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Stable isotope measurement techniques for atmospheric greenhouse gases

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FOREWORD

The technical requirements to perform useful measurements of atmospheric greenhouse gas concentrations and of their isotope ratios are of direct relevance for all laboratories engaged in this field. A meaningful integration of isotopes in global models on sources and sinks of CO_2 and other greenhouse gases depends on strict laboratory protocols and data quality control measures ensuring comparable data in time and space. Only with this precondition met, the isotope techniques can serve as a potentially powerful method for reducing uncertainties in the global CO_2 budgets and for tracing pathways and interaction of terrestrial, oceanic, and atmospheric pools of carbon. Related to the scientific results of a Co-ordinated Research Project (CRP) on Isotope-Aided Studies of Atmospheric Carbon Dioxide and Other Trace Gases — Phase II it was considered that a publication describing the analytical techniques used by leading groups in this field would be a significant contribution to achieve the ultimate goal of comparable and consistent data sets. This publication provides four contributions describing methods for the determination of the isotopic composition of trace gases in atmospheric air and in ice cores.

The preparation of the contributions was co-ordinated by I. Levin, University of Heidelberg, Germany. This report was compiled with the aid of H.A.J. Meijer, Groningen University, Netherlands, who organized the peer review. Special thanks are given to those who contributed to the peer review of the individual contributions. M. Gröning of the Isotope Hydrology Section was the IAEA officer responsible for the publication.

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The contents of this publication are closely related to IAEA-TECDOC-1269, Isotope Aided Studies of Atmospheric Carbon Dioxide and Other Greenhouse Gases — Phase II, in which the scientific outcome of the described greenhouse gas measurements is discussed.

CONTENTS

SUMMARY

The global measurement programmes on greenhouse gas concentrations are often accompanied by measurements of their isotopic composition, providing additional and independent information on the greenhouse gas sources and sinks. The isotopic composition is a powerful marker of the origin of those gases, e.g. in the case of CO_2 with distinct differences between CO_2 produced by natural biogenic activity and fossil fuel combustion.

However, due to the atmospheric mixing the resulting isotope signals as composite of all sources and sinks are rather small. A difference of 0.01‰ in $\delta^{13}C$ in CO_2 on a global scale, for example, resembles a source/sink term either from biospheric/fossil fuel or from oceanic origin of roughly 0.4 Pg of Carbon (for CO_2). Furthermore, an effective source identification of methane requires an accuracy of <0.1‰ in $\delta^{13}C$. Therefore, the contribution of isotope measurements is only valuable if measurements are performed with:

- high individual precision, using specially designed protocols, and suitable machinery
- high accuracy, which includes reliable long-term calibration of the laboratory
- reliable intercalibration between the different laboratories. Assessment of this latter feature requires, among other things, frequent exchange of samples and reference gases.

These requirements have proven to be absolutely non-trivial indeed, and the existing situation is far from satisfactory in this respect.

Many of the techniques used by laboratories active in the field of atmospheric greenhouse gas measurements (sample taking, chemical and physical sample preparation, actual measurement techniques) have matured over many years, sometimes decades. This maturing process has usually led through a terrain full of pitfalls. Even though these technical developments are essential for scientific achievements in this field, they are usually only briefly described in the scientific literature. A comprehensive description can therefore be extremely useful for (new-coming) colleagues who would like to adapt a certain technique. Therefore the participants of an IAEA Co-ordinated Research Project on Isotope-aided Studies of Atmospheric Carbon Dioxide and Other Trace Gases — Phase II agreed to produce technically detailed papers about the main topics in the field of that CRP. For a detailed discussion of the scientific results of that CRP please refer to the related IAEA-TECDOC-1269, Isotope Aided Studies of Atmospheric Carbon Dioxide and Other Greenhouse Gases — Phase II.

This TECDOC contains four detailed technical papers on CO_2 isotopes, CH_4 isotopes, N_2O isotopes, and air extraction from ice cores for isotope measurements. They are meant to be helpful both for experienced users and novices. The main focus of all the contributions was to provide sufficient technical details and numeric data on the operating parameters used to minimize the trial-and-error phase. Special reference was given to issues of quality control and calibration, as these are highly relevant to the comparability of data between laboratories. Rather then writing voluminous overview papers on the respective topic, preference was given to an extended reference list, meant to be useful (and their lecture being nearly mandatory) for any group entering that scientific field. A list of contact addresses is added (or the authors may be contacted) for any further technical question on the topic.

The first contribution describes the currently applied techniques for stable isotope analysis of carbon dioxide. Two of the leading groups in this field are represented here (J. White, D. Ferretti and B. Vaughn from INSTAAR Boulder, R. Francey and C. Allison from CSIRO, Aspendale) and have jointly written this overview.

The second paper deals with the present state of the art isotope measurements on atmospheric methane. Authors from four of the leading laboratories (J. White and J. Miller from INSTAAR Boulder, M. Wahlen from SIO La Jolla, D. Lowe and P. Bergamaschi from NIWA Wellington and I. Levin from IUP Heidelberg) have together produced this contribution.

The third contribution is about isotope measurements of atmospheric N_2O. Due to the low ambient concentration of N_2O, these measurements are far from trivial. T. Rahn and M. Wahlen describe in much detail the technical features of N_2O isotope measurements, as it is in use in their laboratory in SIO La Jolla.

In the forth paper a brief technical overview is presented of the various techniques in use at present to extract air from ice cores for isotope analysis. Authors from four leading groups active in this field (Leuenberger from the Physics Institute of the University of Bern, Bourg from LSCE Paris, Francey from CSIRO Aspendale and Wahlen from SIO La Jolla) have contributed to it.

It is hoped that the four contributions — giving a snapshot of the current technologies used — will facilitate the start of new groups and will give examples and induce more detailed descriptions of new techniques on atmospheric trace gas measurements, which will hopefully be published in the future.

STABLE ISOTOPE MEASUREMENTS OF ATMOSPHERIC CO_2

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Abstract. The measurement of stable carbon isotope ratios of atmospheric carbon dioxide, $\delta^{13}CO_2$ are useful for partitioning surface-atmospheric fluxes into terrestrial and oceanic components. $\delta C^{18}OO$ also has potential for segregating photosynthetic and respiratory fluxes in terrestrial ecosystems. Here we describe in detail the techniques for making these measurements. The primary challenge for all of the techniques used to measure isotopes of atmospheric CO_2 is to achieve acceptable accuracy and precision and to maintain them over the decades needed to observe carbon cycle variability. The keys to success such an approach are diligent intercalibrations of laboratories from around the world, as well as the use of multiple techniques such as dual inlet and GC-IRMS and the intercomparison of such measurements. We focus here on two laboratories, the Stable Isotope Lab at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado is described and the Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research (CSIRO). Different approaches exist at other laboratories (e.g. programs operated by Scripps Institution of Oceanography (SIO) and The Center for Atmospheric and Oceanic Studies, Tohoku University (TU)) however these are not discussed here. Finally, we also discuss the recently developed Gas Chromatography — Isotope Ratio Mass Spectrometry (GC-IRMS) technique which holds significant promise for measuring ultra-small samples of gas with good precision.

1. INTRODUCTION

Carbon and oxygen stable isotope ratios of atmospheric carbon dioxide, $\delta^{13}CO_2$ and $\delta C^{18}OO$, provide important, independent information about carbon sources and sinks. Combined with CO_2 mole fraction measurements, the $\delta^{13}CO_2$ measurements can be used to quantitatively separate fluxes between the atmosphere and the terrestrial biosphere from fluxes between the atmosphere and the ocean [6,18,19,20,29]. This is because C3 plants discriminate against $^{13}CO_2$ during photosynthesis while little isotopic discrimination occurs during carbon uptake and release by the ocean. The $\delta^{13}C$ measurements have mainly been used to indicate the one-way carbon fluxes (in the case of fossil fuel release) or net carbon fluxes (e.g. the resultant of photosynthetic uptake and respiratory releases), whereas $\delta C^{18}OO$ measurements more reflect the large (gross) natural cycling of CO_2 between the atmosphere and surface reservoirs, and are only just beginning to be usefully exploited. The two main mechanisms for controlling $\delta C^{18}OO$ on annual to decadal time scales are oxygen isotopic exchange with soil water and oxygen isotopic exchange with leaf water. This isotope can potentially be used to separate photosynthetic and respiratory fluxes for land plants [e.g. 16, 10,7]. Note, the gross fluxes become a complicating factor in $\delta^{13}C$ interpretation when isotopic disequilibria between the atmosphere and surface reservoirs develop (e.g. due to ^{13}C depleted fossil fuel release) and result in second-order $\delta^{13}C$ changes not reflecting net CO_2 exchange, and require careful consideration of response times of exchange [28]. As the atmosphere integrates surface processes over space and time, CO_2 concentration measurements, combined with isotopic measurements, provide constraints for regional scale sources and sinks of atmospheric CO_2 on time scales of months and longer. Indeed, these measurements provide our primary constraints on surface fluxes and thus the processes and factors, climatic and otherwise, controlling these fluxes. In the future, atmospheric monitoring is also expected to play a central role in verifying any international carbon emission agreements in much the same way that seismic monitoring was used to monitor compliance with nuclear test ban treaties.

The degree to which isotopic measurements made on atmospheric samples are useful is seriously constrained by the precision of the mass spectrometer used. For example, a change of just 0.02 ‰ in $\delta^{13}C$ measured at one site could translate to an equivalent of 1.0×10^9 metric tons of carbon in models of surface fluxes. Such precision is challenging enough on a short-term basis, but this precision is needed over decades if we are to use the data to study trends over longer periods of time. A high precision instrument is required along with diligent, frequent intercalibrations between laboratories.

Here we describe the isotopic measurements made at the Stable Isotope Lab at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado, and briefly refer to different techniques employed at the Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research (CSIRO). The different approaches at these laboratories represents a range of variations in the conventional techniques used to measure the isotopic composition of atmospheric CO_2. Other variations exist, for example the monitoring programs operated by Scripps Institution of Oceanography (SIO) and The Center for Atmospheric and Oceanic Studies, Tohoku University (TU) [19,26]. In addition to discussing traditional dual inlet Isotope Ratio Mass Spectrometry (IRMS) with cryogenic pretreatment of air we also discuss the recently developed Gas Chromatography — Isotope Ratio Mass Spectrometry (GC-IRMS). The latter is less precise than the former but has other attractions such as: smaller sample requirements, no requirement for the N_2O correction due to its contribution of masses 44, 45 and 46, and the elimination of liquid nitrogen use for CO_2 extraction.

2. ISOTOPIC MEASUREMENTS USING DUAL INLET MASS SPECTROMETRY

2.1 Isotopic measurements at the Stable Isotope Lab, INSTAAR

Since 1989, the Stable Isotope Laboratory at INSTAAR, University of Colorado has been measuring the stable isotopic composition of atmospheric CO_2 from weekly flask samples of air obtained from the network of sites operated by the NOAA Carbon Cycle Group, at the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder, Colorado. This operation begun with a selection of six sites and two ships in 1990, the measurement effort has grown to include all 55 sites in the CMDL program. During calendar year 1999 over 11,000 isotopic analyses of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 were made at INSTAAR. This included 7,800 sample flasks and 3,200 air standards used for calibration. In 1990 the program began making measurements with a VG SIRA Series 2 dual inlet mass spectrometer. This instrument and extraction system routinely achieved an overall reproducibility of 0.03 ‰ for $\delta^{1\delta}C$ and 0.05‰ for $\delta^{18}O$ (1δ). This includes errors in the extraction process and is determined from replicate measurements of air standards over many years. A Micromass Optima dual inlet IRMS was used beginning in 1996. This machine is fitted with a custom manifold and extraction system, and is used exclusively for making measurements on atmospheric gases. The overall reproducibility for the Optima system is ±0.01 ‰ $\delta^{13}C$ and ±0.03 ‰ for $\delta^{18}O$.

2.1.1 Sample and standard manifold

The automated flask measurement system is composed of three parts: a 40 port manifold; the CO_2 purification system; and the mass spectrometer. The system performs a number of operations simultaneously (multi-tasks), as one sample is analyzed in the mass spectrometer while CO_2 from the following sample is being purified from the air.

For a measurement run, 20 pairs of 3 L glass flasks are attached to a 40 port manifold using Ultra Torr fittings. The sample flasks used in the NOAA network are Pyrex, taped for safety purposes, and have two stopcocks that allow flushing of the flask when the samples are obtained. Samples are always taken in pairs and filled simultaneously. Results are retained if there is acceptable pair agreement in the isotopic concentrations (discussed below). The flasks are typically over-pressurized by 1.5 atmospheres during sampling, and after other greenhouse gas measurements have taken aliquots, the flasks typically are slightly over one atmosphere pressure when they arrive for isotopic analysis.

Two atmospheric air standards in aluminum tanks AIRCO (BOC Gases Inc, NJ, USA) are also attached to the manifold, using stainless steel tubing (0.0625 in. OD × 0.05 in. ID, with Swaglok-to-VCO fittings), and regulators (High-Purity, Single-Stage, Stainless Steel, model E11-C444A, Air Products and Chemicals, Inc, USA) set to 6 psi. There may be other regulators that can work as well, however, it should be noted that considerable testing led to choosing this regulator over others. For example, a variety of problems have been discovered with regulators that employ Viton seals. Manufacturer's tests for analytical contamination are of limited use, and successful performance of a regulator in this isotopically sensitive system could only be determined by long term testing. This includes extended periods of non-use, to allow for any effects of degassing of sealant materials into the body of the regulator to be seen. Finally a single stage regulator was chosen over a two stage for three reasons: 1) the single stage regulator employs fewer wetted parts, 2) to keep costs down, and 3) a precise outlet pressure is obtained from a two stage regulator is unnecessary, as the flow rate is regulated further downstream by the mass flow controller. Any changes in outlet pressure as the tank drains over time can easily be adjusted.

Air samples from sample flasks or standard tanks enter the manifold through air actuated, low dead volume bellows valves (stainless steel, model SS-6LV-BNBW4, Nupro Company, Willoughby, Ohio, USA). The 14/35 ground glass joints on the flasks seal well with 0.5" Cajon O-ring fittings with thick wall (#2–111, 0.104" thick) Viton-7 o-rings used in place of the standard wall (#2–014, 0.070 in thick) o-rings. Electropolished stainless steel tubing (0.25" O.D. thick wall) is used to connect the flask ports to the Cajon VCO fittings on the manifold.

2.1.2 The CO_2 purification system

Air samples are pulled from the manifold through the extraction system using a rotary vane vacuum pump (model RV-3, BOC-Edwards, Wilmington, MA, USA) at a flow rate of 40 standard cubic centimeters per minute (sccm). The flow is maintained by a mass flow controller (BOC-Edwards, model 825, series B, 0–100 sccm) (Figure 1). During the first minute of air extraction, 40 scc are allowed to waste directly to the vacuum pump, flushing the lines. Following the flush, the sample is then diverted first through a glass water trap, held in an ethanol bath chilled to –85°C by a refrigerated probe (Cryocool, model cc-100, Thermo NESLAB, Portsmouth, NH, USA), and then through a CO_2 trap, cooled to liquid nitrogen temperature. This is basically the Triple Trap extraction system provided by Micromass with two modifications: the addition of a flow controller, and the replacement of the standard water trap with a more efficient one. At the end of the sample extraction time, the flask port is closed, and when the flow rate drops to 10 sccm, a valve is opened that allows the remaining sample air to bypass the mass flow controller (Figure 1).

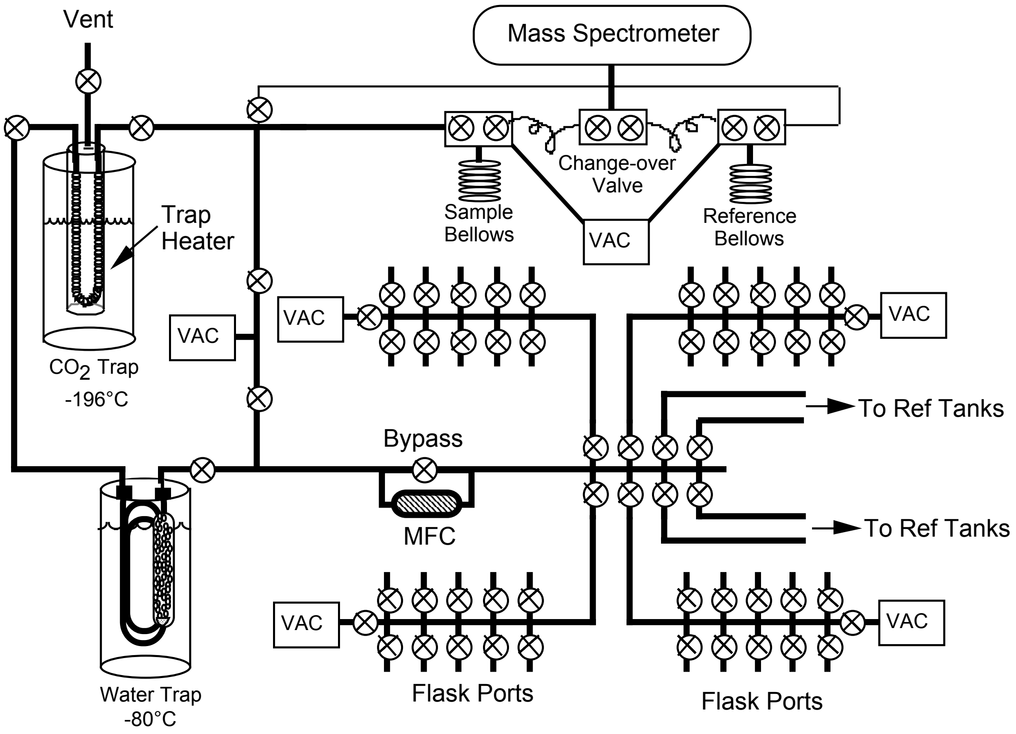

Figure 1. A general schematic showing the flask/reference tank manifold with the extraction system, including mass flow controller, water trap, CO_2 trap, and sample/reference bellows leading to the dual inlet mass spectrometer. The connection from the extraction system to the reference bellows allows large extractions of CO_2 from tank air to be used as reference gas. Tank air CO_2 has isotopic concentrations very similar to flask samples which minimize any gas memory issues in the mass spectrometer source.

As complete removal of water vapor is critical to high precision measurements, and as the efficiency of the water trap determines in part the speed with which air flows though the gas purification system, we use a water trap that employs a number of trapping strategies. The water trap is made of Pyrex with an initial 0.75 in. O.D. vertical section that is filled with glass beads to provide a large, cold surface area (Figure 2a). A 40–60 micron glass frit at the bottom of this section keeps the beads in place and helps prevent ice crystals from escaping this section of the trap. This is followed by two loops of 0.24 in OD glass that are 80% submerged in the ethanol. This section traps and re-traps any water vapor or ice crystals that might have escaped the beads and frit. The glass trap is removable, and is held in place using two 0.25 in. Cajon Ultra Torr fittings. This allows wet traps to be removed and dried offline after each daily run. Traps are dried in a 120˚C oven with air circulation to speed the drying time.

The CO_2 trap is modeled after the Micromass Triple Trap, employing a liquid nitrogen bath, and an open-bottomed 2.0 in. O.D. tube surrounding the ‘U’ shaped sample trap (Figure 2b). The trap is electrically insulated with glass tape, and wrapped with resistive heating wire (~350 cm of 18 gauge, 80% NiChrome wire). With a vent valve on top of the tube closed, the activated heating element boils the LN_2, building N_2 gas pressure in the open bottom tube. This displaces the LN_2, allowing the resistive heating element to further warm the sample to release the previously trapped CO_2.

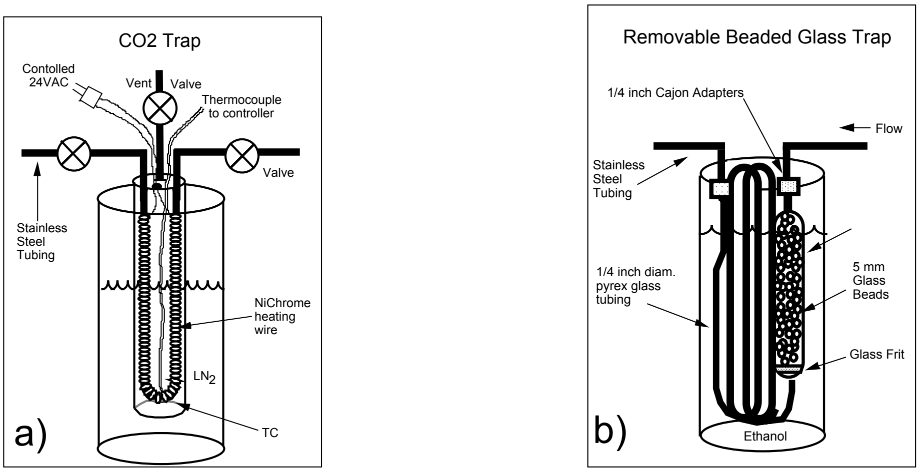

Figure 2. ***a.)*** *The CO_2 trapping system, based on a Micromass design, allows the trap to be alternately controlled to set points of –196°C, –20˚C, and +25°C. Liquid nitrogen provides the low point. The warmer temperatures are reached by controlling a NiChrome heating wire (24VAC) on the trap and closing the top vent on the (2 in. dia.) displacement tube. The resulting pressure of gaseous N_2 displaces the liquid N_2 out the open bottom of the displacement tube, allowing further heating.* ***b)*** *The pyrex beaded water trap incorporates an 40–50 micron glass frit at the bottom of a 0.75 in. dia. tube filled with 5 mm diameter beads. There are two open loops that extend out of the chilled bath, to ensure complete removal of water from the air stream by warming and re-trapping of any mobilized ice crystals.*

Once the CO_2 is extracted from the air and frozen in the trap, the system is pumped to high vacuum (5 E-8 mBar) for 60 seconds. Typically, each 400 cm^3 air sample introduced to the system yields ~6.5 δmol CO_2 for isotopic analysis. The isolated sample is then warmed to –20°C and expanded for 60 seconds into the sample bellows. The mass 44 sample beam is then balanced to match the reference target beam to less than ±2% at 5×10^{-9} A.

2.1.3 The mass spectrometer

The mass spectrometer currently used at SIL is a Micromass Optima dual inlet IRMS machine with an electro-magnet. The mass spectrometry is standard. The CO_2 sample and reference gas flow through matched capillary tubes into the source where they are ionized, repelled and accelerated with electric fields and focused into an ion beam. After exiting the source, the ion beam is deflected by the magnetic field, directed into Faraday cups, where the beam currents are measured for mass 44, 45, and 46. Beam currents are amplified, converted to frequencies, and transmitted to the microprocessor by fiber optic cables. The beams are allowed to stabilize for 60 seconds before measurement. The ratios of beams are calculated from integrations taken during 12 reference/sample switches, with outlier rejection (beyond 1 σ). The number of ref/sam switches is determined by two factors. The lower limit is set by the desired internal precision of less than 0.005 ‰ for δ45. This typically requires 8 switches. As the system multi-tasks, extracting one sample while the previous one is being analyzed, additional time is available for switches. The upper limit on switches thus is set by the time required to extract the next sample.

The carbon and oxygen isotope data are reported as δ values relative to VPDB-CO_2, in units of per mille (‰). 0 ‰ VPDB - CO2 = 41.47 per mil VSMOW. The δ notation is given as:

$$\delta^{13}C= [(^{13}C /^{12}C)_{sam}/(^{13}C /^{12}C)_{ref} - 1] * 1000$$

and applies to $\delta^{18}O$ as well.

2.1.4 Data quality checks

Data quality is checked by three mechanisms: flask pair agreement, outlier rejection, and internal standards run as samples. All data is retained and reported so that users can assess data quality. Flags are provided with the data to signify known problems, however, so that data with known problems can be easily removed before the data is used.

Air samples are taken in paired flasks that are filled simultaneously. For all species, data are retained only from those flasks that demonstrate good agreement between each sample pair. The criteria for acceptable pair agreement used at SIL is agreement with three standard deviations, or $|\Delta\delta^{13}C| <0.03‰$ and $|\Delta\delta^{18}O| <0.15‰$.

Between trips to the sampling sites, the flasks are filled with dry air with known, but non-atmospheric concentrations and isotopic ratios of CO_2 and other gases. Flasks that are improperly flushed with air can thus be identified and the data flagged. In addition, the data are examined as times series and are routinely filtered for outliers relative to the general trends observed. Such outliers may be real and represent unusual climatic or atmospheric circulation features, for example, or they may represent non-baseline conditions when air was coming from known sources of contamination such as nearby industries, or, in the case of ship board sampling, air blown back from the engine exhaust. Again, such data is flagged, but differently for known problems (as in the case of engine exhaust), as opposed to outliers that deviate significantly from the common trend but that may contain desirable information.

As an internal quality check, SIL began in late 1996 to measure three aliquots of air from a cylinder of air in the middle of each daily run on the mass spectrometer. This additional cylinder, called the “quality control tank” or “trap”, is handled in exactly the same manner as the samples, and provides an independent check on the performance of the entire system. The variability of this tank over time is used to determine our overall reproducibility, and problems in the analysis system are frequently first seen and subsequently diagnosed using this trap tank. The recent behavior of the trap tank is shown in Figure 3 and illustrates the value of this quality check. Shown are 10 point running means of the standard deviation (1δ) for $\delta^{13}C$ and $\delta^{18}O$ values of the trap tank. The average standard deviation during the last 160 analysis runs is 0.010 ‰ for $\delta^{13}C$ and 0.042 ‰ for $\delta^{18}O$. Known factors that can cause this number to vary include: source tuning and cleanliness, contamination of the inlet/extraction system by water or organic compounds from gas regulators, and overheating in the CO_2 trap. This latter problem occurs when the autorun sequence stops during heating of the trap to release the CO_2 and the trap temperature exceeds 20°C.

2.1.5 Standards and calibrations

The results are calibrated to external standards, and to internal whole-air references. The internal set of tank-references consists of a hierarchy of 18 aluminum tanks filled with dry atmospheric air obtained from a clean air site located at 4,000 meters elevation on Niwot Ridge in the Rocky Mountains, Colorado, USA. Eight of these tanks are cycled through as the ‘daily’ reference measurement tank, after first performing as the trap tank. Five more tanks are measured on a monthly basis, with one tank purposely 'spiked' with $^{13}CO_2$ to be 2‰ different from the others in δ^{13}C. Five other tanks are analyzed every 6 months, with two of those being spiked by 1‰ and 2‰. The tanks are stored horizontally to help minimize any gravitational fractionation, and each tank is assigned its own regulator for the life of the tank air. Multiple tanks are used to guard against any systematic bias resulting from one drifting tank. It is extremely unlikely that any long-term changes in the isotopic concentration experienced by one tank would be identical for all. The structure of a pyramid of standards is essential for providing long-term continuity and precision.

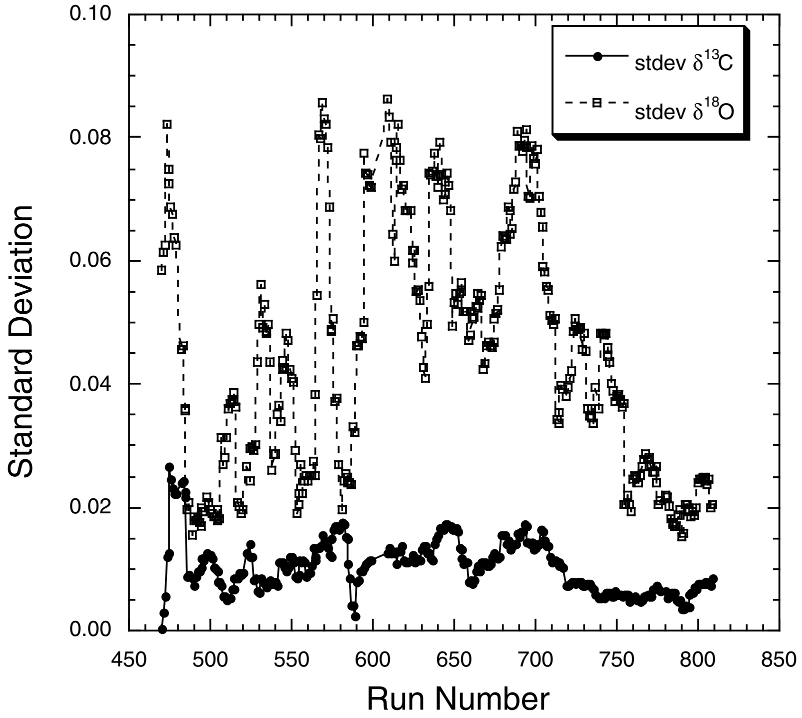

Figure 3. The 10 point running means of the standard deviation of the quality control tank $\delta^{13}C$ and $\delta^{18}O$ as a function of run number.

The standard tanks are tied to the IAEA VPDB CO_2 scale via measurements of carbonates and waters provided by the IAEA and measured by established procedures [9]. As these measurements are made on different extraction systems than the one used for CO_2 in air, we have found that the precision with which air standards can be calibrated to the VPDB CO_2 scale is less than the precision with which air standards can be intercalibrated. Consequently, four labs around the world have been working with the IAEA to resolve internal scale differences and establish air standards for stable isotopes in atmospheric CO_2.

Two types of comparisons between laboratories are maintained as an essential element in the globalization of atmospheric isotopic measurements. The first is an exchange of 5 CLASSIC cylinders circulated by Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research, (CSIRO) among four different labs, including Scripps Institution of Oceanography, (SIO), The Center for Atmospheric and Oceanic Studies, Tohoku University (TU), INSTAAR-CMDL, and CSIRO. Each lab group analyzes the cylinders for CO_2, N_2O, δ^{13}C, and δ^{18}O, and can compare results. While individual labs make their own internal tie to primary carbonate and water (IAEA) standards, the tanks allow very small relative differences between labs to be examined.

The second comparison method between labs is the flask inter-comparison program (ICP). ICP takes an entirely different approach by allowing two or more labs to make measurements on the same flask samples obtained from the same site at the same time, on a regular basis though with lower precision [13,8]. The ICP compliments the cylinder measurements by providing 1) ongoing intercomparisons that allow weekly feedback on sampling and measurement methods, giving laboratories an opportunity to pinpoint problems, and 2) the ICP flask samples are sampled and measured in the same way as the flask measurements themselves, thereby eliminating any potential differences in measurement that may arise from pressurized tanks vs. sample flasks. For example, the ICP program with CSIRO at Cape Grim, Tasmania has identified calibration offsets between the two labs that have led to minor modifications of analysis procedures at both labs. ICP calibrations, combined with rotating tanks such as the CLASSIC tanks, are essential to global integration of greenhouse gas measurements.

2.1.6 Problems with humid air

Drying of air during sampling is clearly important to the quality of the $\delta^{18}O$ measurements, particularly in the relatively small (2.5 L) flasks used in the NOAA network. For samples collected at humid, tropical locations without drying, the $^{18}O/^{16}O$ measurements are highly variable and consistently more depleted in ^{18}O due to the exchange of oxygen atoms between CO_2 and H_2O molecules on the walls of the flasks. Systematic tests at INSTAAR [14] showed that the exchange takes place during storage in the flasks, and that this exchange can occur at humidities less than saturation values. There is also clear dependence on the physical characteristics of each flask. This problem can be seen in the percentage of retained flask pairs, which is much lower for $\delta^{18}O$ (68%) than for $\delta^{13}C$ (94%). The reason for the lower success rate in $\delta^{18}O$ pair agreement is closely tied to the moisture problem, as seen in the trend in low pair agreements at low latitude (generally humid) sites (Figure 4). While seriously contaminated if $\delta^{18}O$ of CO_2 data are obvious (offsets of 4‰), it is impossible to unambiguously determine if $\delta^{18}O$ are slightly affected by exchange with water in the flasks. Consequently, data from 30˚N to 30˚S are all flagged as suspect. Comparisons of “wet” and “dry” air at several locations indicate that sites outside of this range are not affected.

Field testing of a new prototype air sampling apparatus began at SMO in September 1994 and Cape Kumukahi, Hawaii (KUM) in May 1995. The new AIRKIT (Air Kitzis sampler) differs from the previously used MAKS (Martin and Kitzis Sampler) in two important ways. First, it has a thermoelectrically cooled condenser to remove water vapor from the air stream, and secondly it has a microprocessor to control the sampling process so that collecting the sample is more automated and less subject to operator error. The effect of drying the air sample is most dramatic for the measurement of $^{18}O/^{16}O$ in CO_2. Figure 5 shows the dramatic improvement in the $\delta^{18}O$ values of CO_2 from Seychelles, (Mahe Island, 4° 40’ S, 55°10’ E) when the switch to using dried air was made in September 1998. There is also speculation that the $\delta^{13}C$ values may be affected by the moisture as well. In autoruns with larger numbers of "wet" flasks, the trap tank value appears to be very slightly shifted in $\delta^{13}C$ (less than 0.003‰). As the precision of the isotopic measurements improves, this suspected problem may become an issue.

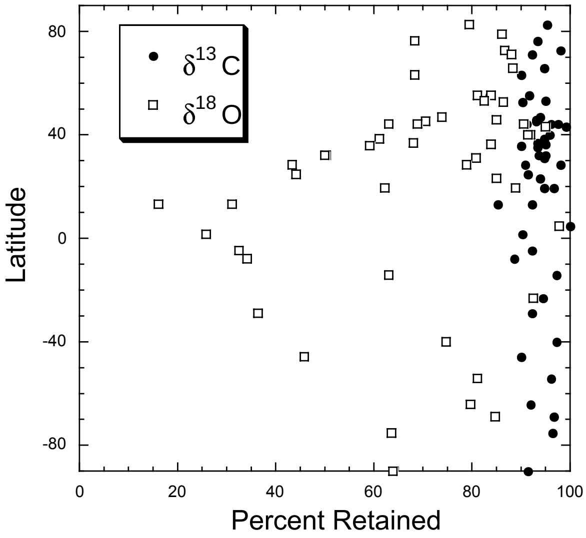

Figure 4. Percentage of flasks from the NOAA network retained for both $\delta^{13}C$ and $\delta^{18}O$ at each site, plotted against latitude. Moisture is a key factor in low retention rates at low latitudes for $\delta^{18}O$.

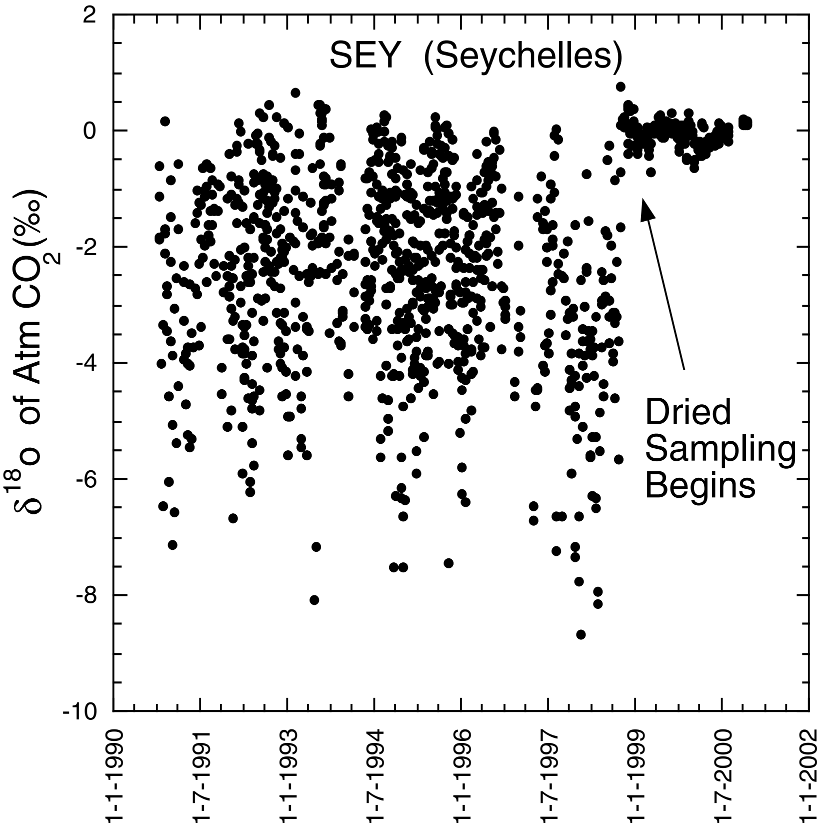

Figure. 5. Oxygen-18 in flask samples from Seychelles (4° 40'S, 55°10' E).

2.2 Isotopic measurements at GASLAB, CSIRO

The long running CSIRO program is documented in a number of technical publications that can be obtained on request, and are briefly summarized here. Two unusual features of the CSIRO program have been: (1) an emphasis on sample drying since inception in 1977, and (2) redundancy in methods of sample collection and sample pre-treatment.

2.2.1 Sample collection and pre-treatment

The Cape Grim *in situ* program commenced in 1977. It involves cryogenic drying, then extraction of CO_2, from around 30 standard liters of air over a two hour period. The extracted CO_2 (about 10 standard ml, 400 μmol) is stored in 100 ml glass flasks fitted with a Teflon o-ring sealed stopcock, and these are returned to CSIRO laboratories at Aspendale for isotopic analysis. Method details, and data from 1982 to the end of 1996 are given in 4 key references [17,18,2].

Flask sampling of whole (dried) air is now conducted from about 13 global sites [15]. A consistent feature of this sampling network has been the chemical drying (magnesium perchlorate) of all flask samples during sample collection. Initially, from 1984, air sampling involved pressurized 5-litre volume glass flasks (8–10 standard liters of air) from 5 sites. The air in the 5 L flasks was completely processed to extract CO_2 with a cryogenic extraction line similar to that used at Cape Grim. The CO_2 samples (about 3 ml, 120 μmol, STP) were stored in 100 ml glass flasks identical to those used for Cape Grim *in situ* samples, until analysis. Since 1992, similarly pressurized 0.5 L glass flasks have been employed, although some 5 L glass flasks are retained for flask storage comparisons. These flasks are processed using a Finnigan MAT (Bremen, Germany) MT Box-C cryogenic separation system that is connected directly to a dedicated inlet of the mass spectrometer system. Typically, 30 ml of air is processed that yields about 10 standard μL (0.4 μmol) of CO_2 for mass spectrometer analysis.

The MT Box-C cryogenic separation system, interfaced directly to MAT252 mass spectrometer, uses a slightly different trapping procedure to that employed at INSTAAR. Sample air passes through two small-volume traps, maintained at –196°C, at a flow rate of about 5 ml/min. H_2O and CO_2 are trapped in the first of these two traps. After processing the required volume of air, the first of these two traps is heated to –100°C and the CO_2 is cryo-distilled into the second trap. The yield of CO_2 is then determined (for use by the automated analysis procedures) and a second cryo-distillation of the CO_2 into a micro-volume trap follows. The CO_2 is analyzed directly from this micro-volume. The entire inlet system is manufactured from stainless steel and all valves in the MT Box-C are constructed from stainless steel with gold seats. The MT Box-C device has a 12-port manifold to which 10 sample flasks and one or two air standards are connected for a typical analysis sequence. Sample flasks are connected to the MT Box-C using Cajon Ultra-Torr fittings fitted with Viton o-rings. Air standards are connected using Swagelok stainless steel fittings. Details of the MT Box-C are given in [15].

N_2O cannot be physically separated using the procedures employed at CSIRO and is co-trapped from air samples with CO_2. The procedure to correct for the presence of N_2O is described previously.

2.2.2 Mass spectrometers used at CSIRO

Between 1977 and 1991, a Micromass 602D dual inlet stable isotope ratio mass spectrometer was employed. In 1991, a Finnigan MAT252 dual inlet mass spectrometer was commissioned and operated in parallel with the 602D for 18 months. Since 1992, the MAT252 has been used for all CO_2 isotopic analysis at CSIRO Atmospheric Research. The basic principles of operation of these mass spectrometers are similar to those described above for the INSTAAR mass spectrometer and are not detailed here.

At CSIRO, we have identified a number of systematic effects in the measurements of stable isotope ratios of CO_2. Two significant effects that are regularly monitored, and for which we have developed correction procedures, are termed the “bleed effect” and the “working gas effect”. The bleed effect arises from the small depletion of $^{12}CO_2$, with respect to $^{13}CO_2$, in the reference CO_2 gas that occurs over time. We treat this effect in two ways. First, we replace the working gas in the bellows frequently to minimize the effect, and second, we quantify the magnitude of the effect and apply a correction to all measured samples based on the elapsed time between loading and use of the reference gas. The working gas effect is a “memory effect” (and is also known as cross contamination) where a small amount of sample gas is analyzed with the reference gas and a small amount of reference gas is analyzed with the reference gas. The result of this effect is to reduce the magnitude of the measured difference between sample and reference gas. Measuring this effect on CO_2 gases with significantly different isotopic composition from the reference gas monitors the effect and allows a correction procedure to be applied. These effects have been described in more detail elsewhere [1,12,24]. Modifications were made to the ion source of the MAT 252 in 1997 that reduced the working gas effect considerably.

2.2.3 Standards and calibrations

The $CO_2\delta^{13}C$ and $\delta^{18}O$ data are reported on the international VPDB-CO_2 scale. First, δ45 and δ46 values of sample CO_2 are obtained with respect to a pure reference CO_2. The reference CO_2 is one of 6 sub samples of an ultra-high purity high-pressure cylinder of CO_2 (HC453) maintained in large-volume glass containers. HC453 has been the sole source of reference CO_2 for use at CSIRO since 1977 and HC453 sub samples were measured against NBS-19 in the 1980's resulting in an assignment of VPDB-CO_2 values of $\delta^{13}C = -6.396‰$, and $\delta^{18}O = -13.176$ ‰ [17]. The link to VPDB-CO_2 has been maintained by comparisons between these sub-samples. Corrections to convert δ45 and δ46 values to preliminary $\delta^{13}C$ and $\delta^{18}O$ are applied using methods described by [4]. This includes correction for the presence of nitrous oxide, co-trapped with the CO_2, using measured concentrations of N_2O and CO_2 in each sample [15].

Final $\delta^{13}C$ and $\delta^{18}O$ values on the VPDB-CO_2 scale are obtained after a correction based on comparison of measured and assigned values in air standards (high-pressure cylinders of air) that are processed every 4 samples. The initial assignment of VPDB-CO_2 isotopic values to air standards was referred to as CG92 [2]. A revised assignment, CG99, was developed during 1999–2000, which takes into account recently identified and independently quantified systematic biases. The CG99 assignment is used here.

CSIRO expressions of the VPDB-CO_2 scale are monitored using a number of high-purity CO_2 standards (GS–19, GS-20, OZTECH-3, OZTECH-30, OZTECH-40) and a number of surveillance standards (high-pressure cylinders of air). The very small sample requirements mean that all high-pressure cylinder air standards used since 1991 remain in the surveillance suite. (Note: Measurements made on all surveillance gases are used solely for diagnostic, not adjustment, purposes).

CSIRO monitors its expression of the VPDB-CO_2 scale relative to those of other laboratories, using a range of samples that includes the three NIST high-purity CO_2 SRMs [30], the IAEA CLASSIC cylinders (two four-laboratory circulations of 5 cylinders) [5], flask air sharing comparisons with several laboratories (for example, ~ six flasks of air per month with NOAA/CMDL since 1992) and through participation in other comparison exercises.

3. ISOTOPIC MEASUREMENTS USING GAS CHROMATOGRAPHY–ISOTOPE RATIO MASS SPECTROMETRY

3.1 Isotopic measurements at NIWA using GC-IRMS

The traditional method used to perform isotopic measurements of atmospheric CO2, dual-inlet IRMS, has the following two problems: 1) co-extraction and analysis of contaminating N_2O with the CO_2 of interest such that post-measurement correction is required and 2) the requirement for relatively large samples of CO_2 (a few tenths to several μmol) [11].

To avoid the problems and sources of error that arise due to this inclusion of N_2O in the CO_2 sample during dual-inlet analysis, either a standardized correction procedure must be used by all laboratories, as recommended by [4], or analysis of N_2O-free samples must be achieved.

To address these shortcomings in the dual inlet technique, a number of labs have been exploring the GC-IRMS technique (Gas Chromatography, Isotope Ratio Mass Spectrometry), which enables N_2O-free, high-precision isotopic analysis of atmospheric CO_2. Typically, GC-IRMS systems have significantly less precision than dual inlet techniques, and thus the primary challenge for GC-IRMS techniques is to achieve acceptable precision in the isotopic measurement. We describe here the system recently developed at NIWA in New Zealand [11].

3.2 Experimental setup at NIWA

3.2.1 GC-IRMS inlet system

The layout of the GC-IRMS system is shown in Figure 6. The basic components are as follows. A 10-port valve (Valco Instruments Co. Inc., Houston, Texas) is used to direct sample air into the GC, an HP5890 Series II (Hewlett Packard, Avondale, Pennsylvania, USA). Switching between sample/reference gases and vacuum on/off is performed with pneumatic valves (Nupro) controlled by LabView™ (National Instruments, Austin, Texas, USA). Sample aliquot introduction into an evacuated sample loop and pressure-equilibration-volume (PEV) before injection is described in section 3.2.3. Gas separation is performed with a packed column described in Section 3.3.1.

After GC separation, sample gas enters the open split interface via a Nafion™ MD — Series Gas Drier (Perma Pure Inc., Toms river, New Jersey,) which is discussed further in Section 3.3.2.1. Two independent air-actuated pistons switch between the sample capillary (deactivated quartz glass, 0.32 mm ID flow rate 3.0 ml/min) and the helium purge gas capillary (deactivated quartz glass, 0.32 mm ID flow rate 5 ml/min). Transfer of sample gas or purge helium from the open split to the IRMS was through a deactivated glass capillary, 0.11 mm ID, 1 m long, (SGE, International Pty Ltd., Ringwood, Victoria, Australia) at a flow rate of 0.3 ml/min. Obtainable precision is critically dependent on the open split design, which is further discussed in Section 3.3.2.2.

Isotopic analysis of CO_2 is performed by a Finnigan MAT 252 IRMS with an accelerating potential of 10 kV. This IRMS utilizes a Multielement — Multicollector (MEMCO) system with Faraday cups connected to feedback resistors of 3×10^8, 3×10^{10}, and 1×10^{11} Ω to simultaneously measure m/e 44, 45, and 46 ion currents, respectively. The IRMS was tuned for a compromise between maximum sensitivity (<1200 molecules/ion) and minimum nonlinearity (<0.10 ‰/V for $\delta^{13}C$ and <0.15 ‰/V for $\delta^{18}O$, respectively) between ~0.2 and 1.5 V (~0.7 to 5 nA) m/e 44. In the course of the development, new Finnigan source slits were installed to the IRMS, the advantages of which are discussed in Section 3.3.1.

3.2.2 Analysis procedure

Routine analysis is provided by injection and analysis of (1) a reference gas aliquot, (2) three aliquots of a sample, and (3) a second aliquot of the same reference gas. The average 44/45 and 46/44 ratios and areas of the two reference gas aliquots are used to calculate $\delta^{13}C$, $\delta^{18}O$, and the CO_2 mixing ratio of the sample, respectively. This bracketing of the sample aliquots with reference gas aliquots further reduces the effect of any instrumental drift that may occur during the period of analysis.

During the analysis procedure the sample loop and adjacent plumbing (see Figure 6) are first purged with reference gas for 30 s at a flow rate of 60 ml/min. The flow is stopped, and pressure equilibrates for 5 s after which injection through both the precolumn and main column occurs for 230 s. Following injection, the precolumn is back flushed for 270 s. Meanwhile, the open split interface switches from directing pure helium to the IRMS to sample effluent, ~60 s before the eluting CO_2 peak. Integration of the CO_2 peak follows. Approximately 45 s after the final integration point of the CO_2 peak, the open split redirects the flow to the IRMS to pure helium.

For sample gas aliquots the sample loop and adjacent plumbing are evacuated rather than pressure flushed. To ensure peak reproducibility, the same amount of gas must be introduced to the IRMS for each sample aliquot. Thus each sample aliquot must be at the same pressure, volume, and temperature (PVT). To facilitate this, a vacuum is applied to the sample flask valve, through the 0.5 ml sample loop and into a 5 ml PEV, 1.36m × 3.175 mm OD (1.016 mm ID.). After introduction of the sample aliquot to the sample loop, the PEV valve is opened to enable sample loop equilibration to ambient pressure. For samples flasks with above ambient pressures, outflow from the PEV to the laboratory atmosphere occurs, and for samples at or below ambient pressure, inflow from the laboratory atmosphere into the PEV occurs. This equilibration is necessary to ensure that sample/reference gas injections are at the same PVT. During this equilibration for samples collected at or below ambient pressure, the PEV is necessary to avoid contamination by stopping “suck back” or inflow of laboratory air into the sample loop. Furthermore, during sample loop filling, up to 5 ml of sample gas purges through the sample loop to ensure that no residual from a previous sample or reference gas is injected as a contaminant.

Initially, for each new sample, the PEV valve is closed, and all plumbing to the flask valve is evacuated by a turbo molecular pump to a pressure of ~0.01 Pa. This volume is filled, re-evacuated, and refilled before an analysis commences. The vacuum pump connection then switches from turbo to roughing pump for the automated run. After the reference gas injection and 450 s prior to each subsequent sample injection, the PEV valve is closed, and the PEV, sample loop, and adjacent plumbing are evacuated. Typically, a vacuum of ~0.02 Pa is obtained in this time, after which the vacuum inlet is closed, and the sample valve opens, filling the sample loop, PEV, and adjacent plumbing. To ensure equilibration between the sample flask and sample loop, the sample valve remains open for 30 s. Pressure equilibration of each sample aliquot to ambient pressure then occurs by opening the PEV valve for 5 s. To avoid sample contamination during pressure equilibration of each sample aliquot, it is critical that inflow of laboratory air into the inlet volume must not pass beyond the PEV.

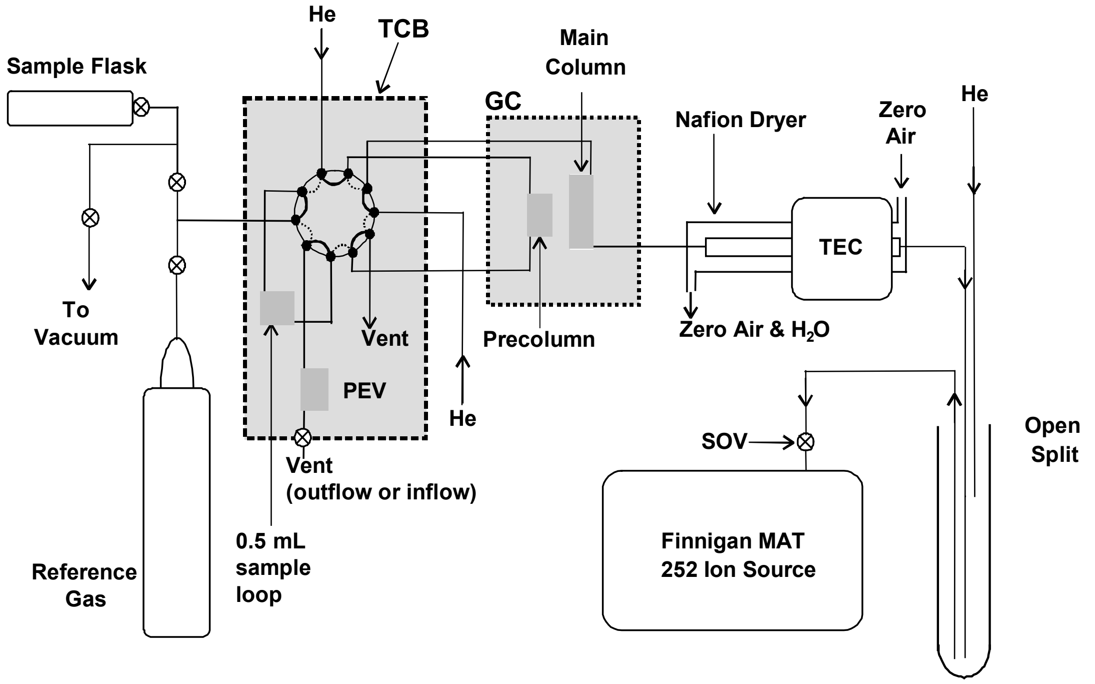

Figure 6. Gas chromatograph—isotope ratio mass spectrometry (GC-IRMS) schematic. The 10-port valve and adjacent plumbing are enclosed in a temperature controlled box (TCB) and automatically switch between load/back flush (solid loops) and inject (dashed loops). Pressure equilibration of sample gas before injection to the GC column occurs in the pressure-equilibration-volumn (PEV). After GC separation, gas effluent flows through a Nafion drier and enters the open split. The Nafion drier is cooled by a thermoelectric cooler (TEC) and is purged by a countercurrent flow of clean dry "zero"air. To enable gas stream switching, the sample and purge helium capillaries alternately move into the immediate proximity of the tip of the transfer capillary, which is permanently positioned at the bottom of the open split. The open split has two positions: (1) "open split in," (sample capillary extended and helium capillary retracted, as shown in figure1), where the Finnigan MAT 252 IRMS receives undiluted GC sample effluent and, (2) "open split out" (sample capillary retracted and helium capillary extended), where the Finnigan MAT 252 IRMS, receives pure helium. The shutoff valve (SOV) is closed to enable operation of the IRMS in dual-inlet mode.

For routine analysis (three aliquots) of air samples collected at ambient pressure, total sample usage is 45 ml. This usage is high compared with the total amount actually injected onto the column (three 0.5 ml aliquots) and is currently limited by the 15 ml inlet volume (sample loop, PEV, and adjacent volume). For routine analysis of an air sample collected to 100 kPa total sample usage is 90 ml. This higher total sample usage (compared to that required for air samples collected at ambient pressure) results because the 15 ml inlet volume is filled to the pressure at which the sample was collected (~100 kPa above ambient pressure), rather than ambient pressure.

3.3 Results and discussion of the GC-IRMS system

3.3.1 Separation of CO_2 and N_2O

Porapak-Q was found to provide the best separation between CO_2 and N_2O. After the installation of the new Finnigan memory effect reducing source slits, the excessive "tailing" of the CO_2 peak was reduced, and the CO_2 — N_2O separation was improved. This made possible complete separation of N_2O from the integrated CO_2 peak (Figure 7) to enable N_2O-free determinations of $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2.

The specifics of the column used is a Porapak-Q, 3.66 m × 1.59 mm OD (1.016 mm ID), stainless steel, 80/100 mesh with a 1.83 m precolumn of the same material (Alltech). This is used at a temperature of 41°C with a helium carrier gas flow rate of 3.0 ml/min.

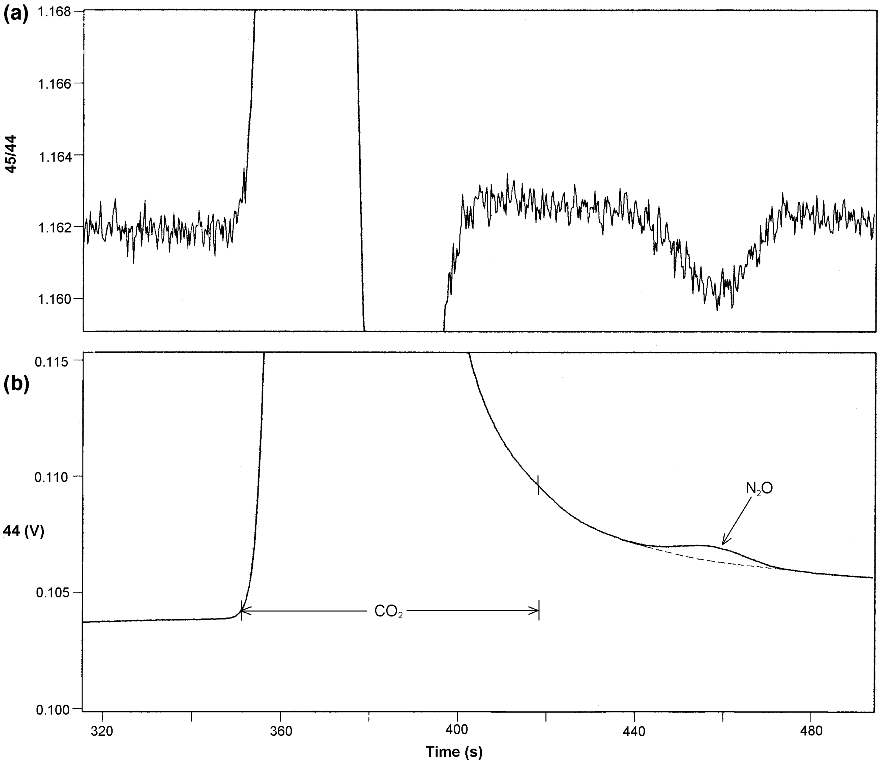

Figure 7. (a) 45/44 isotope ratio and (b) mass 44 chromatogram. Results of separation using the memory effect reducing source slits: The tick marks shown are the positions at which the software starts and ends the peak integration. The 1000 times smaller N_2O peak, which is visible as a small blip on the large CO_2 tail, is completely separated from the integrated CO_2 peak, allowing for a completely N_2O-free calculation of $\delta^{13}C$ and $\delta^{18}O$ in CO_2.

3.3.2 Maximization of signal-to-noise ratio

3.3.2.1 Contamination and carrier gas purity

High carrier gas purity is required to minimize background contamination and noise. This is achieved with the use of an in-line gas purifier (ALL-Pure Helium Purifier, Alltech) to purify helium of purity greater than 99.995% so that contaminants (CO, CO_2, O_2, H_2O, and NMHCs) were reduced to ppb levels.

Entrainment of laboratory air into the inlet system results in increased background levels and noise and loss of precision. This is mainly because laboratory air is relatively "wet," and the formation of HCO_2^+ molecules in the ion source contributes to a loss of precision and accuracy [22]. Thus it is imperative for high-precision results to maintain the inlet system completely leak free and dry. IRMS background water levels are minimized and maintained at a constant level by passing all GC effluent through a Nafion drier consisting of a 610 mm long, 0.762 mm ID Nafion tubular membrane in a 1.59 mm OD stainless steel sheath. Clean, dry "zero" air (dew point < –80 °C) purges the Nafion drier at a flow rate of ~100 ml/min. The Nafion purge flow (~100 ml/min) is high compared to the sample flow (~3 ml/min) to ensure high drier performance [21]. A thermoelectric cooler (TEC) (Tropicool, Christchurch, New Zealand) cooled the second half of the Nafion to 0 °C. By cooling the Nafion the vapor pressure in equilibrium with the membrane decreases, and the effectiveness of the drying is enhanced [21]. The addition of the TEC decreases the dew point of the emerging dried gas from ~ –45°C to < –80°C, corresponding to a drop in background water (m/e 18), as measured on the most sensitive detector in the Finnigan MAT 252 IRMS, from 2.2 to 1.030 V (2.2 to 1.03 pA).

3.3.2.2 Open split design

The open split interface is an integral part of the system as it forms the critical GC-IRMS link and allows for the continuous flow of either sample gas or pure helium into the IRMS. For this application, the open split is designed to minimize entrainment, contamination, and sample dilution and maximize reproducibility and precision. The open split is a Pyrex glass test tube, open at the top, with the following dimensions: 60 mm long, 1.9 mm OD, and 1.3 mm ID. Gas stream switching, previously described in Figure 6, enables a high signal-to-noise ratio. The split ratio is ~1:9; that is, of the sample effluent that enters the open split at 3.0 ml/min, only ~10 % actually enters the ion source at 0.3 ml/min (this factor is currently limited by chromatography and not the open split design). Thus, in the technique described here and for samples at current atmospheric levels, ~8 nmol CO_2 is injected onto the GC column, and 0.8 nmol of this enters the IRMS source.

3.3.3 Reproducibility: temperature and pressure effects

Reproducibility and precision of the measured CO_2 mixing ratio are strongly affected by temperature and pressure variations that occur for each eluting peak during a GC-IRMS analysis. Because of the IRMS nonlinearity, $\delta^{18}O$ and $\delta^{13}C$ measurements are also affected.

Temperature variations are generally nonlinear and non-monotonic over the analysis period and are therefore important for reproducibility. In addition, temperature variations change the value of the high-precision resistor that regulates the magnet current in the Finnigan MAT 252 IRMS, (*W. Brand*, personal communication, 1999). The detected signals are therefore affected because magnetic field strength variations cause the ion beam to be shifted.

The background noise is further magnified when operating in GC-IRMS mode, owing to variations in open split entrainment. This occurs because the relative pressure difference between the slightly above ambient pressure open split (due to the purge helium) and the laboratory is affected by temperature variations. This further highlights the need for a well-designed open split so that minimal (if any) entrainment and IRMS contamination occurs.

The effects of laboratory temperature variations should be minimized by stabilizing the inlet system temperature to <0.2°C/h. Insulation of the inlet system, from the reference gas regulators through to the open split, can achieve this. In addition, temperatures are stabilized in the transfer capillary and SOV to the IRMS to <0.1°C/h by insulation of the section. Furthermore, the sample loop, PEV, and adjacent plumbing are maintained at a stable temperature of 35.00 ± 0.02°C by enclosing this section within an insulated, temperature-controlled box (TCB). Temperature control to this level within the TCB is achieved with the use of an external GC temperature sensor and a 40 W cartridge heater. A 2 W electric fan circulated air within the box, and two thermal masses of 150 ml water and 1.6 kg brass were positioned in the box. These measures reduced the uncontrollable temperature effects due to laboratory air temperature variations and improved technique precision.

3.3.4 Analysis time

The analysis time is determined by the requirements for sufficient N_2O–CO_2 separation, high signal-to-noise ratio, and a sufficient number of reference and sample aliquots for good statistics and to reduce instrumental drifts. The analysis time includes the time required for extraction of CO_2 from the air sample. Increasing the carrier flow rate in the column decreases the analysis time. However, reduced separation and increased sample dilution occurs, resulting in lowered signal strength, reduced signal-to-noise ratio, and lowered precision. A balance between the analysis time, adequate separation, dilution, and precision is achieved at an analysis time of 40 min, which is comparable to that required for dual-inlet analysis.

Using the technique described here, mass spectrometers that have a large memory effect may not be used (without modification) to obtain high-precision, N_2O-free isotopic analyses of atmospheric CO_2 in short analysis times.

3.3.5 Technique performance

Maximum performance can be evaluated by considering the “shot noise limit.” This limit is based on ion collection statistics and refers to the precision that would be obtained if the ion beam were the only significant noise source [27]. Simplified expressions from [25] for the shot noise limited precision (σ_δ) expressed as functions of the integrated m/e 44 signal area (${}^{44}A$, V·s) are

$$\sigma_\delta^2 = 0.00892/{}^{44}A$$

If the integrated ion currents of the reference and sample are not equal, then

$$\sigma_\delta^2 = 0.00446(1/{}^{44}A_{\text{reference}} + 1/{}^{44}A_{\text{sample}})$$

In the initial paper describing this technique by [11] the precision of the technique for $\delta^{13}C$, $\delta^{18}O$, and CO_2 mixing ratio, determined by both analysis of atmospheric air samples and replicate analyses of air standards, was 0.02 ‰, 0.04‰ and 0.4 ppm, respectively. Comparing the observed and theoretical shot noise limited $\delta^{13}C$ precision, it was seen that the technique performs at the shot noise limit of 0.02‰.

Evaluating technique performance over a range of sample sizes can be performed by introducing differing amounts of CO_2 to the ion source of the IRMS by varying the open split dilution. The split ratio of 1:9 was increased by introducing reference and sample CO_2 with the helium capillary also extended and increasing the open split helium purge flow from the normal 5 ml/min to ~20 ml/min. Replicate analyses of an air standard by this method are shown in Figure 8. Over the observed range of 150 pmol to 1 nmol CO_2 in the source, the technique performs within a factor of 1.3 of the shot noise limit. At the lower limit of 150 pmol CO_2 in the source, the technique performs within a factor of 1.5 from the shot noise limit, indicating that the effects of noise or systematic error become more significant at these lower sample sizes.

It can be seen from the theoretical prediction (Figure 8) that by increasing the amount of gas reaching the IRMS source (while maintaining matched reference and sample sizes), higher performance (i.e. lower standard deviation) is possible. However, this performance is ultimately limited by IRMS detector overload, which for eluting CO_2 peaks from the experimental technique presented here in a Finnigan MAT 252 IRMS, would occur at ~4 nmol CO_2 in the source. A shot noise limited precision of 0.01‰ is theoretically possible with 3 nmol CO_2 in the source. This would be possible by this technique if the split ratio could be reduced to ~1:2.2. This precision is comparable to that of the dual inlet technique.

While this theoretical precision has yet to be achieved on a routine basis, GC-IRMS measurements, even at a coarser precision, opens many new doors for analysis of isotopes in atmospheric CO2. These new opportunities for trace gas research are now possible because of the smaller sample requirement of GC-IRMS. The logistics of new sampling methods (e.g. sampling from pilot less aircraft (kites and gliders) and international commercial flights) will be eased as will sampling and analyzing CO_2 from ice cores. Traditionally, large volumes of carbon-containing trace gases are converted off-line to CO_2 for $\delta^{13}C$ analysis, for example, up to 35 L for CH_4 [23]. The GC-IRMS technique developed in this work can be used as a "front end" in a modular approach to GC-IRMS for other carbon-containing trace gases. On-line preparation of trace amounts of gases can be performed by miniaturized versions of existing methods and injected directly into the CO_2 GC-IRMS system presented here for isotopic and mixing ratio analysis.

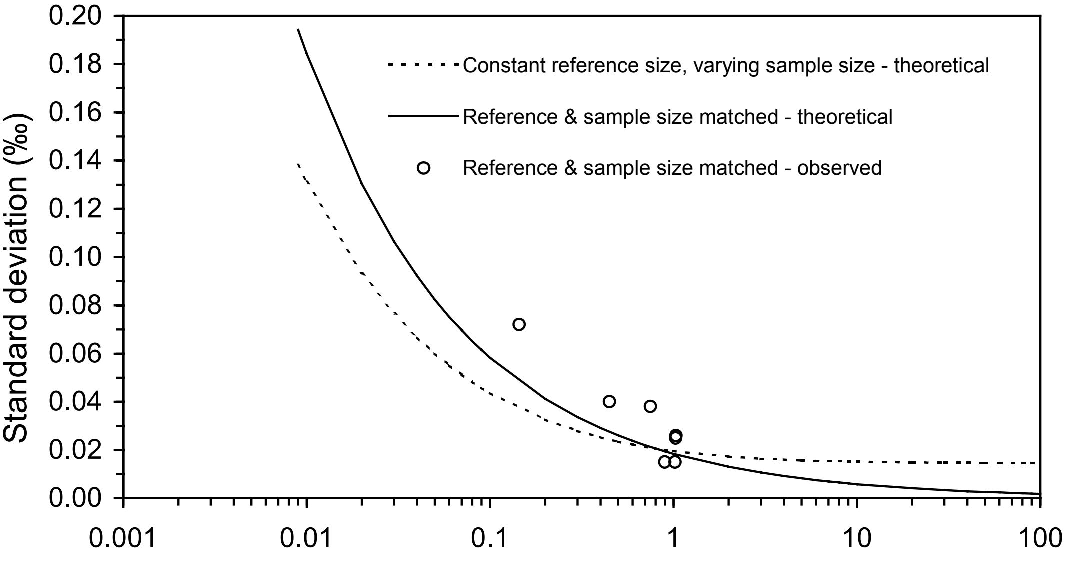

Figure 8. Observed and theoretical (shot noise limited) standard deviations for varying amounts of CO_2 in the IRMS source.

4. CONCLUSIONS

Isotopes in atmospheric CO_2 are key properties for separating terrestrial biospheric and oceanic exchanges of carbon with the atmosphere and for potentially separating regional scale respiratory and photosynthetic fluxes in terrestrial ecosystems. The primary challenge is to achieve acceptable accuracy and precision and to maintain them over the decades needed to observe variability of the carbon cycle. We are pushing our analytical capabilities to their limit in this application of stable isotopes, and small artifacts that may be unobservable or unimportant in normal mass spectrometry will become important.

The keys to success in this approach are diligent intercalibrations of laboratories from around the world, as well as the use of multiple techniques such as dual inlet and GC-IRMS mass spectrometery.

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ISOTOPE MEASUREMENT TECHNIQUES FOR ATMOSPHERIC METHANE

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Abstract. Measurement techniques for the carbon isotopic composition of atmospheric methane ($\delta^{13}C$) are described in detail as applied in several leading institutions active in this field since many years. The standard techniques with offline sample preparation and subsequent measurement by dual inlet isotope ratio mass spectrometry (IRMS) are compared with continuous flow IRMS. The potential use of infrared absorption spectroscopy is briefly discussed. Details on quality control and calibration are provided. Basic analytical aspects for the measurement of other species, ^{2}H and ^{14}C, are also given.

1. INTRODUCTION

Determination of methane in air trapped in bubbles of Antarctic ice show that the burden of atmospheric methane has more than doubled over the last 150 years [1,6] due to an excess of methane sources over sinks. Major sources of atmospheric methane include methanogenesis in wetlands, rice paddies and landfills, enteric fermentation in ruminant animals, venting of natural gas and emissions from biomass burning. More than 90% of methane removal is believed to be due to oxidation in the troposphere by the hydroxyl radical (OH) with removal by soil bacteria and stratospheric losses considered to be less important [2,3,4,5]. An extensive series of mixing ratio measurements made at a number of sites in the northern and southern hemispheres in conjunction with atmospheric chemistry and transport models have been used to develop a consistent picture of the global methane budget [7,8,9]. In addition, measurements of variations in the isotopic composition of atmospheric methane have provided valuable additional constraints on the budget because several of the sources can be distinguished by their characteristic ^{14}C, ^{13}C and ^{2}H signatures [10,11,12,13].

Because atmospheric methane mixing ratios are relatively low, today ca. 1800 ppb, techniques for high precision determinations of its isotopes are non-trivial. The scope of this report is, thus, to provide readers with a summary and a list of references to the scientific literature describing various published techniques used to make isotope measurements in atmospheric methane. The list includes published work known to the authors of this report and we apologise in advance for any omissions. We welcome input from readers with additional information that could be included in future IAEA-TECDOC reports on isotope measurement techniques for atmospheric greenhouse gases. We also provide a list of laboratories that can be contacted for more information.

2. DETERMINATION OF ^{13}C IN ATMOSPHERIC METHANE

2.1 Standard techniques based on offline sample preparation and dual inlet IRMS

Early determinations of ^{13}C in atmospheric methane have been summarised by [14] and early techniques for its measurement have been reported [15,16,17]. Subsequent methods based on these earlier techniques have been published [10,13,18,19,20]. These techniques are all based on the use of isotope ratio mass spectrometry (IRMS) running in dual inlet mode. They require the quantitative extraction of methane from rather large volumes of ambient air, typically 20–500 litres. The methods provide a typical precision of about ±0.05‰, which is sufficient to track the relatively small seasonal cycles and secular trends in ^{13}C in atmospheric methane. However, the methane must first be quantitatively extracted from the air samples and converted to CO_2. This can be done in several ways.

2.1.1 Standard technique used at National Institute of Water and Atmospheric Research, Wellington, New Zealand (NIWA)

For example, [19] have used a vacuum conversion line for a "flow through" procedure based on a method inspired by the early work of Stevens [15]. First the air sample is stripped of remaining water, CO_2, N_2O, and light non-methane hydrocarbons (NMHC) by passage at 1 liter·min^{-1} (controlled by an integrating mass flow controller) through a series of cryogenic traps held at liquid nitrogen temperature. In addition CO is removed from the stream by passage through a 350g bed of Schütze reagent (Leco Corporation, St Joseph, Missouri), where the active reagent is iodine pentoxide on a silica gel support. Subsequently, methane in the air sample is combusted at 750°C in a furnace containing 100g of 1% platinum catalyst supported on 3mm alumina pellets (Aldrich, Milwaukee, Wisconsin). The resulting CO_2, which retains the ^{13}C/^{12}C and ^{14}C/^{12}C ratios from the methane in the air samples, and water from the combustion are collected in cryogenic traps immediately after the furnace. The water is removed at –80°C over alcohol dry ice traps by triple vacuum distilling the CO_2 from the cryogenic traps into small pyrex bottles or flame sealed pyrex tubes. This CO_2 is analyzed for ^{13}C by IRMS and the same gas may be used for ^{14}C determinations [19].

Conversion of the methane in an air sample to CO_2, is done by first flushing the conversion line with about 20 litres of sample immediately followed by the combustion of the methane in about 15 litres of air using the technique described above. At a typical ambient methane mixing ratio of about 1700 ppb, approximately 25μl of CO_2 are derived from the methane in each air sample. Conversion yields for the process are calculated using the collected CO_2 pressure and volume in a calibrated manometer at room temperature compared with the CO_2 expected on the basis of the air sample methane mixing ratio and the amount of air processed as determined by an integrating mass flow controller. Measured yields are approximately 100%, and subject to errors of about 2% in each of manometer pressure times volume determinations and measurement errors in the integrating mass flow controller.

^{13}C/^{12}C ratio measurements of the CO_2 derived from the methane are made using a Finnigan MAT (Bremen, Germany) 252 IRMS running in dual inlet mode. The sample inlet side of the IRMS has been modified by inserting a 500μl cold finger stainless steel volume at the head of the sample capillary with the inlet isolated by a pneumatically actuated gold seated dual valve (Finnigan MAT, Bremen). This allows the direct introduction of 10–80μl CO_2 samples from volumes of either 500μl or 2.5ml into the IRMS ion source. With this inlet system m/z =44 signals are typically 4 volts (collector resistance $3\times10^8\Omega$) and the precision of individual $\delta^{13}C$ determinations (10 changeovers) is typically 0.01‰.

The standard notation: $\delta^{13}C = (R_s/R_r - 1) \times 1000$ [in ‰] is used to report $^{13}C/^{12}C$ ratios as parts per mille (‰) where R_s and R_r are the $^{13}C/^{12}C$ ratios of the unknown sample and a working reference gas, respectively. The working reference is dry CO_2 stored in a 25 liter glass flask at 1.1 bar and is metered as required via 3mm OD stainless steel lines and Nupro (Nupro, Willougby, Ohio) high vacuum valves into the variable volume bellows on the reference side of the MAT 252. The reference CO_2 is made from combusted, purified, land fill methane and mixed with CO_2 derived from marine carbonates to produce a $\delta^{13}C \approx -47$‰, which is in the middle of the range expected for atmospheric methane samples. Two working references denoted CH4WR1 and CH4WR2 were prepared in this fashion. These isotopically "light" CO_2 working reference gases are compared with CO_2 evolved every 6–12 months from NBS19 carbonate supplied by the International Atomic Energy Agency (IAEA), Vienna, Austria [21]. This provides the link to the VPDB scale widely used in the literature and all measurements are reported as ‰ deviations from VPDB. CH4WR1 and CH4WR2 were first determined at $\delta^{13}CH_4 = -47.07 \pm 0.01$ and -47.02 ± 0.01‰ VPDB respectively versus NBS19 in January 1995 and repeated comparisons since then show that any drift in these values is less than 0.005‰ in 3 years. As a control, the two light working reference gases are compared against each other on the MAT 252 IRMS at the start of each day that $\delta^{13}C$ in methane analyses are made.

An additional assurance of calibration is provided by the light barium carbonate reference material IAEA-CO-9, also known as NZCH [21,19]. The published values for this material are $\delta^{13}C = -47.119 \pm 0.149$‰ and $\delta^{18}O = -15.282 \pm 0.093$‰. Quality assurance is provided by the routine measurement of $\delta^{13}CH_4$ in methane mixtures in synthetic air and ambient methane in dry air samples collected at Baring Head, New Zealand and stored or "archived" in stainless steel tanks as described by [22]. These controls provide confidence in the sample preparation and analysis techniques. The overall precision of the technique at 1 sigma level is 0.02‰, as determined by $\delta^{13}C$ in methane analyses of sets of duplicate air samples collected at Baring Head. Inter-calibration has also routinely been carried out with other laboratories making $\delta^{13}CH_4$ measurements in air. For example, a set of 15 air samples exchanged between Paul Quay, University of Washington, Seattle and NIWA and analysed for $\delta^{13}CH_4$ by both labs showed a mean difference of 0.01±0.05‰ [22]. A similar inter calibration exercises is currently in progress with the Geosciences Department, University of California, Irvine and a set of 16 samples exchanged between the two labs from early 1995 to mid 1998 shows a mean analysis difference for $\delta^{13}CH_4$ of 0.01±0.06‰.

2.1.2 Standard technique used at Max Planck Institute for Chemistry, Mainz, Germany (MPIC)

In order to allow also optical isotope ratio measurements on highly preconcentrated CH_4 samples (for δD analysis, see section 3) as well as concomitant analysis of carbon monoxide, a new sample preparation line has been designed [10], based on the techniques developed for CO isotope analysis, followed by a preconcentration unit using activated charcoal. The CO part of this system is as described by [23].

Briefly, the air sample is introduced into the line using a mass flow controller (5 liter·min^{-1}, STP), followed by two ultra-efficient metal Russian Doll traps (RDT) [24] at 77 K in order to remove H_2O, CO_2, N_2O and NMHCs (except ethane). Subsequently the sample air is pumped through Schütze's reagent (I_2O_5 on acidified silica gel), which converts CO quantitatively into CO_2. This CO derived CO_2 is trapped in a succeeding glass RDT [25].

Following the CO extraction, the sample air enters a cold trap (77K) containing 75 g of granular activated charcoal, which quantitatively adsorbs CH_4. Pressure is held below 200 hPa within the entire system to prevent liquefaction of O_2. After processing of the air sample, first the CO derived CO_2 is transfered into a drying finger (containing P_2O_5), subsequently into a calibrated volume, where the pressure is determined precisely, and finally into a sample collection bottle. Desorption of CH_4 from the activated charcoal trap is achieved by heating to 100^oC, during which the desorbing gases are directed through a second small activated charcoal (2 g) trap at 77K. Subsequent desorption of CH_4 from this small trap occurs rapidly at room temperature. By using this second charcoal trap, CH_4 preconcentration to about 3000 µmole/mole is attained allowing the direct δD analysis by tunable diode laser spectroscopy [10] (see section 3). A fraction of the preconcentrated CH_4 sample is introduced into a separate CH_4 combustion line, utilizing platinum as catalyst (800^oC) for the quantitative conversion of CH_4 into CO_2 (in the presence of oxygen, which is admixed to the sample flow). Resulting amounts of H_2O and CO_2 are trapped at 195K (dry ice) and 77K, respectively, and further processing of CO_2 is identical as described above for the CO derived CO_2.

Analysis of stable isotope ratios is performed in the CO derived CO_2 sample ($\delta^{13}C$, $\delta^{18}O$) and in the CH_4 derived CO_2 sample ($\delta^{13}C$) on a dual inlet, multiple collector, isotope ratio mass spectrometer (Finnigan MAT 252). Overall precision of stable isotope analysis is $\pm 0.05‰$ ($\delta^{13}C(CH_4)$) based on experiments of duplicate samples (i.e. including the compressor sampling procedure).

2.1.3 Standard techniques used at the Scripps Institution of Oceanography (SIO), University of California San Diego

In the early 1980s (while MW was in Albany, NY) we were contemplating the possibility of an alternate technique (other than that developed earlier by [15] using the Schutze reagent) to separate CH_4 from air and samples from various methane sources. The motivation was to measure all three isotopes, ^{13}C, D and ^{14}C, in methane in order to better constrain the global methane cycle, but also to simultaneously collect and measure (by proportional counting) ^{85}Kr, a powerful chemically inert tracer for atmospheric air mass movement. As this document is mainly concerned with the technical aspects we refer to some of the underlying aspects and principles of using isotopes to arrive at a refined methane budget and some results in references [13,26].

The system was designed for large air samples for both ambient and sub- or super-ambient CH_4 concentrations. Large samples are required to perform δD and ^{14}C measurements in CH_4. The system was first implemented and used in Albany and then transported to SIO where it is still in use. It consists of three basic parts: 1) a bleed–down train to concentrate CH_4 (and ^{85}Kr) in two steps; 2) a preparative gas chromatograph system to separate CH_4 and ^{85}Kr from remaining small amounts of air; and 3) a combustion system to oxidize CH_4 to CO_2 and H_2O. The individual components are described below.

The samples of atmospheric concentrations (about 400 liter) are first concentrated in a bleed-down system at flow rates of <2.5 liter·min^{-1} (measured with an integrating calibrated mass-flow meter). Two simple traps and one double helical trap filled with quartz wool cooled to 77K first remove all condensibles (such as H_2O, CO_2, N_2O, most non-methane hydrocarbons, etc.). The sample is then passed through a double helical coil filled with ~60 g of granular activated charcoal at 77K (at $<2\times10^4$ Pa to prevent liquefaction of O_2). This process quantitatively retains CH_4 and Kr. Most of the trapped air (~12 liter) is then removed by pumping on the charcoal at –80°C. Desorption of CH_4 and Kr is then achieved by heating the charcoal to 250°C and He carrier gas. The sample, containing at this point CH_4, Kr and several cm^3 of air is then subjected to the above procedure sequentially two more times, but using only ~2 g of charcoal to further reduce the amount of air.

The final product is trapped on a small amount of molecular sieve 5A (MS) at 77K and transferred to the inlet loop (containing charcoal) of the preparatory Gas Chromatograph (GC). This GC is equipped with a 10 m, 1/4 inch ID column, packed with 90% MS and 10% charcoal, a thermal conductivity detector, and parallel collection traps with MS at the exit to collect CH_4 and Kr. Upon desorption by heating the inlet loop the sample is injected into the GC with He as carrier gas. The column completely separates O_2 (including Ar) from N_2 (peak separation ~20 min), CH_4 from N_2 (~10 min) and Kr from CH_4 (~10 min). The effluent CH_4 and Kr are routed through individual collection traps containing MS at 77 K. The overall collection efficiency for the bleed-down and GC separation process is monitored manometrically (by comparison to the original air sample concentration as measured by an analytical GC equipped with a flame ionization detector (precision ±0.5 percent) and is 98±1%. The recovered CH_4 is quantitatively transferred by a small vessel containing a small amount of MS to the combustion system. The combustion system consists of a platinum coated quartz tube, oxygen is added and the sample is converted statically to CO_2 and H_2O at 600°C for one hour. The products are collected on coils at –80°C and 77K, respectively, by double distillation. A small fraction of the produced CO_2 is split for mass spectrometric analyses of $\delta^{13}C$ with the remainder saved for producing AMS targets for ^{14}C analyses. The water is frozen into a flame-off tube containing about 400 mg of granular zinc, stored in a refrigerator and reduced to hydrogen (at 485°C for 45 min) just prior to the mass spectrometric analyses of D/H.

After each run the three systems are cleaned overnight. The charcoal traps in the separation system are heated and initially purged with oxygen to the point that the charcoal is slightly glowing and then left heated and purged with He for about 12 hours. The preparative GC (column, inlet and collection traps) are kept heated and purged with He overnight and the combustion system is heated and evacuated overnight.

A multitude of experiments were and are performed to check on the experimental uncertainty of the results with respect to ^{13}C, D and ^{14}C. Much of this work is described in [13].

Blanks for large samples are negligible. Tests include running inter-calibrated samples, among them natural gas samples (NGS-1A, NGS-2A, NGS-3A, provided by Martin Schoell) inter-calibrated in an IAEA study [27], along with many other documented samples run interspersed with unknown samples. Furthermore we investigated possible fractionation effects for yields not close to unity. By variously manipulating the operating conditions of the bleed-down train and the preparative GC as well as the combustion system we were able to produce a series of results with lower yields. The combination of the bleed-down train and GC, and the combustion produce fractionation, resulting in lower $\delta^{13}C$ at lower yields (Y).

The fractionations follow a Rayleigh type mechanism according to $\varepsilon = [\delta^{13}C(Y) - \delta^{13}C(Y = 1)] / \ln Y$. For the separation process $\varepsilon = 7.5$ per mil and for the combustion $\varepsilon = 2.2$ per mil. Thus, the corrections due to these fractionations are small as the yields are usually close to unity.

Errors associated with the compressor used to collect the large samples in Al cylinders were investigated by compressing an already collected sample into a second cylinder, with the assumption that this incremental sampling would reveal any changes in isotopic composition produced by this procedure. We also compared samples of outside air directly piped into the separation train to samples simultaneously collected by compression. These tests showed that the CH_4 concentration ratio for twice-compressed versus once-compressed samples is 1.003 ±

0.003 and for $\delta^{13}C$ the ratio is 0.998 ± 0.004, indicating that the sampling process produces no statistically significant alteration.

Our procedures for ^{14}C are similar to those described later in this chapter by others, and together with quality control experiments, are documented in [13] and are not repeated here.

Up to 1988 the isotopic measurements were made on a Finnigan MAT 251 IRMS at the Lamont-Doherty Geological Observatory. This machine was calibrated to NBS19. Taking into account all experimental uncertainties we assigned a conservative ±0.2 per mil standard deviation to the $\delta^{13}C$ results. Early in 1990 we acquired a VG Prism II IRMS instrument which turned out to be very efficient and accurate due to a number of reasons. Among them, the instrument is equipped with 4 oil diffusion pumps, two 4 inch pumps, one under the ion source and one under the analyzer, and two 2 inch pumps for the inlet and the waste pump, resulting in a terminal vacuum of about 4×10^{-10} bars.

Furthermore the ionization efficiency is better then 0.5 percent (for every 185 molecules consumed, one arrives in the collector). This instrument is periodically calibrated against NBS19, NBS16 and NBS17 standards. A great number of secondary standards have been calibrated and are used to correct for long and short term (daily) variations in the machine performance. We have also successfully taken part in the IAEA sponsored CLASSIC intercomparison. Thus the ^{13}C experimental uncertainties have been reduced to ±0.05 to 0.1 per mil. For δD the experimental uncertainty is between ±1 and ±3 per mil as determined by reducing SMOW, GISP and SLAP standards prepared daily once or twice, reduced just prior to analysis. These are used as reference gases.

Later we miniaturized the whole separating and combustion system for ^{13}C in CH_4 to accommodate sample sizes down to 2–20 liters at ambient concentrations resulting in CO_2 samples of >2.5 μL. Combustion for e.g. is achieved by using two pellets of platinized Alumina. As our machine produces about 1 nA at the major current per μL of CO_2, results are still useful and meaningful given the large isotopic range, despite a larger experimental error.

2.1.4 Standard technique used at the Institut für Umweltphysik, University of Heidelberg, Germany (IUP)

While both techniques described above (NIWA, MPIC) rely on chemical separation of carbon monoxide via Schütze reagent, the IUP technique uses a preparative GC for their separation [20] and is as such similar to the SIO approach. The measurement principle for stable isotope analyses on atmospheric methane is based on a two-step enrichment of methane from about 400–800 litres of air on activated charcoal by a factor of approximately 10^4. Gas chromatographic separation of the enriched air sample from carbon and hydrogen containing gases other than methane are followed by catalytic conversion of the CH_4 sample on platinum to CO_2 and H_2O. The rather complex Heidelberg laboratory technique, in contrast to that used in other laboratories [18,22] allows the D/H ratio in methane to be determined because atmospheric H_2 gas as well as ethane (C_2H_6) are removed quantitatively during the enrichment and gas chromatographic separation steps. However, for the purpose of δD analyses on CH_4 via H_2O large sample sizes are needed to minimise contamination with atmospheric water being present on all surfaces of the line (see below). CO_2 from the CH_4 combustion is directly analysed for $^{13}C/^{12}C$ ratio by isotope ratio mass spectrometry (IRMS MAT252, Finnigan, Bremen, Germany). The remaining sample gas is break-sealed and a subset is sent to an AMS laboratory (Zürich or Groningen) for radiocarbon measurement [20]. H_2O, carrying the D/H signature of the CH_4 sample, is further reduced to H_2 gas on zinc and analysed by IRMS (MAT 230, Varian, Bremen).

First enrichment on activated charcoal

For the first CH_4 enrichment the air sample (collected in a high pressure gas cylinder) is run through a cold trap at –196°C (liquid Nitrogen, lN_2) followed by a large charcoal trap (400g F12/470, Chemviron Carbon, Belgium) kept at the same temperature (flow rate: 0.8–1.5 liter·min^{-1}). The pressure in the system is kept below 400 hPa to prevent O_2 to condense in the traps. Atmospheric CO_2 and traces of H_2O are removed in the first trap while CO, CH_4 and other light hydrocarbons as well as noble gases (except for He) are trapped on the charcoal. When the enrichment is finished the charcoal is warmed up in a water bath at 6.5 °C for 29 min. During this process, most of the adsorbed gases like N_2 and O_2 are blown off while CH_4 stays in the adsorbed phase. The first enrichment step is normally run overnight before the sample is further processed on the following day.

Second enrichment

A small charcoal trap for the second enrichment is integrated in the GC and conversion line (Figure 1).

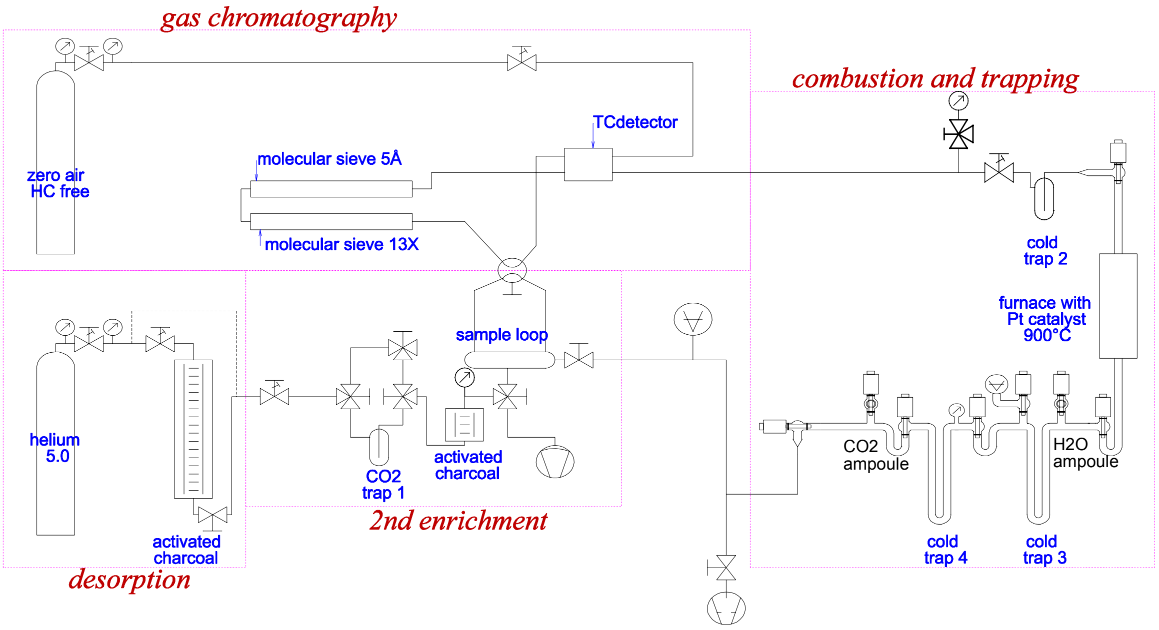

Figure 1. Sketch of the preparation line used for the enrichment and conversion of methane for stable isotope ratio analysis [28].

The large charcoal trap containing the adsorbed methane sample is now warmed up to 70°C and filled with helium to 5000 hPa over pressure. The He-diluted sample is then flushed (250 ml·min^{-1}, $p < 400$hPa) through a cold trap (#1) at lN_2 temperature to condense CO_2 followed by the small charcoal trap (15g of Desorex F12, Degussa AG, Hanau, Germany) at lN_2 temperature. During this process, the temperature of the large charcoal trap is increased to 135°C. The last portion of the sample gas is flushed with He into the second charcoal while the temperature is further increased to 150°C. Flushing is continued for 40 min after which less than 5‰ (detection limit) of the sample remains in the first adsorber. Then the second charcoal trap is warmed up at room temperature under He flow (160ml·min^{-1}) for 5 min. The charcoal outlet is switched to an evacuated sample loop (140 ml) and the small charcoal trap is heated up to 135°C in 5 min. The desorbed sample is now transferred to the sample loop under He gas flow (30 ml min^{-1}). The remaining desorbing gases inclusive the CH_4 in the charcoal are further flushed into the sample loop until the pressure in the system has reached 1250 hPa.

Preparative gas chromatography and combustion of CH_4 to CO_2 and H_2O

Gas chromatographic separation of CH_4 from CO (and CO_2 catalytically generated during heating of the charcoals in the presence of O_2) as well as C_2H_6 and possible remaining traces of H_2 is performed at room temperature on two columns (molecular sieve 13X and 5Å, 60cm, 7mm id) using zero air (180 ml·min^{-1}) as carrier gas. The methane peak is registered with a thermoconductivity detector (Gow-Mac Instr., Shannon, Ireland). The pressure after the columns is kept constant at 1000 hPa using a needle valve. After the needle valve the pressure is kept constant at 400 hPa before the flow passes a second cold trap (#2) at lN2 temperature (safety trap for CO_2 bleeding from the columns). For the time span (about 3 min) when the complete CH_4 peak leaves the columns (methane has a retention time of about 5:45 min, depending on the room temperature), the sample gas is run through the catalyst (Platinum powder on quartz wool at 900°C). Here the CH_4 in the sample stream is quantitatively oxidised to CO_2 and H_2O. The oxidation products are frozen out in two cold traps (# 3 & 4) at lN_2 temperature. The catalyst is then flushed with zero air for another 15 min to remove remaining CO_2 and H_2O from the catalyst. The flow is stopped and the combustion/trapping system (Fig.1) is evacuated to 10^{-3} hPa. CO_2 and H_2O are finally separated by vacuum distillation using Isopropanol/dry-ice mixtures and lN_2 and are frozen into separate glass ampoules for analysis. Based on the NOAA calibration scale, the mean yield of the methane extraction and conversion procedure is (99.7 ± 3)%. The uncertainty is mainly due to the errors in the flow measurement of the first enrichment step.

Quality control checks and correction factors for systematic errors

During the methane extraction and conversion procedures, all steps have to be quantitative and free of contamination. For regular checks of the complete sample preparation line, blank and standard samples have been run. For this purpose, methane standard gases have been prepared from gas distributed in the Heidelberg city network (EG94, EG95) and from a biogas reactor (Staighof). These gases have been purified from H_2S, Non Methane Hydrocarbons, H_2, CO and CO_2 in several purification steps using Fe_2O_3, molecular sieve 4Å, cryogenic traps and an activated charcoal adsorber at lN_2 temperature. The purified gas was then diluted with N_2 to a concentration of approx. 1% CH_4 in N_2 and stored in high pressure aluminium tanks. The standard gases have been used regularly from 1994 onwards in different dilutions with zero-air down to atmospheric mixing ratios to either check the GC and conversion line or the complete air sample preparation system. The standard deviations of the individual analyses lies between ±0.04 (EG95 and Staighof) and ±0.11 ‰ (EG 94 L). Standard deviations of the δD values of the standard gases vary between ±5 and ±8 ‰.

Calibration with pure CO_2 standards

The $^{13}C/^{12}C$ ratio of methane is measured on its combustion product CO_2. Until November 1993, a Finnigan MAT-230 IRMS, and from there onwards, a MAT-252 system was used. For the period of November 1993 to March 1995 samples were analysed on both machines. Routinely at both spectrometers we use as our internal working standard gas *Oberlahnstein* ($\delta^{13}C_{VPDB}$ = –4.46‰) which is compared every day with a more depleted standard gas *Pflanzenstandard* ($\delta^{13}C_{VPDB}$ = –24.80‰). From the comparison of the two machines using results obtained from measurements against *Oberlahnstein*, for the very depleted $\delta^{13}C$-CH_4 samples a mean difference of 0.21‰ was observed, with MAT-252 results being more enriched. It turned out that this difference is mainly caused by a memory effect ("cross-contamination") from the very enriched standard gas in the MAT-252 ion source. Therefore, from July 1996 onwards, a dedicated standard, *CO_2-Reinst* ($\delta^{13}C_{VPDB}$ = –49.98‰ when analysed against *Oberlahnstein* on MAT-252) was routinely used for analysis of CH_4-derived CO_2. In February 1999, a new ion source has been installed into the Heidelberg MAT-252. In addition, the mass spectrometer has been calibrated with reference materials from IAEA (NIST RM 8562–8564, $\delta^{13}C_{VPDB}$ = –3.76‰, $\delta^{13}C_{VPDB}$ = –41.56‰, $\delta^{13}C_{VPDB}$ = –10.45‰). As a consequence of this calibration, new $\delta^{13}C_{VPDB}$ values were obtained for our working gases (*Oberlahnstein*: $\delta^{13}C_{VPDB}$ = –4.42‰, *CO_2-Reinst*: $\delta^{13}C_{VPDB}$ = –50.42‰). All samples were subsequently corrected for the cross-contamination effect, and are related to the new standard values.

2.2 Determination of ^{13}C in atmospheric methane by continuous flow IRMS

All the methods described above are rather labour intensive and require large scale "off line" vacuum processing equipment. New research suggests that "on line" processing of air samples may be a fast and effective way of providing ^{13}C analyses from the methane in relatively small amounts of ambient air. This technique is based on the method of continuous flow IRMS first developed by [29] designed to measure ^{13}C in picogram amounts of organic material. Worthwhile references to check for this exciting new technique are [30,31]. Most progress on the technique for methane has been achieved at the University of Colorado, INSTARR and their used technique is reported here.

2.2.1 Methods at INSTAAR/NOAA

Sample analysis can be separated into six steps: sample introduction, methane pre-concentration, cryo-focusing, chromatographic separation, combustion, and mass spectrometric analysis. The details of the standards used, batch analysis and quality control will also be discussed below.

Sample collection and introduction

Samples are all ambient air collected at sampling sites of the NOAA/CMDL Cooperative Air Sampling Network [32]. Air is pumped into a pair of serially connected 2.5 L glass flasks fitted with two glass-piston stopcocks sealed with Teflon O-rings. Conway et al. [32] have described the collection method in detail. Standard gas is collected in Al 150 aluminum high-pressure cylinders at the NOAA/CMDL co-operative site at Niwot Ridge, Colorado, USA (3040m, 40°N, 105°W).

Samples are pressurized to roughly 0.2 bar above ambient pressure, resulting in 2.0 to 3.0 standard liters of air, depending on the altitude of the collection site. Upon arrival in Boulder, Colorado, flasks are analyzed for mole fractions of CH_4, CO_2, CO, H_2, N_2O, SF_6, and the carbon and oxygen isotopic composition of CO_2. On average, the flasks contain less than 1.5 standard liters of air by the time they are analyzed for $^{13}C/^{12}C$ ratio of methane. This relatively small volume was a major constraint in the design of the analysis system. Air pressure in the flasks is also significantly less than ambient when extracted for measurement.

Flasks are attached to a manifold described in detail by [33] in preparation for analysis. The circular manifold is evacuated up to the stopcocks on the glass flasks by a rotary pump (Edwards E2M5) to a pressure less than 3×10^{-2} mbar. The stopcocks on the flasks are then opened allowing the air inside to expand through tubing to an eight-port stream selection valve (Valco SD8, Valcon M rotor) fitted to a sixteen position electric actuator. These extra actuation positions allow the manifold to be in a "blank" position between the analysis of samples. When a flask is ready to be analyzed, a diaphragm pump then pulls air out of the flask through a mass flow controller (Edwards 1605) at a flow rate of 100 sccm.

The air then flows through an Ascarite II (NaOH on a silica substrate) and $Mg(ClO_4)_2$ trap to remove CO_2 and water vapour from the sample. The CO_2/water trap is a 15cm × 6mm i.d. glass trap consisting of a six cm layer of Ascarite II sandwiched between two, 2 cm layers of $Mg(ClO_4)_2$, with small plugs of glass wool at each end. The Cajon Ultra-Torr fitting holding the trap on the downstream side also has a 10 μm stainless steel frit to prevent particles from entering the rest of the system. After leaving the trap, the air flows to a 40 ml sample loop positioned on a six-port, two-position injection valve (Valco 6-UW, Valcon E rotor). After flushing the sample loop and trap for 120 seconds, the injection valve is switched so that a flow of He (99.999 % purity, further purified by Alltech "All-Pure" He purifier) flushes the sample loop to another six-port, two-position valve containing the pre-concentrator (Figure 2).

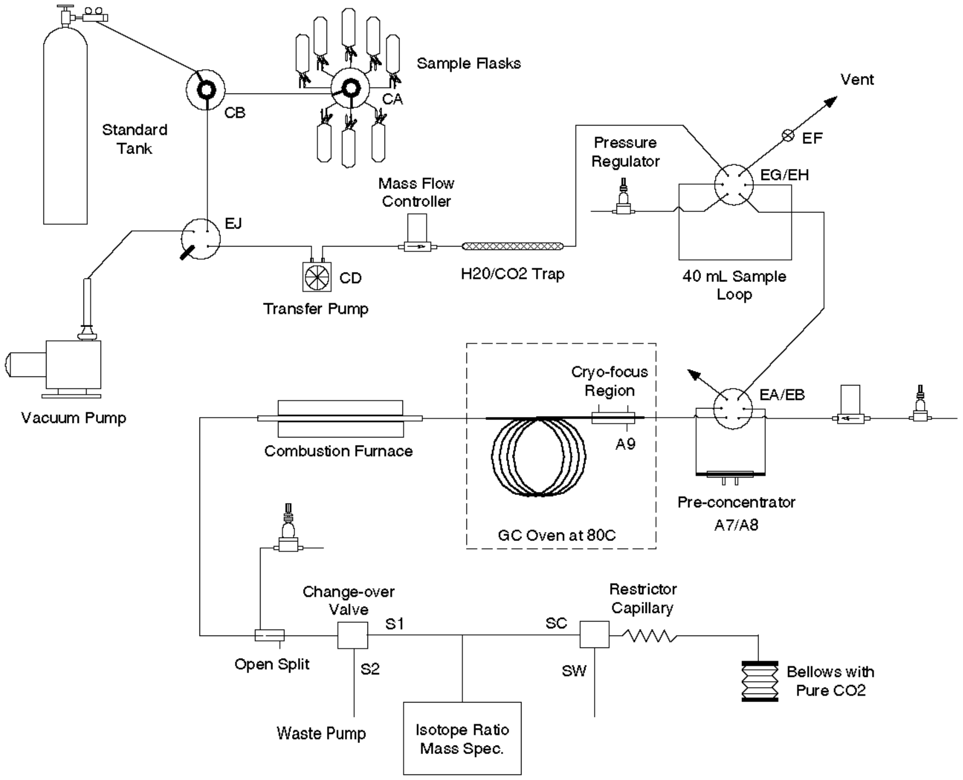

Figure 2. Plumbing diagram of Gas Chromatography – Isotope Ratio Mass Spectrometry System (INSTAAR,NOAA).

Note that the flowrate of the He stream is only pressure regulated resulting in changing flowrates with temperature and flowpath. The flowrates through the pre-concentrator at room temperature and at -120^{o}C are 22 sccm and 30 sccm, respectively. The introduction of air from a standard tank is essentially the same, except that the air flows through the diaphragm pump while it is off. A downstream regulator pressure of 0.2 bar above ambient pressure or greater on the standard tank is needed to overcome the resistance of the water/CO_2 trap and maintain a flow of 100 sccm. A total of approximately 250 standard ml are used in each sample analysis. This volume is more than four times the volume of tubing that is flushed but decreases the chances that the trap contains any "memory" of the previous sample from run to run.

Sample pre-concentration

Pre-concentration of the CH_4 within the air sample is necessary to ensure that N_2, O_2, and Ar do not co-elute with methane from the analytical column. N_2 entering the combustion furnace can form N_2O, which interferes with the m/z = 44 and 45 signals that result from CH_4-derived CO_2. In general, we want only CH_4-derived CO_2 (and He) in the mass spectrometer during its analysis. The goal of the pre-concentration step is to isolate methane on a substrate while N_2, O_2, and Ar are vented. Our pre-concentrator is based on the design of [30], but we have modified their design for ease of automation (see Figure 3).

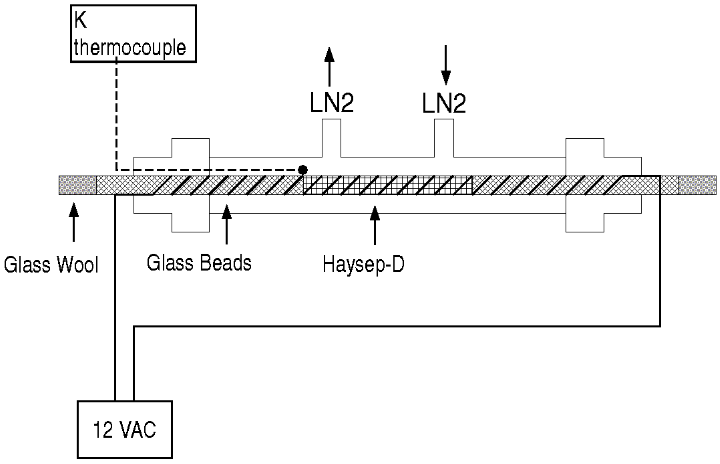

Figure 3. Methane pre-concentrating device.

The pre-concentrator is a linear 1/8” o.d. (0.085” i.d.) × 20 cm stainless steel column packed with 4 cm of 80/100 mesh Haysep-D surrounded by 5 cm of 60/80 mesh glass beads and 1 cm of glass wool on either side. The column is encased in a 12cm×6mm i.d. glass tube, fitted with two 1/4” o.d. side-arms, as shown in Figure 3. A 1 cm thick insulating layer of open-cell foam covers the glass tube. The column is held in place within the glass tube by a pair of 1/2” to 1/4” Cajon Ultra-Torr fittings through which the column extends. The central 10 cm of the column is wrapped with fiberglass insulated NiCr wire (0.23 mm diameter, Omega). The wire is wrapped over a narrow gauge K-type (alumel/chromel) thermocouple positioned about 2 cm from the center of the column, just beside the liquid N_2 outlet (Figure 3). The column is fitted to the six-port, two-position valve with 1/16” stainless steel tubing and 1/16” to 1/8” reducing unions fitted with 10 μm screens (Valco) and sealed with Teflon ferrules.

The column is maintained at -120^oC by opening and closing a solenoid valve on a pressurized liquid N_2 tank. The valve is controlled by the central computer, which monitors the thermocouple with a frequency of about 5 Hz. Cold N_2, mainly in the vapor phase, enters through one of the side-arms on the glass outer jacket and exhausts through the other side-arm and the gaps between the 1/8” o.d. column and the 1/4” ends of the Ultra-Torr fittings. Tests demonstrated that allowing liquid nitrogen to exhaust through the exit side-arm and both ends of the glass jackets provided the most uniform temperatures. [30] used an ethanol slush (-118^0C) to maintain the temperature of their pre-column. This plastic, freezing ethanol requires substantial attention to maintain and is not conducive to automation.

The pre-concentrator is kept at –120 ± 5°C for 3 minutes prior to the sample injection to ensure that the entire diameter of the column has cooled. Once the sample air has been injected onto the pre-concentrator, it is held at –120°C for 2 minutes allowing the bulk of the "air" to vent. Immediately after the cooling is stopped, the NiCr wire (total resistance=19.7Ω) is heated to 0°C by applying a 12 V potential across the NiCr wire. The central computer controls the warm temperature in the same manner as the cryogenic temperature. As soon as the heating begins, the six-port valve is switched so that the ~ 30 sccm flow of He through the pre-concentrator is replaced by a 2.0 sccm electronically controlled flow (Tylan FC-260). The low flow is required by the analytical column and ensures a reasonable split ratio prior to entering the mass spectrometer. 0°C was chosen to minimize the amount of water vapor released by the pre-concentrator on to the cryo-focus stage. After the elution of CH_4, the high He flow is returned to the pre-concentrator and it is heated to 110°C for 5 minutes to purge the column of H_2O and any other remaining condensables.

The temperatures and timings for the pre-concentrator were determined by analyzing both the venting flow and the slow eluting flow with a flame ionization detector (FID). At the measured temperature of –120°C methane was retained indefinitely on the pre-column. Although the FID is not directly sensitive to air, the flow disturbance caused by its elution is evident at about 15 seconds. The additional 105 seconds was used to let the tail elute. A column heating rate of about 40°C/minute, corresponding to an application of a 12 V potential resulted in the elution of methane at 45 seconds (after the valve switch and the start of heating) with a peak width of about 30 seconds. Tests using an NDIR analyzer (Li-Cor 6251) indicated that CO_2 co-elutes with methane in the absence of the pre-sample loop CO_2/H_2O trap.

Sample cryo-focusing and separation

The methane eluting from the pre-concentrator is transferred to the GC through a 0.32mm i.d. deactivated fused silica transfer capillary (SGE). There it is cryo-focused at the head of the analytical column (Molecular Sieve 5Å, 0.32 mm × 25 m, Chrompack) so that its peak width can be reduced. The cryo-focusing is achieved by cooling the first 10 cm of the column to about –150°C. The head of the column is encased in a section of 1/4" o.d. stainless steel tubing with a tee at one end, and a cross at the other (Swagelok). The column is held in place by custom-drilled 1/4" – 0.5 mm graphitized–vespel reducing ferrules. The tee is used as the inlet for liquid N_2 while the cross is used as an outlet and as a port for a K-type thermocouple. The cryogenic temperature is controlled by the central computer in the identical manner as the pre-concentrator. The head of the column is cooled one minute prior to the heating of the pre-concentrator to ensure that all eluting methane is trapped. It is held at –150°C for an additional 2 minutes, which corresponds to the FID-determined elution of methane from the pre-column plus one additional minute of "safety" time. The head of the column is heated by stopping the flow of liquid N_2 and simply allowing the cryo-focus device to warm to the GC temperature of 80°C. The column warms to 0°C within about 3 minutes, although methane probably begins to desorb from the column at about –100°C. [30] cryo-focused the methane outside the GC in an ethanol slush on approximately one meter of 0.32 mm Poraplot-Q. In addition to the difficulty of using freezing ethanol as a temperature bath, the strong retention of CH_4 on Molecular Sieve 5Å allows for a much smaller length of column to be used in cryo-focusing.

Methane and residual air from the pre-concentration step, along with air from leaks and carrier gas impurities are cryo-focused on the head of the analytical column. Some of this air passes through at –150°C, but the portion that is retained must be fully separated prior to combustion and analysis in the mass spectrometer. Although the dominant choice of analytical column in similar systems has been 0.32 mm × 25 m Poraplot Q [30,31,34] we have found that the separation of CH_4 from air is greatly enhanced on Molecular Sieve 5Å. At a GC oven temperature of 80^{o}C, O_2 elutes at 100, N_2 at 150, and CH_4 at 190 seconds after the warming of the cryo-focus region. The GC effluent prior to the elution of CH_4 is diverted from the source of the mass spectrometer through a change-over valve located downstream of the open-split (Figure 2). The excellent separation ensures that when CH_4 is present in the combustion furnace and the analyzer section of the mass spectrometer, no other species (other than He carrier gas) are present. The peak width (FWHM) of the methane peak is 5 seconds as determined by FID and is not substantially different as measured by the mass spectrometer after combustion. The peak height is typically about 9 nA (Figure 4) but can vary depending upon both the sensitivity of the analyzer and the temperature and retention characteristics of the cryo-focus unit. CO elutes at 350 seconds, but the ratio of its peak area to that of methane indicates that only a portion of the initial CO in the sample is trapped during methane pre-concentration. Although the Molecular Sieve column has excellent separating characteristics, it irreversibly adsorbs water and CO_2 at room temperature. The presence of the trap upstream of the sample loop prevents the majority of water and CO_2 from reaching the column, but the column must be baked out every 500 samples or so at greater than 200^{o}C so that the adsorbed water and CO_2 can elute.

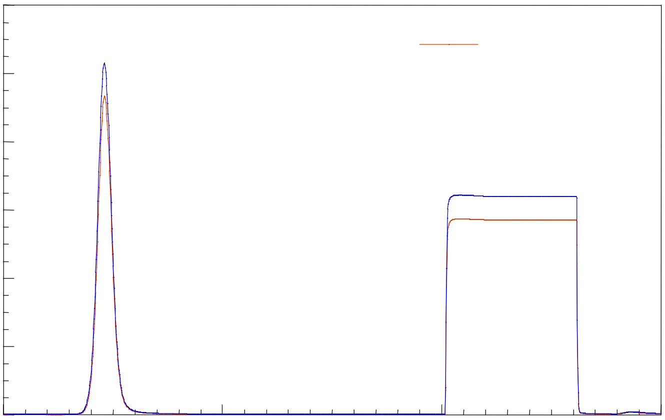

Figure 4. Typical sample air or standard gas analysis showing sample/standard and reference peaks.

Sample combustion

After eluting from the capillary column the methane peak is transferred to the combustion furnace via a small section of 0.32 mm i.d. fused silica capillary. The combustion furnace is composed of a 3 mm o.d. × 0.5 mm i.d. × 300 mm high density alumina tube (Alsint, Bolt Technical Ceramics) mounted co-axially within a 400 W cylindrical heater. The combustion tube is attached to transfer capillaries on either end by 1/8" – 1/16" reducing unions (Valco), and the seal is made with 1/8" graphitized-vespel ferrules and 1/16" gold-plated stainless steel ferrules (Valco). The output of the heater is controlled by an electronic temperature controller (Omega 9000A) using an R-type (Platinum and Rhodium/Platinum) thermocouple. The ceramic tube extends 6 cm beyond the edges of the heater to ensure that the fittings remain cool. Glass wool is used to plug both ends of the annulus between the combustion tube and the heater to minimize the temperature gradient within the heated zone.

The combustion tube is filled with Ni and Pt wires running the length of the furnace. The Ni wire is used as a substrate for oxygen required in combustion, and the Pt wire serves as a catalyst [30]. In order to maximize the amount of oxygen available for combustion and the surface area available for catalysis, six 0.05 mm Ni (99.994% purity) and two 0.05 mm Pt wires (99.95 % purity) are used (Alfa Aesar). [30] on the other hand, used 3 Ni and one Pt wire of larger diameter. All wires were braided together to facilitate insertion. The furnace is maintained at 1150°C to promote combustion; lower temperatures appear to allow some methane to remain not combusted [30]. The furnace was initially oxidized by passing pure oxygen (99.999% purity) through the furnace at 5 sccm, at 500°C for 4–6 hours, and then at 1150°C for 10–12 hours [30]. However, repeated oxidation does not appear to be necessary. This is, most likely, because of the small amount of oxygen eluting through the column and passing into the furnace every time a sample is analyzed. The increased surface area of Ni wire, compared to that of [30], may also provide a larger reservoir of oxygen available for combustion. This design yields a consistent amount of CO_2, no CH_4 and no CO, as measured by the mass spectrometer, FID, and reduction gas analyzer, respectively. Based on these tests we infer a combustion efficiency of 100%.

Although water is produced in the combustion of methane, it is not removed from the He stream prior to admittance to the mass spectrometer. Normally, transient amounts of water are removed so that the rate of the gas phase ion-molecule reaction between CO_2 and H^+ is constant in the source of the mass spectrometer. In this reaction, a proton bonds to the CO_2 resulting in a species of m/z = 45 that does not correspond to CO_2 containing ^{13}C. This reaction occurs in all IRMSs, but is "invisible" when its contribution is the same for both running gas and sample gas. In our case the rate of this reaction is substantially higher when our CH_4-derived CO_2 peak enters the source, resulting in a systematic error to our measurements. Such systematic errors can be accounted for by calibration. However, random variations in the H_2O peak and drifts in the background concentration of H_2O in the source over time do contribute to imprecision in our measurements. Fortunately, these random errors are small as shown below.

Mass spectrometric analysis

After the CH_4-derived CO_2 peak leaves the combustion furnace it is transferred to an open split, described in detail by [30]. The split consists of a 0.11 mm i.d. capillary placed 4 cm within a 0.32 mm i.d. capillary that is bathed in He. A 1 m section of the 0.11 mm capillary leads through the change-over valve to the source region of the mass spectrometer, resulting in a pressure of $5–6 \times 10^{-6}$ mbar. The split ratio is approximately 1:6. Although a larger split ratio would allow more CH_4-derived CO_2 to be analyzed, the mass spectrometer cannot tolerate pressures of greater than 1×10^{-5} mbar.

Once inside the mass spectrometer, the CH_4-derived CO_2 is ionized and the signals for m/z = 44, 45, and 46 are simultaneously measured. After the tail of that peak has completely disappeared, after about one minute, a pulse of pure CO_2 "running gas" ("Bone-dry" quality) from the bellows of the dual-inlet portion of the mass spectrometer is mixed into the He stream and admitted to the source region (Figure 2). This square peak of CO_2 is thirty seconds wide with a height of about 6 nA. The CO-derived CO_2 peak elutes about 20 seconds after the end of the CO_2 peak. Once the baseline has returned to normal, the signal collection is stopped.

Each aliquot of air, from either a sample flask or standard tank is measured relative to running gas, so that short-term drifts at frequencies lower than ~0.01 Hz. in the source or analyzer regions of the mass spectrometer are taken into account. Specifically, the m/z = 44, 45, and 46 peak areas are integrated for both the sample and running gas peaks and ratios of the areas are calculated. The data analysis software measures the signal levels at the beginning and end of the data collection period, linearly interpolates between those points, and subtracts these "zero" lines from the raw signals. The m/z= 44, 45, and 46 peaks have slightly different elution times, requiring each peak to have unique integration limits. The software makes an "isotope-shift" correction to the m/z = 45 and 46 peaks that are typically –40 ms and +20 ms, respectively. In order to correct for the contribution of $^{12}C^{16}O^{17}O$ to the m/z = 45 signal, a "Craig Correction" is made [35] based on the size of the m/z=46 peak. Finally, the $\delta^{13}C$ value of the sample peak is calculated relative to that of the running gas, and then converted to the VPDB scale using the user-entered VPDB value of the running gas.

The $\delta^{13}C$ value of our running gas is –36.9‰ as determined on a dual inlet instrument (VG – Optima) in our lab. However, we cannot be certain that this is the $\delta^{13}C$ value that is admitted to the source. The running gas is probably fractionated in the stainless steel capillaries between the bellows and the mass spectrometer, and the degree of fractionation can vary with the pressure in the bellows. In addition, it is possible that fractionation can occur in the introduction of running gas to the bellows from our CO_2 source, and through leaks in the dual inlet of the mass spectrometer. Other day to day variability may result from changing baseline conditions and its effect on zero – subtraction. The consequence of these errors is that at this point the calculated delta values of both our samples and standards differ from their true values by +1.0 ± 0.2 ‰, on average.

Standard gases and calibration

In order to know the "true" value of our samples and standards, our primary standards are externally calibrated using traditional, dual-inlet, off-line techniques. Four primary standards have been calibrated by Dr. Stanley Tyler at the University of California, Irvine, using a technique based on that of [16,19,36]. The isotopic composition of most of our samples and secondary standards have been determined relative to these primary standards. All standards consist of whole air that has been dried by $Mg(ClO_4)_2$ and pumped into aluminum cylinders to a pressure of about 150 bar at Niwot Ridge, CO. In the future, at least one of our primary standards will be re-measured by the Tyler group to check for any drift in the $\delta^{13}C$ value over time. All measurements are reported relative to VPDB [37].

Analysis sequence

Each sample flask is measured as part of a batch of eight. The run starts with the analysis of five consecutive aliquots of standard air, of which the first is typically an outlier (greater than 2σ), and always rejected. The measurement of the flask samples then begins, and each sample analysis is alternated with a standard analysis until all eight samples have been measured. The batch analysis ends with the measurement of four consecutive aliquots of standard gas. Once the first standard measurement has been excluded, the standard measurements are averaged in three groups of five, i.e. run #s 2,3,4,5 and 7; 9,11,13,15 and 17; and 19,21,22,23,24. In this way, the drift of the total system over times of about two hours is tracked. Standard gas and sample gas are alternately introduced to the system to reduce the chances of "memory" of a previous sample affecting future samples. Standard gas $\delta^{13}C$ values are linearly interpolated between the averages of groups 1,2, and 3. Flask sample $\delta^{13}C$ values are then re-calculated relative to the interpolated standard gas values to correct for drift. Drifts of about 0.1 ‰ are typically observed between the beginning and end of a run, with the ending standard gas $\delta^{13}C$ values heavier than those at the start. The most likely explanation for this drift is the accumulation of water vapor in the source region of the mass spectrometer over the course of the run. The water produced as a result of methane combustion may not be pumped away from the tubing downstream of the furnace, and the source, as fast as it is produced. From one sample/standard analysis to the next, this effect would be difficult to observe, but over the six hour period of the run, we would expect to observe some accumulation. Regardless of the cause of the drift, our frequent use of standard gas gives us confidence in the accuracy of our measurements relative to that of the standards.

Quality control

a) Flask tests:

In order to quantify any systematic biases in the measurement of air from under-pressure flasks versus that from over-pressure tanks, we conducted systematic flask tests. Eight flasks were filled from a tank of standard gas to a pressure of about 0.5 bar, which is the typical pressure of flasks when they are analyzed. The $\delta^{13}C$ values of these flasks were measured, in the manner stated above, and compared to the $\delta^{13}C$ values of the standard aliquots of the same batch analysis. The test was repeated twice on these flasks, in order to simulate up to three total measurements. No systematic bias could be detected within the noise ($1\sigma \cong 0.05$ ‰) to which all samples and standards were subject. Additionally, the $\delta^{13}C$ values of the flasks from the first and third runs were not distinguishable, implying that we can sample a flask at least three times without error.

b) Flask pair differences:

One measure of the precision of flask analyses is the difference between the $\delta^{13}C$ value of a single flask and its mate. The mean pair difference is –0.016‰ (first flask measured minus the second), and the mean of the absolute values of pair differences is 0.089‰ (n=326). The distribution of pair differences is well approximated by a normal distribution (Figure 5), and centered approximately on zero, indicating that there is no systematic bias in the order in which a pair of flasks is measured. The $\delta^{13}C$ values of a flask pair are averaged, and the standard deviation of this value is $1/\sqrt{2}$ of the pair difference, 0.063 ‰. Among good pairs, *i.e.* rejecting "outliers" with a pair difference greater than 0.2 ‰, the mean absolute value is 0.069 ‰ (n=306) and the standard deviation is 0.050 ‰.

c) Precision of standards:

We can also use the standard deviation of the standards in a batch analysis as a proxy for the precision of flask measurements. The mean standard deviation of the standards in any given run is 0.08‰ ± 0.02‰ (1σ, n= 90) (Figure 6).

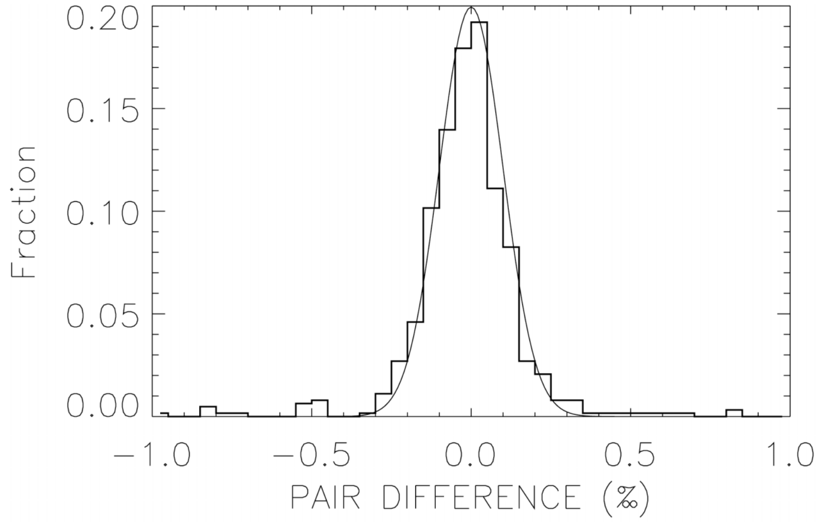

Figure 5. Histogram showing the distribution of differences between δ values of 365 pairs of flasks collected simultaneously (1st flask – 2nd flask). The super-imposed gaussian has a width of sigma = 0.08‰.

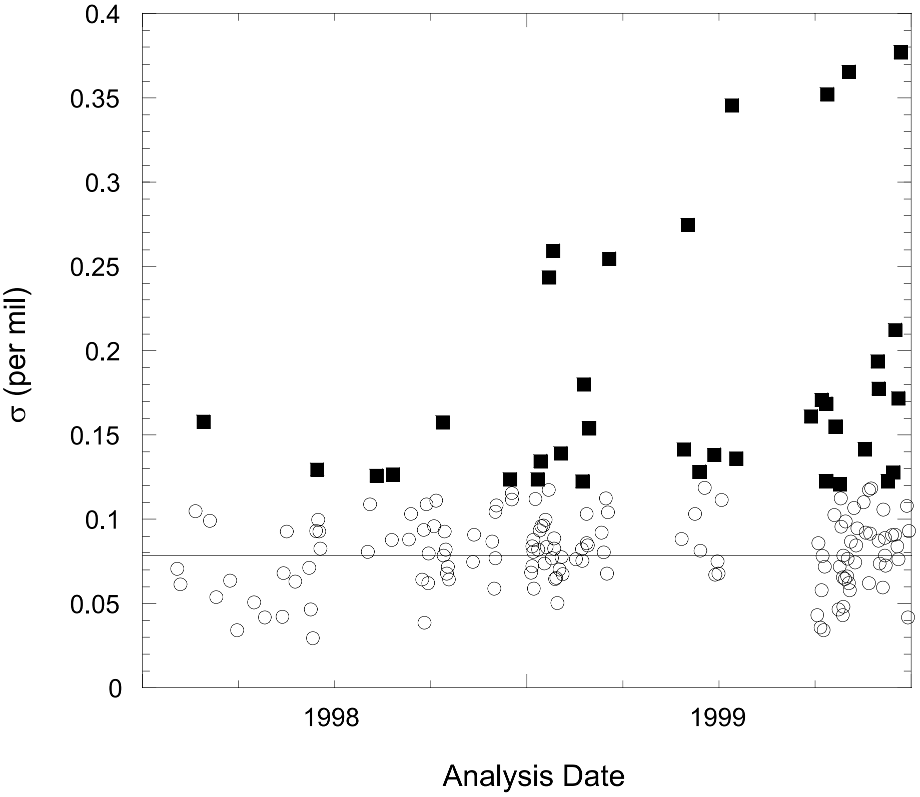

Figure 6. Standard deviation of standard air aliquots during batch analyses over time. Squares represent rejected runs and circles are retained. Solid line is the long-term mean of retained runs, 0.08 ‰.

However, since all measurements are corrected for the drift of standards during a run, we calculate the absolute difference between the measured $\delta^{13}C$ value and the $\delta^{13}C$ value of the linearly interpolated drift line, at the same point in time. The standard deviation of these differences is 0.04‰ ± 0.01‰. Once corrected for drift, the precision of our measurements approaches that of conventional, off-line analysis performed on large samples [18,19,38]. Assuming Poisson statistics apply, the shot-noise limited precision is ~0.02‰, and we are within a factor of 2 of this limit.

2.3 Determination of ^{13}C by infrared absorption spectroscopy

As fundamental alternative to IRMS measurements optical techniques have been developed for direct analysis of $^{13}CH_4/^{12}CH_4$ ratios using either tunable diode laser absorption spectroscopy (TDLAS) [39] or fourier transform infrared spectroscopy (FTIR) [40,41]. These techniques are based on the difference of rotational-vibrational transitions and the corresponding infrared spectra for the different CH_4 isotopomers. The general advantage of these techniques is that they do not necessitate any sample preparation apart from CH_4 preconcentration and drying. However, the precision of these techniques (0.5‰ for TDLAS, a few ‰ for FTIR) have so far not reached the precision required for atmospheric $^{13}CH_4$ analysis. On the other hand, the TDLAS techniques allows the most precise δD measurements in atmospheric methane today (precision 0.5–1‰) [10], and will be discussed in more detail in Section 3.

Furthermore, worthwhile mentioning is the application of the TDLAS and FTIR technique for isotope studies on CH_4 sources and sinks [10,41–44].

3. DETERMINATION OF ^{2}H IN ATMOSPHERIC METHANE

3.1 Technique used at IUP

Conversion of H_2O to H_2 for IRMS

For the deuterium analysis in CH_4 the H_2O sample derived from CH_4 combustion is reduced to hydrogen gas which is then measured in a MAT 230 mass spectrometer for its D/H ratio. The water from the H_2O ampoules (ca. 5 µl, see above) is vacuum distilled onto pre-cleaned and dried zinc reactant. In earlier years, we used the method developed by Coleman et al. [45] and Hayes and Johnson [46], and zinc provided by Hayes, University of Illinois. This specifically prepared "Hayes-zinc" was, however, not available for a long time so that alternative zinc granulate had to be tested. H_2O reduction was finally performed with 1.6 g zinc coarse powder (BDH Laboratory Supplies, Poole, England) at 500°C for 30 min.

Effect of isotope exchange with surface water in the combustion and trapping system

The general problem of contamination occurring with deuterium analyses in methane, particularly for methane source determinations (very depleted δD values), could be quantified through a deuterium intercomparison exercise with the MPI for Chemistry, Mainz, on their Tunable Diode Laser System [10] and standards analysed at the Federal Institute of Geosciences and Natural Resources, Hannover : A systematic deuterium shift occurs in the Heidelberg line on methane samples resp. the water from methane combustion, and also, by the same amount, on water standards injected directly into the combustion part of our line. This shift can, however, not be explained by contamination (*addition*) of atmospheric water as the H_2 yield from the converted H_2O lies within a range of 95–100 % of the expected one. We rather explain the observed δD shift by *isotopic exchange* with a permanent water film covering the glass walls. In the case of atmospheric samples with δD of –80‰, i.e. a correction of +(5.5±1.5)‰ has to be applied (for details, see [28]).

The deuterium analysis of CH_4 standards shows a reproducibility of δD = ±5 to 8‰ and has been improved in the last year to ±1.5‰ also for duplicate analyses of methane in air samples. This is, however, still not precise enough to resolve seasonal cycles of δD-CH_4 at clean air stations, particularly in the southern hemisphere.

Calibration with pure H_2 standards

The H_2 samples derived from the H_2O reduction were measured against a secondary working standard (δD_{VSMOW} = –60‰) which was calibrated against IAEA water standards VSMOW and SLAP to derive the VSMOW scale. As for $\delta^{13}C$ the day-to-day performance of the Varian MAT230 was checked using a second laboratory standard with a δD value of –22.5‰. The deviations from the long term mean value of this lab standard over the period of 1994 to 1998 was in the order of ±1‰. This effect may cause systematic variations in isotopically very depleted samples if compared to the working gas. However, for the atmospheric methane samples a possible variation is only in the range of ±0.5‰.

Taking into account all systematic corrections as well as the variability in sample collection, storage and preparation, the standard deviation of $\delta^{13}C$ and δD analysis of atmospheric CH_4 samples prepared before November 1994 is estimated for $\delta^{13}C$ to ±0.15‰, resp. for δD to ±7‰ and for samples prepared after that date for $\delta^{13}C$ to ±0.09‰ resp. for δD to ±5‰.

4. DETERMINATIONS OF ^{14}C IN ATMOSPHERIC METHANE

Several groups have reported ^{14}C determinations in atmospheric methane [e.g. 13,18,19]. ^{14}C determinations in atmospheric methane are potentially very valuable because they provide a unique and powerful way of distinguishing between biogenic (modern ^{14}C) and fossil (radiocarbon dead) sources of atmospheric methane [13,47]. Unfortunately, however, the ability of ^{14}C measurements to determine the fossil methane component of atmospheric methane is compromised by the difficulty of estimating precisely the production of $^{14}CH_4$ by light water nuclear power plants.

As described in section 2.1 above [19] have developed a “flow through” procedure for the determination of ^{13}C in atmospheric methane. The identical method is also used for the determination of ^{14}C in atmospheric methane, but a far larger sample size is used, typically 500 litres of air. After IRMS determinations of ^{13}C in the CO_2 derived from the methane in the air, the CO_2 is frozen back and used to make a graphite target using procedures developed by [48]. These targets, containing about 0.4 mg of the original carbon from the methane in the air sample, are measured for ^{14}C using accelerator mass spectrometry (AMS).

At Heidelberg, sample sizes for stable isotope analysis (400–800 litres of air, resp. 0.3–0.6 mg C) are usually sufficient for ^{14}C target preparation and subsequent ^{14}C analysis by AMS. Graphite targets are prepared adding high purity H_2 to the CO_2 sample with Fe powder as catalyst [49].

5. LIST OF LABORATORIES FOR FURTHER INFORMATION ON STABLE ISOTOPE AND ^{14}C DETERMINATIONS IN ATMOSPHERIC METHANE

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MASS SPECTROMETRIC METHOD FOR THE DETERMINATION OF THE STABLE ISOTOPIC CONTENT OF NITROUS OXIDE BY THE TECHNIQUE OF DIRECT INJECTION

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Abstract. A method for the direct isotopic analysis of N_2O has been developed for VG-Prism II dynamic dual inlet stable isotope mass spectrometer. Tests have shown extreme sensitivity to contamination by carbon dioxide with a dependence of 6.8‰ per % CO_2 for $\delta^{15}N$ and 12.4‰ per % CO_2 for $\delta^{18}O$. Trace amounts of CO_2 have proven difficult to eliminate, particularly for small sample sizes. In order to ensure accurate analyses an indicator of CO_2 contamination must be monitored and corrections applied when necessary. We have found that ions with mass to charge ratios of 12 and 22 are excellent proxies for CO_2 contamination. Empirical relationships between these indicator species and CO_2 contamination are documented which allow for corrections to be applied to raw data. Additional corrections required due to the presence of isobaric molecules containing ^{17}O are described. Issues of standardization are discussed and sample handling procedures described. Finally, these methods and corrections are applied to a suite of stratospheric air samples.

1. INTRODUCTION

Early investigations of the stable isotopic signature of nitrous oxide employed infrared absorption techniques [1,2] or required decomposition of N_2O with subsequent mass spectrometric analysis of the reaction products, N_2 and CO_2 [3-10]. These techniques required large sample sizes and extensive preparatory procedures limiting the amount of data which could be produced. These methods were employed rather than direct injection of N_2O into the mass spectrometer in order to avoid contamination by carbon dioxide which has the same molecular masses as N_2O and is 1000 times more abundant in a typical sample. The potential for direct injection of N_2O into a mass spectrometer was first realized by Kim and Craig [11]. Separation of N_2O and CO_2 was performed with a gas chromatograph and assumed to be 100% complete. A thorough treatment of the method was performed by Tanaka et al. [12] who showed that erroneous enrichment of $\delta^{15}N$ and $\delta^{18}O$ could occur when even trace amounts of CO_2 were present. Since the ionization characteristics for each individual mass spectrometer are unique, we have adapted the methods described by [12] and developed a sample handling and mass spectrometric analytical protocol for our VG-Prism II mass spectrometer.

2. N_2O ANALYSIS AND NECESSARY CORRECTIONS

2.1 Delta 45 and 46 dependence on CO_2 contamination

Initially we would like to have an estimate of the effect a trace amount of CO_2 would have on a sample of N_2O. If only first order effects are considered we can use the natural abundance of the respective isotopes to get an approximation of the shift which a small amount of CO_2 contamination might cause. Table 1 shows the natural abundance of the stable isotopes of C, N, and O as well as the probabilities for the various mass combinations.

Table 1. The natural abundances of the stable isotopes of N, C, and O and the probabilities of the various combinations which are pertinent to mass spectrometric analysis of N_2O

^{14}N	0.99635	^{12}C	0.98892	^{16}O	0.99759
^{15}N	0.00365	^{13}C	0.01108	^{17}O	0.00037
				^{18}O	0.00204
M/z = 44		$^{14}N^{14}N^{16}O$	0.990321	$^{12}C^{16}O^{16}O$	0.984159
M/z = 45		$^{15}N^{14}N^{16}O$	0.003628	$^{13}C^{16}O^{16}O$	0.011027
		$^{14}N^{15}N^{16}O$	0.003628	$^{12}C^{17}O^{16}O$	0.000365
		$^{14}N^{14}N^{17}O$	0.000367	$^{12}C^{16}O^{17}O$	0.000365
	Σ 45		0.007623		0.011757
M/z = 46		$^{14}N^{14}N^{18}O$	0.002025	$^{12}C^{18}O^{16}O$	0.002013
		$^{15}N^{15}N^{16}O$	0.000013	$^{12}C^{16}O^{18}O$	0.002013
		$^{15}N^{14}N^{17}O$	0.000001	$^{13}C^{17}O^{16}O$	0.000004
		$^{14}N^{15}N^{17}O$	0.000001	$^{13}C^{16}O^{17}O$	0.000004
				$^{12}C^{17}O^{17}O$	0.000000
	Σ 46		0.020411		0.004033

Substituting into the standard delta notation and weighting the N_2O and CO_2 terms accordingly:

$$\delta 45 = \left[\frac{\dfrac{\sum 45_{N_2O} + \sum 45_{CO_2}}{44_{N_2O} + 44_{CO_2}}}{\dfrac{\sum 45_{N_2O}}{44_{N_2O}}} - 1 \right] \times 1000 \qquad (1)$$

yields a predicted dependence of 5.2 ‰ per % CO_2. A similar substitution for δ46 predicts a correction of 9.8 ‰ per % CO_2. If we take into account that the ionization efficiency of N_2O is 0.706 times the efficiency of CO_2 then the calculated dependencies increase to 7.4 and 14.0 ‰ for $\delta^{45}N_2O$ and $\delta^{46}N_2O$ respectively.

To test these effects we purchased 15 pounds of VLSI grade nitrous oxide (99.998 % specified purity, 99.9995 % tested purity, batch #90153; Air Products and Chemicals, Inc., Tamaqua, PA) and transferred 200 psi to an evacuated 15 liter aluminum cylinder which was designated the Standard Nitrous Oxide Working-gas (SNOW). A series of glass flasks of known volume were filled with SNOW to specified pressures and doped with carefully measured aliquots of CO_2. The resultant mixtures of known concentration were analyzed on a VG-Prism II triple collector mass spectrometer. The results of these analyses are plotted in Figure 1. In reasonable agreement with the expected values, the dependence is 6.89 and 12.66 ‰ per % CO_2 for δ45 and δ46, respectively.

2.2 Mass 12 and mass 22 as indicators of CO_2 contamination

With the empirical dependence of δ45 and δ46 on CO_2 determined, it is then possible to apply a correction to routine analyses if a reliable proxy indicator can be monitored. Since atomic carbon is a fragment common to the cracking of a CO_2 molecule, a peak with a mass to charge ratio (m/z) of 12 should serve as a good indicator of the presence of CO_2. In the presence of organic contaminants however, monitoring m/z = 12 will result in an erroneous over correction. A more unambiguous indicator is doubly charged CO_2 at m/z = 22 since the second ionization efficiency of N_2O is negligible (13).

Since the mass difference between the indicator masses and the parent mass is so great, the beams can not be monitored simultaneously. The peak jump routine of the mass spectrometer was modified such that time series of the m/z = 12, 22, and 44 peaks could be monitored following each standard isotope ratio run. A typical decay series is shown in Figure 2. Fitting the decay series with second order polynomials we can then solve for the m/z = 12 and 22 peak heights at a specified m/z = 44 beam current.

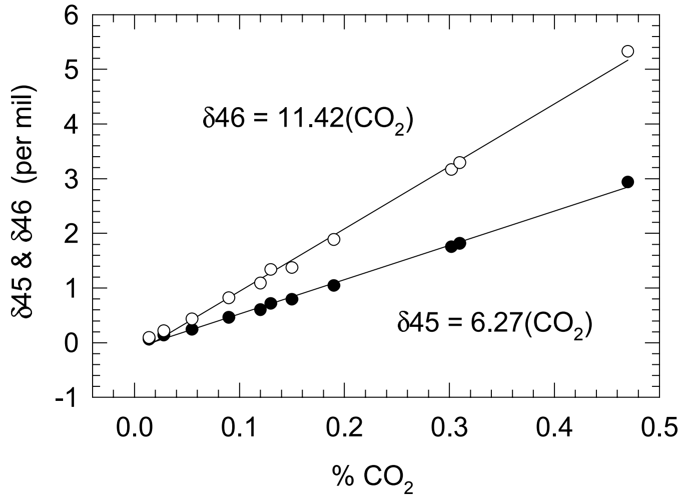

FIG. 1. Dependence of N_2O δ45 and δ46 on CO_2 contamination.

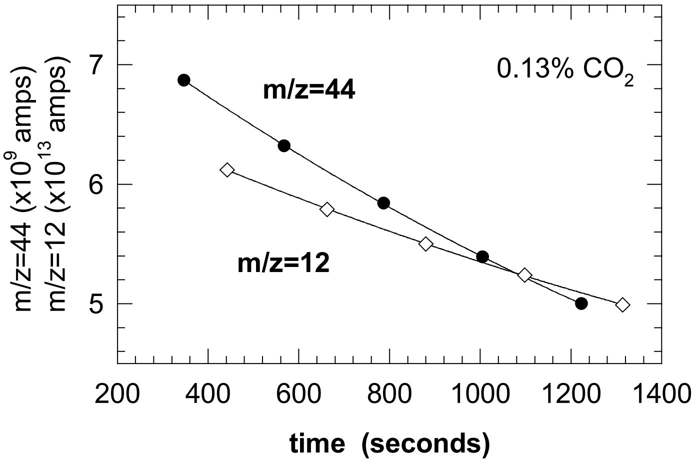

FIG. 2. Example of beam decay over time as determined from peak jump integrations of 20 seconds.

Repeating this procedure with each of the doped standards results in a set of calibration curves (Fig. 3) from which one can calculate the percent CO_2 contamination from the measured m/z = 12 (or 22) peak intensity. The doped standards are periodically measured to monitor small changes in the calibration curves which result from naturally occurring drift of the mass spectrometer ion source. Samples analyzed in the same manor can then be monitored for m/z = 12 and 22 and corrections applied when necessary. Both indicator species are monitored as a double check. Since the CO_2 contamination which is being measured is in trace amounts of already small samples, its actual isotopic content is not measurable and in any case will contribute only to second order effects. Data reduction is performed with the graphics software SigmaPlot ® with subroutines written specifically for N_2O isotope analysis.

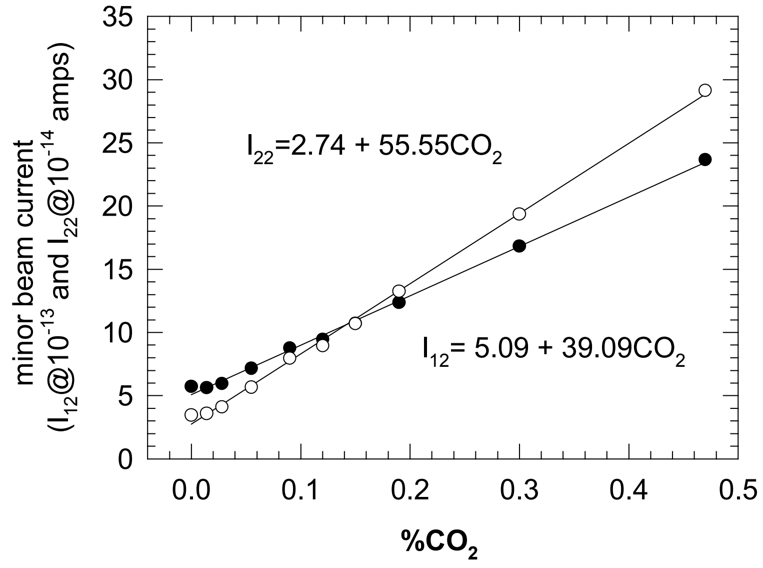

FIG. 3. Minor beam dependence on CO2 contamination normalized to m/z = 44 at 7 nA.

2.3 Oxygen 17 corrections

As in the case of carbon dioxide, mass spectrometric analyses of N_2O at mass 45 and 46 cannot discriminate between contributions from the species of interest, ^{15}N and ^{18}O, and the isobaric species containing ^{17}O. Thorough treatments of the problem have been performed [12, 10]. If R_{45}, R_{46}, R_{45s}, and R_{46s} are the mass 45/44 and mass 46/44 ratios with the subscript 's' denoting standard, then:

$R_{45} = 2R_{15} + R_{17}$ (2) and

$R_{46} = R_{18} + 2R_{15}R_{17} + (R_{15})^2$ (3)

where R_{15} denotes the $^{15}N/^{14}N$ ratio; R_{17} denotes $^{17}O/^{16}O$; and R_{18} denotes $^{18}O/^{16}O$. The quantities of interest are

$\delta^{15}N = (R_{15}/R_{15s} - 1)1000$ (4) and

$\delta^{18}O = (R_{18}/R_{18s} - 1)1000$ (5)

which can be solved if R_{15} and R_{18} are known. Utilizing the raw data from the mass spectrometer for δ45 and δ46, the R_{45} and R_{46} values can be back calculated from the standard delta equation. These can in turn be substituted into equations 2 and 3 which can be solved for R_{15} and R_{18} if the value for R_{17} is known. We adopt the theoretical relationship developed by Craig [14] for the correction of CO_2 analyses which states that:

$$R_{17}/R_{17s} = (R_{18}/R_{18s})^{½} \qquad (6).$$

A first approximation is made by assuming $R_{17} = R_{17s}$. Several iterations employing equations 2, 3, and 6 result in conversion for the value of R_{17} and we can then solve for the 'correct' values of $\delta^{15}N$ and $\delta^{18}O$.

Equation 6 assumes a mass dependent relationship between ^{17}O and ^{18}O of the reference and the sample. The assumption is generally valid for the reference but it has been shown [15] that tropospheric N_2O has a consistent mass independent signature of $^{17}\Delta \cong 1$ ‰ ($^{17}\Delta = \delta^{17}O - 0.515\delta^{18}O$). Corrections could be made by measuring $\delta^{17}O$ in each sample but current methods [16] require a separate analytical procedure converting N_2O to O_2. This would of course negate the advantage gained by employing the direct injection technique. Alternatively, δ47 could also be measured during direct injection from which one could then determine the quantity R_{47}. The quantity $R_{47} = 2R_{15}R_{18} + R_{17}(R_{15})^2$ could then be combined with Equations 2 and 3 and the system would no longer be indeterminate. The change in the correction which would result from this mass independent signature is, however, less than the precision of the current analytical procedures. In the future, as analytical precision improves, it may be necessary to take the proper steps to include this additional correction.

2.4 Standardization

Results of isotopic analysis of N_2O are reported relative to known isotopic standards. In the case of ^{15}N, the commonly accepted standard is atmospheric N_2. For ^{18}O, results are usually reported relative either to atmospheric O_2 or to Vienna Standard Mean Ocean Water (VSMOW). With early mass spectrometric methods, determining $\delta^{15}N$ was relatively straightforward since the technique required direct comparison to N_2 after decomposition of the sample. Analysis of $\delta^{18}O$ was less straightforward since the oxygen from the reacted N_2O was either reduced to water with H in the presence of a metal catalyst (with subsequent equilibration with CO_2), or was reacted with graphite at high temperature to produce CO_2. In either case, analysis of the resultant CO_2 was easily cross referenced to the common standards of O_{2atm} or SMOW.

Direct injection of N_2O precludes direct comparison to the recommended standards. Samples must therefore be measured against a standard which has been dissociated and analyzed as described above, or a standard which has been calibrated to one such. We have calibrated SNOW against the standard known as 'Albany Tank' (AT) which has reported isotopic values of $\delta^{15}N_{AT\text{-}N2} = 2.50$‰ and $\delta^{18}O_{AT\text{-}O2} = 12.96$ ‰ [12]. Triplicate analysis of AT versus SNOW are shown in Table 2.

Applying the standard equation for reference conversion [14]:

$$\delta_{x\text{-}std1} = \delta_{x\text{-}std2} + \delta_{std2\text{-}std1} + (\delta_{x\text{-}std2} \times \delta_{std2\text{-}std1} \times 10^{-3}) \qquad (7)$$

we calculate $\delta^{15}N_{SNOW\text{-}N2} = 1.31$ ‰ and $\delta^{18}O_{SNOW\text{-}O2} = 18.46$‰.

Table 2. Results of the triplicate analyses of the reference gas 'Albany tank' (AT). Columns 2 and 3 are the raw δ45 and δ46 for AT relative to snow. Columns 4 and 5 are the results of the residual CO_2 analyses for M/Z = 12 and 22. Columns 6 and 7 are the converted values for δ45 and δ46 of snow relative to AT. Columns 8 and 9 are the ^{17}O corrected $\delta^{15}N$ and $\delta^{18}O$ values for snow relative to AT. Columns 10 and 11 show the results of the final conversions for referencing to N_{2ATM} and O_{2ATM}.

#	δ^{45} AT-SNOW	δ^{46} AT-SNOW	% CO_2 (from 12)	% CO_2 (from 22)	δ^{45} SNOW-AT	δ^{46} SNOW-AT	$\delta^{15}N$ SNOW-AT	$\delta^{18}O$ SNOW-AT	$\delta^{15}N$ SNOW-N2	$\delta^{18}O$ SNOW-O2
1	1.019	-5.310	0.00	0.00	-1.018	5.338	-1.207	5.394	1.290	18.424
2	0.963	-5.398	0.00	0.00	-0.962	5.427	-1.150	5.482	1.347	18.513
3	1.019	-5.340	0.00	0.00	-1.018	5.369	-1.207	5.425	1.290	18.455
Avg	1.000	-5.349							1.309	18.464
1 σ	0.032	0.045							0.030	0.050

Working standards have also been traded with several other laboratories which are active in N_2O isotopic research. It is hoped that eventually a thorough inter-laboratory calibration will be completed which will allow for more meaningful comparisons of data sets.

2.5 Sample extraction protocol

Tests with the mass spectrometer were conducted to determine the smallest sample size which could be reliably and reproducibly measured. A sample size of 0.4 to 0.6 μmol (~10 μl STP) N_2O was determined to be optimal when used in conjunction with the internal cold finger. Samples of smaller size resulted in reduced signal strength and samples of larger size resulted in over-pressurizing the cold finger volume. Since the atmospheric concentration of N_2O is ~315 ppb, 30 to 40 liters of tropospheric air provide the ideal amount of purified N_2O for direct injection.

A vacuum extraction line dedicated to the extraction of N_2O from atmospheric samples was constructed and is illustrated in Figure 4. Samples are passed through a flow integrator and over a large column of ascarite before being inlet to T1. Scrubbing of the sample with ascarite (NaOH) efficiently removes the majority of CO_2 but also produces a significant amount of water. The majority of the water is removed with an ethanol/liquid N_2 cold trap at T1. Liquid N_2 cold traps at T2 and T3 collect the remaining condensable gases while the non-condensable gases are passed to a turbo-molecular vacuum pump through the main valve V14. A cold ethanol trap replaces the liquid N_2 trap at T2 to retain any water while the N_2O and residual CO_2 are transferred to T3. With V3 closed, the ethanol and liquid N_2 dewars are leap-frogged to traps T3 and T4.

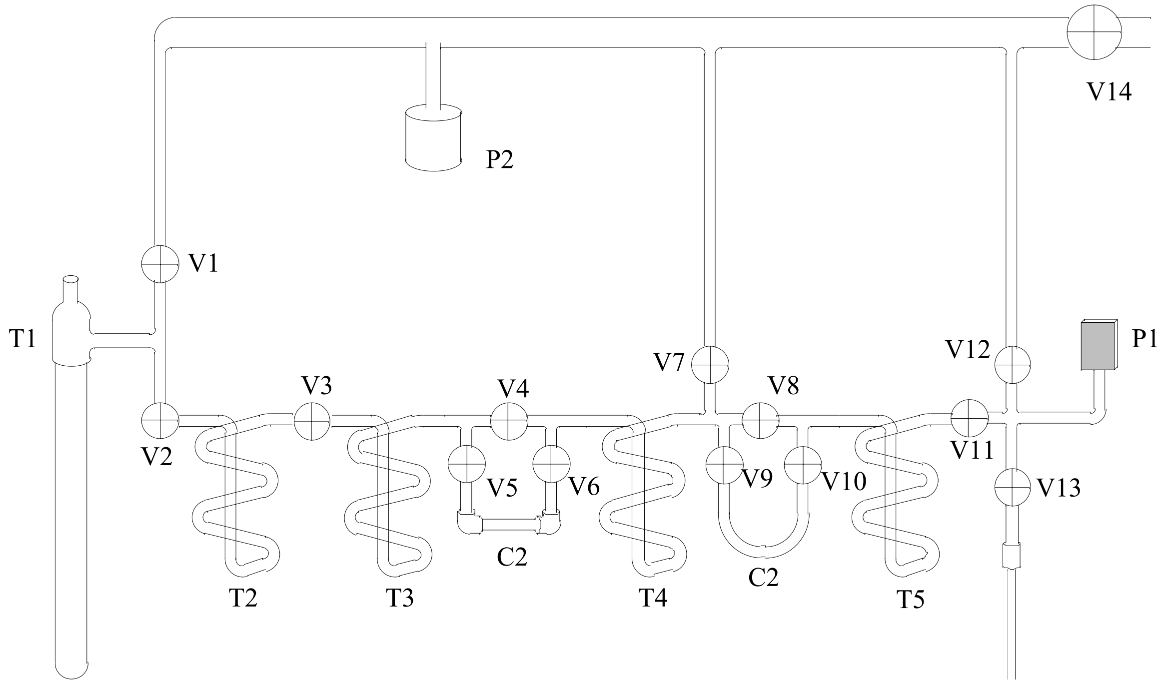

FIG. 4. Schematic representation of the extraction line for purification of nitrous oxide from atmospheric air samples. Details in text.

The sample pass from T3 to T4 is routed through the bypass at V5 and through a small column of ascarite at C1. The ascarite column at C1 removes any residual CO_2 and is attached to the line with Ultra-torr ® high-vacuum connectors to facilitate ease of replacement. With the sample now trapped at T4, the ethanol and liquid N_2 dewars are moved to T4 and T5 and the sample is passed through an additional bypass at V9. The column C1, is filled with 300 mg of Silicalite and is permanently attached to the vacuum line with blown glass joints. Silicalite is an organophilic molecular sieve which efficiently retains trace amounts of light organics [17] which can subsequently interfere with mass spectrometer analyses. After isolation at T5, the sample is warmed and expanded to fill the calibrated volume between valves V8, V10, V12, V13, and the pressure transducer P1. The pressure measured at P1 and the calibrated volume are used to calculate the sample size which is compared with the previously measured sample concentration and the flow meter reading to determine the yield of the extraction. The sample is finally collected on a flame sealed glass finger with liquid N_2 at V13.

The extraction procedure was tested for systematic isotope effects after making several artificial ‘air’ tanks by mixing aliquots of pure N_2O with a mixture of 80% N_2 20% O_2. Tanks were mixed to concentrations varying from 700 ppb to 500 ppm. Tests were completed at various flow rates, with and without bypass through C1 and C2. Elution times through C1 and C2 were systematically varied. Yields were consistently between 98 and 100 % and no fractionation was observed when the flow rate was maintained below 1 liter per minute and elution times were set at 3 minutes and 15 minutes for C1 and C2, respectively.

2.6 Stratospheric sample results

Between January, 1988 and April, 1989 a suite of high volume stratospheric samples was collected during routine flights of NASA's WB-57F aircraft stationed at Ellington Field in Houston, Texas. Samples were collected in 15 liter aluminum spheres and pressurized to ~ 2000 psi with an oil lubricated compressor known as the P-system [18]. Samples were analyzed for CH_4, $\delta^{13}CH_4$, δCH_3D, CO_2, N_2O, and ^{85}Kr and the remaining gas was archived for future use. Local tropopause heights at the time of flight were determined from US Weather Service balloon-sonde data.

During the period that the N_2O direct injection technique was being developed for the mass spectrometer in 1995-96, the archived stratospheric samples were analyzed again for N_2O concentration to ensure sample stability. The sampling dates, locations, and altitudes are shown in Table 3 along with the results of the original N_2O analyses and the repeated analyses. Concentrations show good stability within the precision of the gas chromatograph results.

Two additional stratospheric samples were obtained from balloon flights in northern Europe in February, 1988 (courtesy of Dr. U. Schmidt). The pertinent information on these data are also included in Table 3 although these samples were pre-concentrated so the final concentration could not be double checked.

Samples collected with the P-system were processed on the extraction line as described above. Unfortunately, the oil lubricated pump contributed excess amounts of light hydrocarbons which proved difficult to separate from the nitrous oxide. It was determined that additional processing by gas chromatography would be necessary. A liquid N_2 cold trap was added to the outlet of a gas chromatograph equipped with a thermal conductivity detector. Tests with the artificial air standards were conducted to determine the optimal operating conditions of the gas chromatograph. Initially, the yields were consistently less than 70 percent. The entire flow system of the GC was disassembled, cleaned, and reassembled with new connectors.

With these modifications, the yield improved to a consistent 90 percent. Considering the small sample sizes being processed (~10 to 20 μl), it might be expected that a small portion of the sample would be lost due to retention on the chromatographic column. If a portion of the sample were being retained on the column packing material (Poropac Q ®), it would be expected that the isotopically heavy species would be preferentially retained with δ46 showing approximately double the fractionation of δ45. Table 4 shows the results of two sets of artificial air samples; the first set being processed on the standard extraction line only and the second set being processed through the standard line with subsequent treatment by the gas chromatograph. As expected, the GC processed samples are routinely light with the shifts in δ46 and δ45 having a ratio slightly greater than two.

The WB-57F samples were then processed through the GC and the raw values adjusted according to the offsets calculated in Table 4. Corrections for ^{17}O and conversion to the isotopic standards N_{2atm} and O_{2atm} were applied as specified in the previous sections. The balloon samples were not contaminated with excess hydrocarbons and therefore were not processed through the gas chromatograph. The final results of all stratospheric samples are tabulated in Table 5.

Interpretation of these results is discussed in detail elsewhere [19-21]. We do, however, make the following observations. Several of the samples were analyzed in duplicate and at different sizes. Reproducibility is generally within ±0.2‰ which is excellent considering the multiple preparatory steps and the amount of handling involved. The final four samples in the table are the two balloon samples and two low volume extractions of the tropospheric air tank 64284. Since the balloon samples were of particularly small size (1.5 and 2.6 μl), there was concern that signal strength in the mass spectrometer would be insufficient. The low volume extractions from the tropospheric tank compare favorably with the duplicate analyses at larger volume in the upper portion of Table 5 although precision is somewhat reduced. With these observations we conclude that the results of these analyses are representative of stratospheric conditions. As this document is mainly concerned with analytical techniques we refer to scientific discussions and the reasons for the heavy enrichment in the stratospheric N_2O isotopes to relevant publications [19-21].

Table 3. Sample dates, locations, and altitudes of stratospheric samples as well as the initial concentrations of N_2O as measured in 1989 and the repeat analyses of 1995. Also included is the pressure in the sample cylinder at the time of extraction. HGT. > T = height above the local tropopause. NA = not applicable. NM = not measured.

Sample	Date Collected	Lat/Long	Alt (km)	Hgt > T (km)	C_{89} (ppb)	C_{95} (ppb)	P_{95} (psi)
M2726	1/27/88	46N/94W	17.4	6.6	239	236	890
M0131	5/10/88	39N/94W	18.3	4.8	234	227	880
E1983	5/10/88	45N/94W	16.8	4.4	243	248	900
E1690	4/12/89	40N/94W	15.3	4.3	245	252	710
M3033	4/12/89	48N/94W	17.4	6.7	186	183	640
LL21119	2/10/88	68N/20E	14.4	NM	273	NM	NA
LL21109	2/10/88	68N/20E	22.6	NM	126	NM	NA
64284	5/19/94	33N/117W	0	NA	NA	320	~2000

Table 4. Comparison of artificial air standards which were processed with and without additional gas chromatographic separation. The adjustment applied to the stratospheric samples is the difference between the average values.

	n	Avg. Yield	δ^{45}	1 σ (45)	δ^{46}	1 σ (46)
GC	4	98 %	0.015	0.017	-4.373	0.032
No GC	3	90 %	-0.673	0.112	-5.912	0.084
Δ (No GC-GC)			0.688		1.539	

Table 5. Results of analyses of stratospheric samples. Corrections were applied as described in the text. The CO_2 contamination reported is that calculated from M/Z = 22 correction. NK = not known. NA = not applicable

Sample	Conc (ppb)	Size (ul)	yield [%]	$\delta45_{raw}$ [‰]	$\delta46_{raw}$ [‰]	CO_2 [%]	$\delta45_{corr}$ [‰]	$\delta46_{corr}$ [‰]	$\delta45_{GCadj}$ [‰]	$\delta46_{GCadj}$ [‰]	$\delta^{15}N_{N2}$ [‰]	$\delta^{18}O_{O2}$ [‰]
64284	320	11.0	89	4.96	2.54	0.112	4.28	1.23	4.97	2.77	6.47	21.23
64284	320	11.7	89	5.14	3.07	0.154	4.21	1.27	4.90	2.81	6.40	21.27
E1690	248	12.5	90	7.93	5.33	0.140	7.08	3.69	7.77	5.23	9.35	23.71
E1690	248	12.2	88	7.59	4.53	0.092	7.03	3.45	7.72	4.99	9.31	23.41
E1983	245	13.3	85	9.66	8.09	0.316	7.75	4.39	8.44	5.93	10.04	24.42
M2726	238	15.9	88	8.45	5.55	0.100	7.84	4.38	8.53	5.92	10.14	24.41
M0131	230	11.7	88	8.83	5.84	0.078	8.36	4.93	9.05	6.47	10.67	24.96
M0131	230	21.8	87	9.05	6.40	0.059	8.69	5.70	9.38	7.24	11.00	25.75
M3033	185	15.5	93	11.92	8.10	0.024	11.78	7.82	12.47	9.36	14.20	27.88
M3033	185	14.6	88	11.96	8.49	0.064	11.58	7.75	12.27	9.29	13.99	27.81
64284	320	2.4	100	7.59	6.51	0.287	5.93	3.35	NA	NA	7.47	21.81
64284	320	1.6	100	7.53	5.72	0.417	5.12	1.13	NA	NA	6.67	19.55
LL21119	273	2.6	NK	7.47	4.93	0.182	6.41	2.92	NA	NA	7.98	21.36
LL21109	126	1.5	NK	40.08	43.08	2.474	25.76	15.86	NA	NA	28.02	34.34

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EXTRACTION OF TRAPPED GASES IN ICE CORES FOR ISOTOPE ANALYSIS

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Abstract. The use of ice cores for paleoclimatic investigations is discussed in terms of their application for dating, temperature indication, spatial time marker synchronization, trace gas fluxes, solar variability indication and changes in the Dole effect. The different existing techniques for the extraction of gases from ice cores are discussed. These techniques, all to be carried out under vacuum, are melt-extraction, dry-extraction methods and the sublimation technique. Advantages and disadvantages of the individual methods are listed. An extensive list of references is provided for further detailed information.

1. INTRODUCTION

A number of paleoclimatic archives are available for reconstruction purposes, including ocean sediments, peat bogs and lake sediments, tree ring records, historical documents and ice cores. The advantage of ice cores lies in the well ordered and complete collection of climate (H_2O isotopes), climate forcing (greenhouse gases) and solar variability (^{10}Be and ^{36}Cl) information partly with a sub-annual resolution covering the last 500 000 years.

Ice core records with the full width of information can be obtained from sites where melting and sublimation is minimised. Therefore, the central parts of Antarctica and Greenland, as well as some smaller ice caps in the Arctic, are suitable. Ice domes or ridges, where horizontal ice movement can mainly be ignored in interpreting records, are often preferred drilling sites. In contrast most of alpine glaciers are not cold enough and can be used only for certain investigations with parameters which are hardly influenced by melting and associated processes. The feasibility of ice to act as an archive is based on the sequential accumulation of snow, containing a snapshot of the atmosphere's condition. During the transformation — 'snow–firn–ice' — information can be stored in three reservoirs: (1) the water itself — more precisely its isotopic composition — contains a record of climate variability in particular the local temperature; (2) particles and soluble gases are trapped in snow flakes or at the snow surface and record the chemistry of the lower atmosphere; (3) the gases, which are closed off from the free atmosphere when a certain firn density is reached, hence the gas age is different from the age of the surrounding ice.

1.1 Dating

Dating of the ice cores is essential in order to reconstruct the temporal development of any parameter. There are different dating methods: (1) annual layer counting — parameter like the isotopic composition of water ($\delta^{18}O_{ice}$, δD_{ice}), electrical conductivity measurement (ECM), dust or most chemical components (H_2O_2, NH_4 etc.) show seasonal variations; (2) time markers, such as known volcanic eruptions or nuclear weapon tests; (3) ice flow modelling. Annual layer counting is preferred when the accumulation rate is sufficiently high. In deeper ice, and for low accumulation sites, ice flow modelling combined with time markers from different archives is generally used. A brief description will be given about the accuracy of ice core dating.

1.2 H_2O isotopes as temperature indicator

The „key“ parameter in any ice core record are the H_2O isotope records. Both the oxygen and hydrogen isotope ratios can be measured and yield information about temperature and water vapour history (sources). The principles of using H_2O isotopes as a paleothermometer was already discussed by several authors starting with simple Rayleigh distillation [1, 2, 3, 4, 5, 6, 7]. The relationship between H_2O isotopes and temperature was derived spatially for Greenland for example by [8]. Despite critical discussion of using such a spatial relation it was actually used by many scientists for temporal variations. Borehole temperature logging in combination with heat diffusion backcalculations has provided a better insight of past temperature changes and hence the long-term temporal relationship between temperature and H_2O isotopes. This new calibrations for long-term changes was recently supplemented for short-term events by another calibration technique using nitrogen isotopes ($\delta^{15}N$) of N_2 which are partly influenced by thermal diffusion [9, 10, 11].

1.3 Isotopes as synchronisation tool

A fact which is obvious from the deep ice cores recovered so far are the fast variations during glacial times. These variations are more pronounced in Greenland ice compared to Antarctica. Based on these changes, which are common for a lot of parameters such as the H_2O isotopes, methane and many chemical species etc., one can in principal synchronise ice core records from different sites. However, for a synchronisation one has to differentiate between ice (H_2O isotopes), impurities of the ice (chemical species, dust etc.), which underlie both strong local influences and trapped air properties, which are more of global character (short mixing time of the atmosphere of 1–2 years). Two recently established tools are using the global parameters of the isotopic composition of atmospheric oxygen ($\delta^{18}O_{atm}$) by [12] and of methane by [13, 14, 15]. Due to the much shorter atmospheric lifetime for methane than for oxygen, methane is a better recorder of short-term variations and hence better suited for exact synchronisation of different records. But even using so called global parameters as synchronisation tool have their difficulties, which are namely coupled with gas-ice age differences as well as the spread of air ages. Both are among others dependent on the local accumulation rate and temperature. When considering only record comparisons within a single ice core, for example $\delta^{18}O_{ice}$ with a gas record (CO_2 , CH_4, N_2O), then $\delta^{15}N$ is very useful since it can be used to derive exact estimates of gas-ice age differences. Similarly, noble gas ratios or noble gas isotope ratios can also be used to estimate this difference [16].

1.4 Isotopes of trace gases as flux markers

Carbon, oxygen, hydrogen and nitrogen isotopes of the most important greenhouse gases CO_2, CH_4 and N_2O — **except** water vapour — are very useful tool**s** for tracing the partitioning of fluxes into the different reservoirs (ocean, atmosphere, biosphere) as shown by several publications as shown below. For detailed information about the importance of biological CO_2 pump, CO_2 isotope disequilibrium, carbonate dissolution and other part of the global carbon cycle please consult the following selected papers [17, 18, 19, 20, 21, 22, 23, 24]. This list is by far incomplete but it allows you a first approach to this topic.

1.5 Isotopes as indicators of gravitational and thermal diffusion corrections

In the diffusive zone of the ice sheet overlaying firn zone two alteration of the air composition occurs due to external forcing of air movement. First of all the earth's gravitation field leads to an enrichment of the heavy isotopes and elements at close-off depths compared to the free atmosphere. Secondly similarly acts a temperature gradient between surface and close-off depth in that the heavier molecule migrates towards the colder end. Both influences can be studied by looking at the isotopic composition of nitrogen ($\delta^{15}N$) since this parameter is believed to be constant in the atmosphere over time periods of 10^5 years, as generally accepted. Information about this topic can be found in the following publications [25, 26, 27, 28].

1.6 Oxygen Isotope as an indicator of a changing Dole effect

The past atmospheric oxygen isotopic composition of ice cores is a global parameter. Together with the corresponding oceanic $\delta^{18}O$ as measured on sea-sediments, mainly derived from benthic foraminifera, one get an idea of the variation of the so-called Dole effect (i.e. the differences of $\delta^{18}O_{atm}$-$\delta^{18}O_{sea}$) [29] and [30].

1.7 ^{10}Be and ^{36}Cl as solar variability indicators

These two isotope are cosmogenically produced. The production rates of these species are modulated by both the magnetic fields carried by solar wind as well as those associated with the geomagnetic dipole moment. Therefore, a large potential for retrieving information about changes of solar variability as well as changes in the magnetic fields in the past is given for those species.[31, 32, 33, 34, 35].

In the following section we will briefly summarise the principal methods which are used to analyse the above mentioned parameters. We will focus mainly on the gas species and their isotopes rather than on direct measurements of ice matrix components and or chemical inclusions.

2. METHODS

First of all one has to distinguish between techniques used for gas extraction or for chemical and matrix component. For the latter two purposes mainly a melting of ice is adequate. For H_2O isotopes only a simple melting is necessary. For Be and Cl isotopes a chemical absorbent is mounted into the melt water line. However, there are different ice melting devices (melt heads) available, some of them were specifically developed for certain tasks such as CFA (continuous flow technique) which is used to determine parameters such as Ca^{++}, Na^+, Cl^-, NH_4^+, H_2O_2 and many more. But most of engineering time was spent on extraction systems for gases.

There are three main techniques used for extracting gases from ice cores, which will be discussed below. Historically the melt-extraction (1) is the oldest method used, followed by the various dry extraction techniques (2) after having problems with CO_2 contamination (in particular from carbonate dissolution in acidic ice or oxidation of organic acids) with the melt-extraction. The third technique is based on the sublimation of the ice (3) to circumvent the potential contamination problems associated with water chemistry. All three methods have in common that the procedure has to be undertaken under vacuum. For extraction types (1) and (3), the extraction efficiency is close to 100% whereas for extraction (2) it is variable depending on time, crushed ice particle size and air inclusion state (bubbles, clathrates, mixture of both). The air in the ice is first enclosed in air bubbles which with increasing pressure lower their volume according to rules of a Van der Waal gas. At a certain depth depending on hydrostatic pressure and site temperature the bubbles are transformed into air-hydrates (clathrates), which are somewhat like a football-like cage made-up of water molecules which themselves host gas molecules. Description of the main extraction devices, their advantages and disadvantages as well as their main applications are listed below.

(1) Melt extraction

The ice is melted by heating the ice under vacuum, therefore releasing the occluded gases from the bubbles. Slow refreezing of the water forces the gases to leave to the headspace of the extraction chamber (usually glass containers made up from two parts sealed with either a synthetic product or soft metal), which are then either cryogenically condensed (by a closed-cycled helium cooler or a liquid helium) or compressed. To optimize the gas extraction efficiency the heating/refrezeeing cycle is repeated up to three times. References describing this technique are [36, 37, 38, 39]. In recent times this technique was modified to process rather small samples (10–20 g of ice) for methane concentration analysis and isotope and elemental measurements of the main air components [40, 41, 14] and [10, 42].

Advantages:

- close to 100% extraction efficiency
- simple and fast extraction
- no or hardly detectable fractionation for close to 100% extraction efficiency

Disadvantages:

- cannot be used for highly water soluble gas species (e.g. CO_2)
- contamination potential via water chemistry
- contamination by ad/disorption processes
- water vapor transport effects
- extraction efficiency has to be checked to prevent fractionations due to different solubilities

Applied to the following species:

• CH_4 and N_2O concentration (latter is rather surprising)	[14], [43], [44]
• $\delta^{18}O_{atm}$, $\delta^{15}N$	[42], [10]
• elemental ratios of main air components (O_2/N_2, AR/N_2)	[10]
• noble gas ratios (Kr/Ar, Xe/Kr)	[16]
• $\delta^{18}O_{ice}$ (ice melting only)	[45], [46]

(2) Dry extraction

Several techniques for dry extraction have been suggested and are actually in use. In the following these different types of dry extraction systems are briefly described and noted for which purpose they are used. General advantages/disadvantages compared to the melt-extraction can be given as:

Advantages:

- no interaction with wet chemistry (when working at low temperatures, <-15°C, lower temperatures usually result in lower contaminations)
- combinations of trace gas analyses including CO_2 on the same sample are possible
- close to 100% extraction of opened air bubbles

Disadvantages:

- incomplete gas extraction (depending on the size ratio of remaining ice particles and the mean bubble or clathrate distance; especially important for clathrate ice)
- contamination problems associated with moving parts (for example: metal-metal friction produces methane)
- contamination problems associated with desorption processes, especially from metal surfaces (therefore good preconditioning is necessary) or the whole extraction system has to be heated to minimize adsorption/desorption processes, especially for CO2.

Needle-crusher

Another technique developed at Bern by [47] is the needle-crusher for small ice samples of less than 20g. Under vacuum an array of needles is repeatedly pneumatically driven into the ice sample splitting it into small pieces, releasing thereby the enclosed air. This air is then expanded into an infra-red laser absorption spectrometer cell, where the CO_2 concentration is determined. The extraction efficiency is of the order of 80% for bubble ice and around 45–70% for clathrate ice [*48*].

A similar technique is in use at Scripps [49]. We evacuate the crusher and crush the ice (4–6 cm^3) at -70^oC, and condense the whole liberated air sample at about 20 K into mini-cold traps cooled by a closed cycle He refrigerator. We admit three standard air gases (165–328 ppm CO_2))over the crushed ice for every three samples to closely simulate the standardization procedure to the ice air extractions. These standard gases are then treated identical to the samples. The traps containing samples and standards are subsequently warmed to -70^oC, the gas is mixed with a bellow assembly (to overcome stratification due to different condensation temperatures) and dispensed into the IR cell by the bellow assembly. Measurements are made by tunable diode laser spectroscopy on a single vibrational-rotational line. Each sample is measured at exactly the same pressure and temperature. Our depth resolution is about 1 cm.

Advantages:

- fast crushing technique for small samples (<20g)
- good extraction efficiency for bubble ice
- very well reproducible

Disadvantages:

- not well suitable for clathrate ice (increasing CO_2 concentration with time)

Applications:

- for CO_2 concentration its isotopic composition

Ball-mill

The ball-mill was developed by [50] to test whether another extraction technique than the previously described needle-crusher would lead to similar results. The ice is powdered by balls within a stainless steel container thus pulverizing the ice and releasing the air. The depth resolution due to the larger sample size is somewhat less.

Advantages:

- fast and easy for middle sized samples (50g>sample <100g)
- good crushing efficiency for both bubble and clathrate ice

Disadvantages:

- not suitable for methane measurements (methane production by metal-metal friction)
- potential of sealing the gas outlet by ice powder

Applications:

- mainly for CO_2, also used for nitrous oxide (N_2O)

Ice mill

The ice mill was especially developed for carbon isotope measurements on CO_2. It was design by [51] for ice samples between 100 to 1000g, making it ideally for extraction of a few microliters of carbon dioxide for mass-spectrometric measurements using a dual inlet system. It furthermore was used for a few radiocarbon measurements. The ice is crushed in a evacuated stainless steel container by a milling cutter. The escaping air from the opened bubbles is collected by condensation at 15K with a closed-cycled helium cooler (Leybold-Heraeus or CTI Cyrogenics).

Advantages:

- large size sample possible
- controllable particle size by additional weights
- fast extraction time and condensation time (<12min)
- tested and suitable for isotope measurements

Disadvantages:

- potential of strong contaminations for CH_4, CO_2, N_2O after removing of ball-bearing silver coating within the ice mill
- rather long time for pre-conditioning

Applications:

• mainly for carbon isotopes ($\delta^{13}C$, $\delta^{18}O$)	[60], [20]
• $\delta^{15}N$, $\delta^{18}O_{atm}$	[52]
• elemental ratios such as $\delta O_2/N_2$, dAr/N_2 etc.	

Cheese Grater (taken from CO_2 -Paper by [53])

The technique quickly extracts air from the bubbles without melting the ice or exposing the released air to moving metal components, both of which could influence the trace gas composition [54, 55]. Briefly, samples weighing 500–1500 gram are prepared by selecting crack-free ice and trimming away the outer 5–20 mm. Each sample is sealed in a polyethylene bag flushed with high purity nitrogen and cooled to –80°C. It is then placed in the extraction flask where it is evacuated and then grinded to fine chips. The released air is dried cryogenically at –100°C and collected cryogenically in electropolished stainless steel "traps", cooled to about –255°C by a closed-cycle helium cooler. The precision is extremely good due to the large sample size which is applicable for high accumulation rate sites.

The measuring procedure at Scripps for $\delta^{13}CO_2$ uses a somewhat similar techniques for liberating the air. About 200 g of carefully trimmed ice is crushed under vacuum in a rotary, inwardly spiked stainless steel cylinder (about 5 L volume) in a –27°C freezer for 30 minutes.

Advantages:

- fast extraction and condensation method (<10min)
- large sample processing is possible (up 1400g)
- tested for several trace gas concentrations and isotope species
- low contamination (at least true for the system at DAR, Aspendale)

Disadvantages:

- lower sample limit is around 200g at least for the Australian Cheese Grater Technique (since a remaining ellipsoidal ball of around 70g is present after crushing)

Applications:

- CO_2 , CH_4, N_2O, CO, H_2
- $\delta^{13}C$, $\delta^{18}O$ on CO_2, C-14, $\delta^{13}CH_4$

New ice mill

A sample of up to 20g is crushed in a sealed container by a milling cutter and the gas escaping from the opened bubbles is flushed with helium to a Porapak column where it is stored until its injection into the gas chromatograph. To avoid any contamination with CH4 produced by friction in the gear section, a helium-flushed rotary feed-through is used. CH4 analyses on ice samples of about 10g from the last 1000 years give precise and reproducible results [56].

Advantages:

- very small sample can be processed (5g<sample<20g)
- hardly no contamination
- direct gas trapping and injection to the chromatograph

Disadvantages:

- rather difficult in maintenance

Applications:

- so far for methane
- potential for CO_2 and N_2O

(3) Sublimation technique

[57] and [58] recently reported the use of sublimation of the ice as a technique for extraction of air samples from ice cores. They applied this technique to extract air samples for the determination of the isotopic composition of CO_2. More recently, [59] used a similar gas extraction approach combined with a frequency-modulated high-resolution infrared absorption spectrometer with tuneable diode lasers (FM-TDLAS) for analysing trace gas concentrations of CO_2, CH_4 and N_2O.

The sublimation extraction technique utilises sublimation of the ice sample in a high-vacuum apparatus at temperatures well below the triple point of ice-water-vapour (0°C). The energy needed for the sublimation is transferred to the ice sample by near infrared irradiation. The released water vapour and the air from the bubbles are refrozen in consecutive cold traps at temperatures appropriate to separate both components. The air is cryogenically trapped at 14K with a closed-cycled helium cooler. The temperature of the ice during sublimation is monitored via the water vapour pressure above the ice and kept below –20°C (equivalent to 1hPa vapour pressure) to prevent melting and the formation of the quasi-liquid layer on the ice surface at temperatures between –4°C and –2°C and at the interface between the ice and glass. This prevents chemical reactions in the liquid phase from producing excess CO_2 from carbonate dust.

Advantages:

- No contamination from liquid phase chemical reactions under careful maintained conditions
- 100% extraction efficiency

Disadvantages:

- Rather long sublimation times (30–45min for 50g ice)
- Additionally long pre-conditioning time required
- contamination problems due to wall desorption processes
- contamination potential by accumulation of chemicals and particulates

Applications:

- applied for radiocarbon analyses on CO_2
- CO_2 , CH_4, N_2O

(4) Steps following the gas extraction (example $\delta^{13}C$ on CO_2)

Detailed information for $\delta^{13}C$ on CO_2 measuring procedure at SIO

The measuring procedure at Scripps for $\delta^{13}CO_2$ uses a somewhat similar techniques for liberating the air. About 200 g of carefully trimmed ice is crushed under vacuum in a rotary, inwardly spiked stainless steel cylinder (about 5 L volume) in a –27°C freezer for 30 minutes. The CO_2 thus liberated from the ice is extracted in a glass vacuum line by passing it through a –90°C acetone/liquid nitrogen (LN) cooled trap to remove water and two –196°C traps to retain CO_2. The CO_2 is transferred from the first LN trap to the second by warming the first to –90°C (and similarly to the third) and ultimately trapped into a Pyrex tube at –196°C which is flame sealed. We introduce multiple times standard air of precisely known isotopic $^{13}CO_2$ over the uncrushed ice before and later over the crushed ice and retrieve and treat it identically to the ice air samples. We observe a small reproducible negative fractionation which we correct for. The samples (standards and ice air) are analyzed on a VG Prism II IRMS for the isotopic composition of C and O. The performance of the mass spectrometer is frequently calibrated against NIST standards (NBS 19, 16, and 17) and the Netherlands standards GS 19 and 20, and we have a numerous set of equally calibrated secondary standards (both air and carbonate standards, for atmospheric and marine work). Typically we run 3 to 4 standards for 15samples to monitor and correct minor short term variations of machine performance over a day. Other corrections made to the raw isotopic data include a correction for the ^{17}O isotope (Craig correction), gravitational correction (using $\delta^{15}N$ data when available). An additional N_2O correction is based on measurements of mixtures of CO_2 and N_2O to arrive at the specific correction for our machine. We use the published values of N_2O concentration in ice air as the raw data from which we calculate the corrections for N_2O.

Our precision on a single sample is about 0.075 per mil for $^{13}CO_2$. Including the errors for the gravitational correction by ^{15}N, it becomes 0.085 per mil. However duplicate and triplicate analyses indicate errors of 0.060 and 0.049 per mil, respectively.

(5) Additional remarks:

Problems of sample handling, transfer, and storing

It is a general experience that the more manipulations and handling steps a sample has to go through the larger will be the potential to get contaminated. Therefore, a condensed and slim but still sufficient sampling procedure is a first step to expect reproducible results. Secondly, it is important to follow a very strict protocol when processing a sample since many handling steps have often time- or pressure-dependent characteristics (such as adsorption/desorption or extraction efficiencies etc.). Thirdly, fractionation inherently belong to sample gas expansion manipulations, therefore great attention has to be paid to this steps. In particular by introducing samples into a analyzer systems (gaschromatographs or mass spectrometers) this has to be in mind. Fourthly, there are a lot of effects associated with measuring procedures as well, which is thoroughly discussed at least for mass spectrometer analysis in [17].

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