at $m/z = 33$–36, which contained less nitrogen impurity (see Table 1) than sample B. The deduced ratio consistency factor for this sample was $\chi(^{18}O) = 0.0001$ (21), where the main contribution to the uncertainty originated from poor statistics due to the minor abundant $^{16}O^{17}O$ isotopic species, as measured at $m/z = 33$.

5.2. Equilibration of the oxygen test mixture

For equilibration, ideally, the gas molecules are condensed on the surface of the catalyst at a low temperature. Metal powder is commonly used as catalyst providing a maximum surface area for fast reaction. During subsequent heating, the gas molecules are cracked into atoms and the isotopes are statistically redistributed. At the time when the gas reached room temperature again, the isotopes have their most probable distribution, i.e., statistical equilibrium [28].

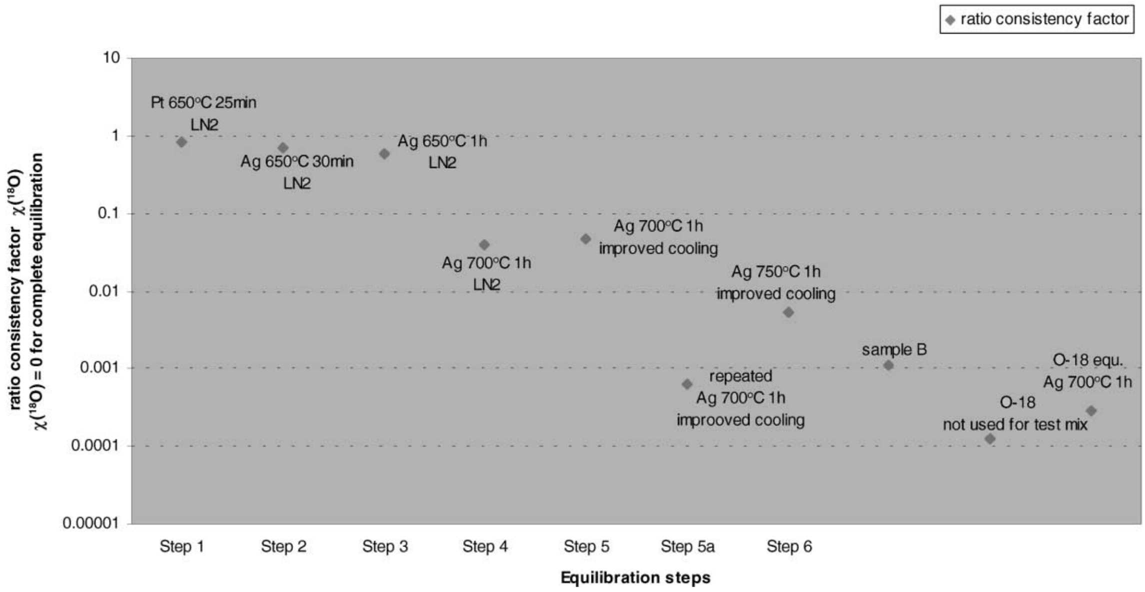

Fig. 3. Optimisation of isotopic equilibration procedure: ratio consistency factor $\chi(^{18}O)$ for each equilibration step of the oxygen test mixture, for sample B and the enriched $^{18}O_2$ that was not used for isotope mixing.

Primarily the equilibration of the prepared oxygen test mixture was carried out in the same way as the previously performed equilibration of CO_2 gas in the scope of a study on gas adsorption in mass spectrometric measurements [16]. The oxygen molecules were condensed on a platinum catalyst with the mixing cylinder cooled in liquid nitrogen for 15 min and then heated for 20 min to about 650 °C. The obtained ratio consistency factor $\chi(^{18}\mathrm{O}) = 0.847\ (34)$ showed that the prepared oxygen mixture was not in isotopic equilibrium. Subsequently, further experiments were carried out to establish isotopic equilibrium in the prepared oxygen mixture by using a silver catalyst, raising the temperature to 700 °C, increasing the exposure time and applying improved cooling (−208 °C). In Fig. 3, the obtained ratio consistency factors $\chi(^{18}\mathrm{O})$ for equilibration optimisation of the prepared oxygen mixture are displayed. The ratio consistency factors for isotope amount ratio measurements of sample B and for the measured oxygen sample highly enriched in ($^{18}\mathrm{O}$) are also included in Fig. 3. Finally, equilibration to a consistency factor of $\chi(^{18}\mathrm{O}) = 0.0006\ (21)$ was achieved. To be complete, the conversion factor for $\chi(^{17}\mathrm{O}) = 0.007$ with a combined uncertainty u_c of 0.13 is also given. The drastically increased uncertainty for $\chi(^{17}\mathrm{O})$ compared to $\chi(^{18}\mathrm{O})$ originates from poor signal statistics for measurements of the prepared test mixture at $m/z = 35$, because there was no enriched $^{17}\mathrm{O}$ added.

6. Results

6.1. Comparison of computed to directly observed isotope amount ratios for non-equilibrated mixing and for isotopic equilibrium of the prepared oxygen mixture

Samples that are not following the equilibrium distribution are subject to redistribution during the measurement itself, catalysed by the dissociative adsorption of oxygen at 75 °C in the inlet system. This means that the values of $\ln J$ vs. time deviate from the linear trend, with the tendency to shift the gas isotopic composition towards equilibrium. Such a deviation from ideal gas behaviour was observed for a 5 hour measurement of the unequilibrated oxygen mixture.

Unequilibrated and equilibrated isotope ratios of the prepared oxygen mixture, with their combined uncertainties, were calculated. The measured isotopic composition of the "parent gases" and the weighing results served as input data to perform this calculation. Finally, one could compare theoretical and measured values of $J_{k/l}$ with their combined uncertainties, both before and after equilibration. The isotope amount ratios $R_{k/l}$ ($k = 33$–36, $l = 32$) for the unequilibrated mixture as well as for the equilibrated mixture are given in Table 4. The computed and measured values agree very well, which indicates high quality mixing and measurement performance in this study.

Table 4
Measured and computed isotope amount ratios of the oxygen test mixture before and after equilibration with combined uncertainties u_c (applying to the last two digits)

Amount ratios	Before equilibration			After equilibration		
	Observed	Computed	Difference × 10^3	Computed	Observed	Difference × 10^3
$R_{33/32}$	0.0007921 (11)	0.0007855 (20)	0.0065 (23)	0.001429 (42)	0.0014435 (12)	0.014 (41)
$R_{34/32}$	0.0048772 (70)	0.004913 (49)	−0.067 (50)	0.0339 (19)	0.0340377 (12)	0.1 (1.9)
$R_{35/32}$	0.0006387 (69)	0.000633 (39)	0.005 (40)	0.0000242 (15)	0.0000244 (31)	0.0003 (15)
$R_{36/32}$	0.0143286 (11)	0.01424 (89)	0.09 (88)	0.000288 (32)	0.0002900 (14)	0.002 (31)

Table 5
Derived isotope amount ratios and conversion factors for the equilibrated oxygen test mixture with combined uncertainties u_c (applying to the last two digits)

Amount ratios	After equilibration		Conversion factor ($K_{conv} = R_{prep}/R_{meas}$)
	Observed	Computed	
$R_{17/16}$	0.00072176 (60)	0.000715 (21)	0.990 (28)
$R_{18/16}$	0.01701858 (85)	0.01696 (93)	0.997 (54)

6.2. Determination of "preliminary" conversion factors for amount ratio measurements of oxygen in view of the aimed preparation of a primary isotope gas standard (PIGS) for oxygen

The main feature of a PIGS compared to a conventional isotopic reference material is, that the certified values for isotope amount ratios are obtained by measurements calibrated by means of synthetically prepared mixtures of enriched isotopes [29]. To achieve this, the directly extrapolated ion current ratios $J^0_{i/j}$ have to be related to the isotope amount ratio $R^0_{i/j}$ by means of conversion factors K_{conv} as determined by means of synthetic isotope mixtures.

$$R^0_{i/j} = \frac{n(^i\mathrm{O})}{n(^j O)} = K_{conv} \times J^0_{i/j}$$

K_{conv} accounts for possible small residual systematic effects of unknown origin. Applying Eq. (1) the isotope amount ratios $n(^{17}\mathrm{O})/n(^{16}\mathrm{O})$ and $n(^{18}\mathrm{O})/n(^{16}\mathrm{O})$ were derived from the measurements of the major abundant oxygen species. In Table 5 the calculated isotope amount ratios $R_{i/j}$ of the equilibrated oxygen mixture are compared to the derived values of $J_{i/j}$ as observed for direct measurements of this test mixture ($i = 17, 18$, $j = 16$). The conversion factors were found to be $K_{conv} = 0.997$ (54) for $n(^{18}\mathrm{O})/n(^{16}\mathrm{O})$ and $K_{conv} = 0.990$ (28) for $n(^{17}\mathrm{O})/n(^{16}\mathrm{O})$. To be complete, Fig. 4 displays the

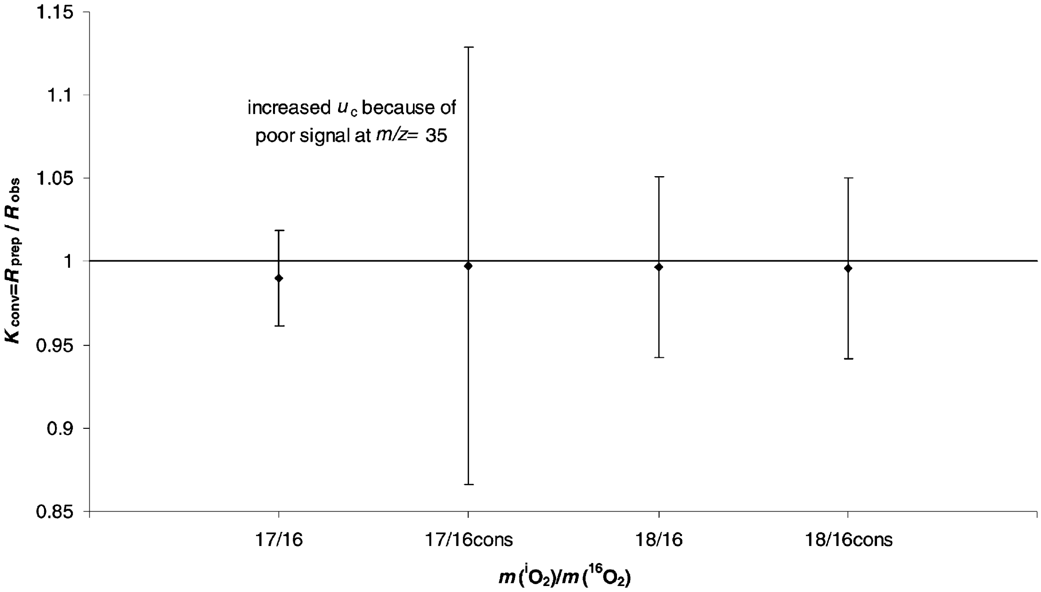

Fig. 4. Consistent conversion factors K_{conv} for the prepared oxygen mixture with combined uncertainties u_c.

conversion factors as derived from the measurements of the major abundant isotopic species as well as the so-called "consistent" conversion factors. $K_{\text{conv}} = 0.996$ (54) for $[n(^{18}\text{O})/n(^{16}\text{O})]_{\text{cons}}$ and $K_{\text{conv}} = 1.00$ (13) for $[n(^{18}\text{O})/n(^{16}\text{O})]_{\text{cons}}$, were derived from the measurements of the minor abundant species, applying Eq. (2). It can be seen that all conversion factors are equal to unity within u_c. Thus, K_{conv} for $n(^{18}\text{O})/n(^{16}\text{O})$ is perfectly consistent, K_{conv} for $n(^{17}\text{O})/n(^{16}\text{O})$ is also consistent but due to poor signal statistics only within highly increased uncertainty.

7. Discussion about areas of improvement

The main uncertainty contribution on the results originates from the weighing of the "parent gases". From former experience, improvement can be made using more sophisticated weighing equipment with automated data collection [30].

A critical point in order to decrease the measurement uncertainty is to investigate the bias in results for ion current readings of minor abundant oxygen isotopic species through a more profound understanding of occurring isobaric interferences. For this investigation enriched oxygen gas of high purity will have to be used in order to observe the interferences from oxygen compounds formation or/and multiple charged isobaric ions from other compounds. This could be done by means of long duration measurements of oxygen enriched in ^{18}O. Possible $^{12}\text{C}^{18}\text{O}$ formation during the measurement could be detected via measurements at $m/z = 30$, without interferences originating from nitrogen. Moreover, although in this study no significant O_2H formation was observed, it cannot be completely excluded either, for oxygen measurements in the future. Measurements of oxygen enriched in ^{18}O could reveal possible $^{18}\text{O}_2\text{H}$ formation at $m/z = 37$.

To improve the oxygen measurements, particularly at $m/z = 32$, in view of the preparation of a PIGS

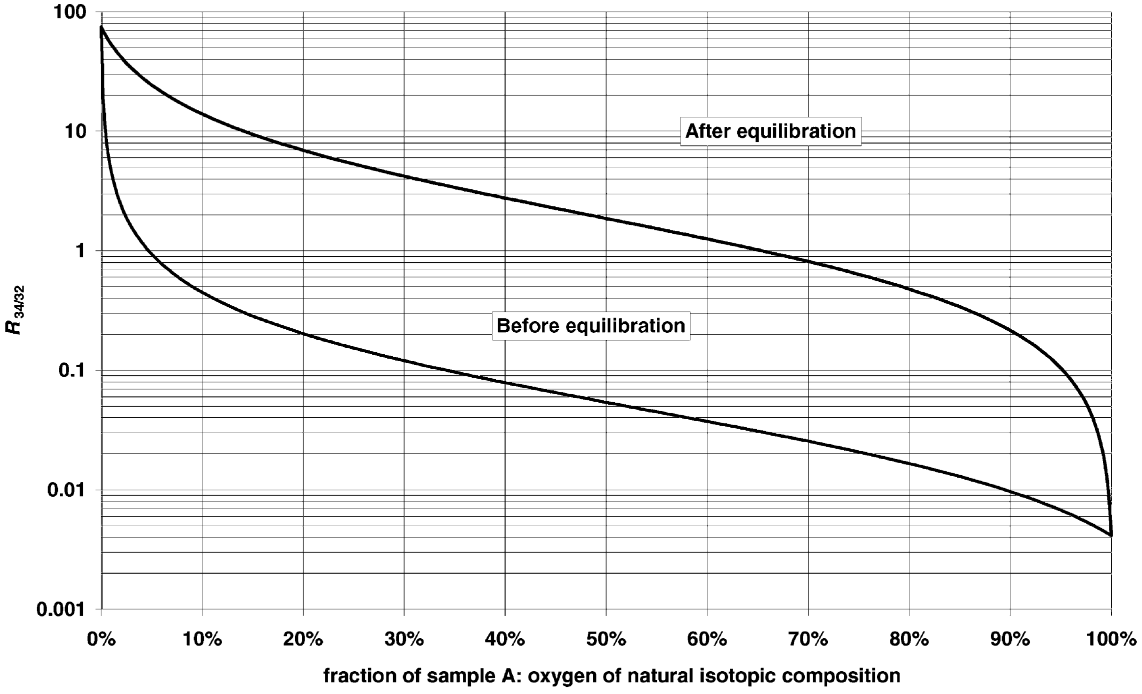

Fig. 5. Computed unequilibrated and equilibrated $R_{34/32}$ vs. mixing ratio.

for oxygen, it will be necessary to minimise isobaric interferences, if possible, and to find an algorithm to be applied as correction, independent of the isotope enrichment factor of the measured oxygen sample. Kinetics of oxygen compounds formation in the mass spectrometer also plays an important role in order to optimise the measurement time. Furthermore, applying an appropriate model for isotope specific oxygen adsorption in mass spectrometric measurements should allow correcting for deviations of $\ln R$ vs. time from the linear trend not originating from isobaric interference. All those effects, which are directly linked to the reliability of measurement results within smallest achievable uncertainty, will be further investigated.

Although, one has to be aware that there is a limit to the improvement of the uncertainty of the consistency factor due to poor ion currents for measurements of minor abundant isotopic species. This is of course depending on the enrichment of the "parent gases" and the mixing ratio of the prepared mixture. As an example, Fig. 5 simulates the trend of the measured ratio $R_{34/32}$ depending on the mixing ratio for unequilibrated and equilibrated mixing of sample A with sample B. The difference in the prepared isotope ratios for isotope mixtures before and after equilibration has its minimum when only a very small amount of sample B is "spiked" to the major component. The maximum deviation is to be found for mixing ratio of the two mixture components closely to 1:1. In general, it can be stated that the ratio consistency factor $\chi({}^{i}\mathrm{O})$, which is a measure of the closeness to ideal isotopic equilibrium of the prepared mixture, has to be calculated from the measurement results of the most abundant isotopic species to obtain reliable results within reasonable uncertainties.

Another aspect of improvement is the optimisation of the equilibration process. More tests have to be performed to find out if subsequent equilibration steps would still be necessary if one immediately performed the first step with improved cooling condensation and high-temperature equilibration on a Ag-catalyst.

8. Conclusions

A method was developed to attain isotopic equilibrium in a synthetic oxygen isotope mixture. Equilibration to a consistency factor of $\chi({}^{18}\mathrm{O}) = 0.0006$ (21) was achieved for a two component isotopic test mixture of oxygen, i.e., the values of the conversion factor K_{conv} determined via $(R_{18/16\,\mathrm{prep}}/R_{18/16\,\mathrm{obs}})$ and its consistent K_{conv} determined via $(R_{18/16\,\mathrm{prep}}/R_{18/16\,\mathrm{obs\,(consistent)}})$ agreed to within 6×10^{-4}.

In other words, an oxygen mixture with a determined ratio consistency factor of $\chi({}^{18}\mathrm{O}) = 0.0006$ (21) theoretically has the potential to yield a conversion factor K_{conv} for $n({}^{18}\mathrm{O})/n({}^{16}\mathrm{O})$ that is equal to unity within the 4th decimal.

This work was performed as a preliminary study in view of the preparation of a set of three-component synthetic oxygen mixtures, mixing oxygen highly enriched in ${}^{16}\mathrm{O}$, ${}^{17}\mathrm{O}$ and ${}^{18}\mathrm{O}$. The intention is to mix this set of oxygen mixtures in such a way that the prepared isotope amount ratios reflect oxygen ratios as measured in real samples, which are commonly expressed as differences on the $\delta^{18}\mathrm{O}$ scale. By means of the preparation of a preliminary test mixture of oxygen the areas for improvement for the envisaged challenging task of preparing a primary isotopic gas standard for oxygen in the future were identified.

It can be concluded from the results of this study on oxygen equilibration, that it is feasible to prepare isotope mixtures of oxygen with conversion factors only deviating in the 4th decimal from unity, provided that enriched "parent gases" of high purity and equipment, that allows weighings to a relative uncertainty of 10^{-3} or better, are used. In view of the ultimate aim of preparing a primary isotopic gas standard for oxygen this is a very promising outcome of this study.

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