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Absolute measurement of the abundance of atmospheric carbon monoxide

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Abstract. The main aspects of an absolute method for measurement of the mixing ratio of atmospheric carbon monoxide (CO) are presented. The method is based on cryogenic extraction of CO from air after oxidation to CO₂ followed by accurate volumetric determination. Gravimetric measurement is used to determine the quantity of sample air processed. In routine operation the overall error can be kept below 1%. Furthermore, the results of a laboratory intercomparison are analyzed. It is shown how offsets in the commonly applied analytical methods can occur and how these can seriously affect results obtained at the low concentration end (<100 nmole/mole).

1. Introduction

The need to better know the budget of CO is reflected by the scale of international efforts in measuring and modeling the distribution and interactions of this ubiquitous chemically active trace gas [Novelli, 1999; Sanhueza *et al.*, 1997; Moxley and Smit, 1998; Reichle *et al.*, 1999; Connors *et al.*, 1999; Bakwin *et al.*, 1994; Novelli *et al.*, 1998b, and the special issue of *Chemosphere: Global Change Science*, September 1999, 28 further papers]. Being the main reaction partner of hydroxyl (OH), changes in CO affect OH and vice versa. Because of the central role of OH in the chemistry of the atmosphere, CO is an important trace gas.

Closely related to the cycle of CO is that of ¹⁴CO, which shares the same sinks, namely OH and soils. Given that the major origin of the ¹⁴C in ¹⁴CO is cosmogenic, and therefore independent of the sources of CO itself, ¹⁴CO is of interest, even though it presents only a very small fraction of tropospheric CO ranging between 10⁻¹¹ and 10⁻¹². This is equivalent to only about 5 to 20 molecules per cm³ air STP. Nonetheless, ¹⁴CO is a unique useful tracer for diagnosing OH distribution, large-scale hemispheric circulation, and fluxes from the stratosphere into the troposphere [Volz *et al.*, 1981; Brenninkmeijer, 1993; Brenninkmeijer and Röckmann, 1998; Brenninkmeijer *et al.*, 1992; Mak and Southon, 1998; Jöckel *et al.*, 2000; Quay *et al.*, 2000]. Because determination of the abundance of ¹⁴CO is based on that of CO, the ability to make accurate and precise observation of CO is of direct relevance for ¹⁴CO applications.

Of importance is how frequently, how precisely, and how accurately atmospheric CO should be measured. The question of frequency and precision is linked to the variability of CO which is dominated by its lifetime and influenced by localized sources. Generally the requirements are not as high as for CO₂, CH₄, and N₂O, and a 1% precision is considered adequate. The accuracy with which one has to know the mixing ratio of CO is rather fundamental because of the long term atmospheric changes. Besides the analysis of samples of air on site or in the laboratory, remote sensing via satellite borne optical detectors is rapidly gaining importance (e.g. Measurement of Air Pollution from Space (MAPS), Measurement of Pollution in the Troposphere (MOPITT), and Scanning Imaging Absorption Spectrometer for Atmospheric

Chartography (SCIAMACHY)). Validation of data obtained by such remote sensing instruments is important.

Relevant is also the question whether there have been gradual changes in OH [Crutzen and Zimmermann, 1991; Krol *et al.*, 1998; Prinn *et al.*, 1995]. For establishing the causes, knowledge about changes in CO and also CH₄ of similar precision is necessary. The same applies to ¹⁴CO, for which it may be particularly important to have accurate observations because of its unique potential as a long term diagnostic for changes the oxidative capacity of the atmosphere. Although one may never be able to model atmospheric CO (or ¹⁴CO for that matter) with such a high degree of confidence that changes of the order of 1% would matter, there is no doubt that it would be unwise not to have accurate information at present. Even though it seems that an accuracy of 1% is feasible, there have been serious problems.

Most of the techniques for measuring CO are described by Novelli [1999]. The analysis of CO is almost exclusively based on relative methods, that is the comparison with standard mixtures of CO, and the procuring and maintaining of traceable standards is difficult at times. Since the discovery of large differences between CO calibration scales used by different laboratories [Novelli *et al.*, 1991], good progress in standardization has been made [Novelli *et al.*, 1994; 1998a]. Primary gravimetric standard mixtures have been prepared and standards were prepared for laboratory intercomparison. [Novelli *et al.*, 1994]. Two intercomparisons have been organized by National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL), in 1994 and 1999. These “ring tests” enable direct comparison and allow the various laboratories to systematically follow and diagnose drifts in CO standards. This paper discusses an absolute method for the determination of CO. Its results differ significantly from those of several other laboratories in the 50 to 100 nmole/mole range, and the possible reasons will be discussed.

2. Experimental Methods

2.1. Extraction System

The technique of Stevens [Stevens and Krout, 1972] for the isotopic analysis of CO is used. In essence, CO₂ is removed from air, after which the CO content is oxidized and subsequently collected as CO₂. The mixing ratio of CO is obtained by determining the mole fraction of CO₂. The system (Figure 1) is an improved

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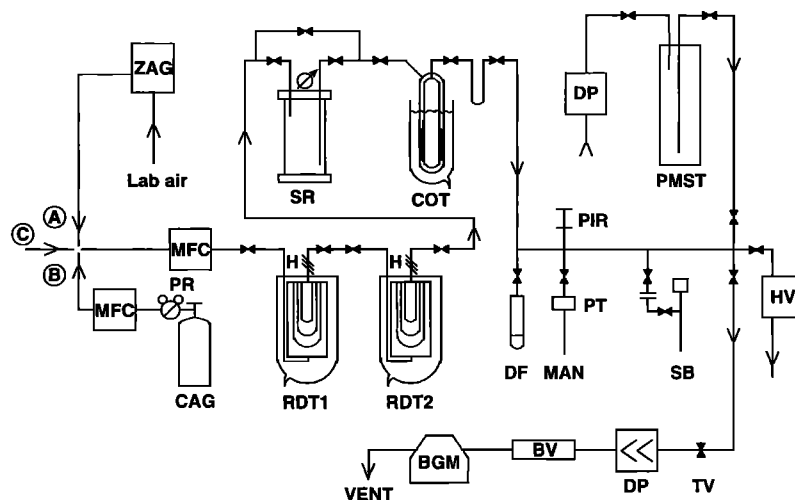


Figure 1. The CO extraction system. The following abbreviations were used: ZAG, zero gas generator; CAG, calibration gas; PR, pressure regulator; MFC, mass flow controller; RDT, Russian doll trap; SR, Schütze reactor; COT, collection trap; H, heater; DP, diaphragm pump; PMST, purge molecular sieve trap; DF, drying finger; MAN, manometer; PT, pressure transducer; SB, sample bottle; PIR, Pirani vacuum gauge; HV, high vacuum pump stand; BV, buffer volume; TV, throttle valve; BGM, bellows gas meter.

version of a predecessor [Brenninkmeijer, 1993]. The main properties of the CO extraction procedure are as follows: (1) It is an absolute method in which the CO is quantitatively extracted; (2) it is an integrating method, which implies that by increasing the sample size through processing more air, the signal-to-noise ratio improves; and (3) the method has a low detection limit in the sub-nmole/mole range.

The flow of sample air (5 L min^{-1} STP) is regulated with a thermal mass flow controller (Hastings type HFC-202F). Condensable compounds are removed by two ultra efficient Russian Doll traps submerged in liquid nitrogen [Brenninkmeijer, 1991]. Such traps consist of stainless steel cylinders incorporating three concentric borosilicate glass fiber thimbles. Cooling at the outlet of these traps is prevented by sheathed thermocouples heater elements [Brenninkmeijer and Hemmingsen, 1988]. After removal of all CO_2 , N_2O , and hydrocarbons (C_3 and higher), CO is oxidized to CO_2 in a reactor (kept at 35°C) filled with 0.8 l of Schütze's reagent [Smiley, 1965], which consists of acidified I_2O_5 on silicagel. The reagent does not induce isotopic exchange and is very efficient in oxidizing CO.

The small quantity of CO_2 from the oxidation of CO is trapped at liquid nitrogen temperature in a glass Russian Doll trap [Brenninkmeijer and Röckmann, 1996]. Measurement of the quantity of CO_2 produced is volumetric. The respective manometer consists of a volume isolated with a 5 mm bore O-ring glass valve [Brenninkmeijer, 1981] and is fitted with a piezo-resistive absolute pressure transducer (Institute of Geological and Nuclear Sciences (IGNS), model 9401). The volume being only 0.816 cm^3 increases the pressure obtained and therefore the resolution.

2.2. Extraction Procedure

When not in use, the system is back-flushed with laboratory air cleaned using a 10 L reactor with 13X synthetic zeolite. The Schütze reagent is kept sealed off. Air samples are processed as follows. Back-flushing is terminated, and the two Russian Doll traps are submerged one after the other in liquid nitrogen. Sample air is admitted via the mass flow controller, and pumped away using the diaphragm pump (Vacubrand, type MZ4, O-ring set for improved sealing was used). At an initial flow rate of 1.5 L min^{-1} the system pressure reaches 50 hPa. The system is flushed for 10

min after which the air is shunted through the Schütze reactor. The system is flushed for 10 min and the collection trap cooled. After 1 min, the glass fiber thimbles have reached liquid nitrogen temperature, and sample collection of CO_2 commences. The integrator of the flow controller is initialized, and the gas meter readings are recorded. Subsequently, the flow is increased to 5 L min^{-1} upon which the pressure increases to 180 hPa. This is the highest possible pressure for optimizing the residence time of CO molecules in the Schütze reactor without freezing out oxygen in the traps.

After processing 350 to 400 l of air the flow is throttled to 1.5 L min^{-1} and terminated after 1 min. The bypass is opened, and the Schütze reactor is isolated. The inlet valve of the collection trap is closed. The process pump valve is closed at 5 hPa, and the valve to high vacuum pumping stage (Pfeiffer molecular drag pump) is opened to evacuate the collection trap. Subsequently, the U tube is submerged in liquid nitrogen, its outlet valve is closed, and the large dewar surrounding the collection trap is removed. During 5 min the sample CO_2 is distilled into the U tube. After further evacuation, the inlet valve of the U tube is closed, and the sample CO_2 is distilled into a small finger containing P_2O_5 for removing traces of water. Next the CO_2 is transferred into a manometer by cryogenic distillation. After measuring pressure (typically 20 to 60 hPa) and the temperature, the sample CO_2 is distilled into a sample bottle for transfer to the mass spectrometer. The manual procedure can be automated by using methods developed before [Brenninkmeijer, 1983].

2.3. Determination of the Quantity of Air

Calculation of the mixing ratio is based on the volume of CO-derived CO_2 and the quantity of dry air processed. The quantity of air is determined using the electronic mass flow controller. This device is calibrated using a gas burette. Furthermore, a bellows type gas meter integrates the amount of air at the exhaust of the system. A buffer volume between the diaphragm pump and the meter reduces pressure pulses and improves the accuracy of the reading.

To ensure precise and accurate measurement of the amount of air, the cylinder containing the air to be processed is at times placed on an electronic balance. With a resolution and stability of 0.05 gram, the amount of air processed, which typically is 350 L,

can be measured to better than 0.1%. There are three devices metering the amount of air processed (the correction for the amount of air CO₂ extracted by the Russian Doll cleaning traps is too small to be significant), namely the integrating mass flow controller, the bellows gas meter, and the electronic balance. The most accurate and precise measurement is by the electronic balance.

2.4. Volumetric Determinations of CO₂

The determination of the small amount of CO₂ recovered is critical. The volume of the manometer, the pressure, and the temperature have to be known accurately. The electronic pressure transducer has in the range 0 to 200 hPa a resolution of 0.01 hPa. The zero readings of this gauge over a period of 1 year ranged without adjustment around 0.1 hPa, with a standard deviation of less than 0.1 hPa. The day to day variability is typically 0.02 hPa, and before each measurement a zero reading is made for correction. The atmospheric pressure reading of the gauge is compared every day with that of a precise atmospheric pressure gauge (Paroscientific, Digiquartz 740). This instrument is extremely stable, has a resolution of 0.001 hPa, and is calibrated against the readings from the weather service. Furthermore, the linearity of the pressure sensor is better than 0.1%. Note that the linearity in the actual volumetric measurement also assumes a constancy of the volume. To ensure reproducibility and minimal volume variations, a 5 mm Vacutap [Brenninkmeijer and Louwers, 1985] is used. Tests performed by repeated sealing of the manometer volume show that the error made is less than 0.1%.

The volume of the manometer is established using a calibrated volume. This consists of a valve sealing off a short section of stainless steel tubing cut from a longer section. By several times filling this longer section with water and accurately weighing, the volume of the short section (0.2442 cm³) was determined with high accuracy. By filling this calibration volume with dry CO₂ at a well-defined pressure (mostly near 1000 hPa) and temperature, and transferring this CO₂ into the manometer accurate calibrations are made. To exclude measurement errors or mistakes, several approaches were used, which lead to the values in Table 1. In the first series of tests the calibration volume was filled with CO₂ at near atmospheric pressure, cross-checked with the Digiquartz instrument. This CO₂ was distilled into the manometer volume, and a pressure reduction of 0.3001 occurred, leading to the manometer volume given in the table. This value is subsequently corrected using the van der Waals equation. The end result is 816.1 μL. In the next series of tests the calibration volume was filled to lower starting pressures. In this instance the van der Waals correction becomes negligible; however, the starting pressure is not known as well as in the preceding case (no direct comparison at near atmospheric pressure is possible). The end result is 815.9 μL. This also confirms the high degree of linearity of the pressure transducers used.

The problem intrinsic to determining the manometer volume accurately is that internal volume measurement is difficult. Independent confirmation of the volume calibration was therefore carried out using external volume determinations. Three identical cylindrical stainless steel needles, with a diameter of 1.5 mm, were

accurately measured using a micrometer. By doing tests as described above using two or three needles inserted into the calibration volume (thus reducing its volume), a value of 815.1 μL was obtained for the manometer. (In this determination the volume of the needles, provided they are identical, does not play a role.) Finally, by also using the calculated volume of the needles, a value of 816.8 μL was obtained. The averaged value is 816.0 ± 1 μL.

2.5. Verification by Calibration Runs

Regular calibration runs are performed injecting isotopically defined CO into a flow of air devoid of CO (zero air). A main reason for calibration is to establish the effect of the oxidation step on the oxygen isotopic composition of the CO₂ produced. As the careful work by Stevens has shown, this oxidation solely adds an oxygen atom to the CO molecule, and there is no isotopic exchange with the CO₂ produced [Brenninkmeijer, 1993; Brenninkmeijer and Röckmann, 1997]. In addition to the isotopic information, the calibration runs give a diagnostic of how well the system produces quantitative conversion and recovery of CO as is discussed below.

A certain quantity of CO is injected and exactly this should be recovered as CO₂. The quantity of air processed during a calibration run is not of primary importance provided the zero air is devoid of CO. The flow rates of both the zero air and CO injected can be varied thus providing different concentrations of CO. The zero air is produced using heated reactors that contain 1 L of Hopcalite, or a Pt on aluminum-oxide catalyst (Merck). Temperatures of 100 to 200°C are applied. After oxidation of the CO content, the air is passed through a bed of 13X synthetic zeolite. This strips out water, CO₂, and other impurities. With the zero air generators air without CO can be produced (less than 0.5 nmole/mole) at flow rates of up to 20 L min⁻¹. It is assumed that at 5 L min⁻¹ the zero air contains less than 0.1 nmole/mole CO. Tests in which the molecular sieve of the zero air generator is replaced by Drierite (Hammond, Ohio), which does not remove CO₂, do not show any difference in yield or isotopic composition. This is proof of the extreme efficiency of the two Russian Doll traps (combined >99.99997% CO₂ removal). The small quantity of condensables (CO₂ and SO₂) that is recovered in a zero run is subtracted from the quantity obtained for a sample.

Experience shows that the zero yield of the system increases when not in use. After one run the zero yield returns to a low level between 0.1 and 0.2 hPa. This is equivalent to approximately 0.25 to 0.5 nmole/mole for a 350 L air sample. A correction for this is applied, and the remaining uncertainty is less than 0.1 nmole/mole. Thus, for air samples containing 50 to 200 nmole/mole CO, the uncertainty in the blank correction introduces an error of 0.2 to 0.05%.

For calibration, CO is not injected as pure CO gas, but as a mixture of 269 ± 3 μmole/mole CO in nitrogen gas. This mixture is metered using a thermal mass flow controller (Hastings HFC-202A) which is occasionally calibrated with a gas burette. According to the supplier of the mixture (NZIG, Lower Hutt), it contained 271 ppm by volume CO; according to a bulk analysis carried out in the laboratory in New Zealand it contained 269 ± 3

Table 1. Determination of the Volume of the Manometer^a

	Standard	Low Pressure	2-3 needles	2 Needles Absolute ^b
Ratio	0.3001±0.0001	0.2993±0.0001	n.a. ^c	0.16795±0.0002
Volume, μL	813.73±0.3	815.9±0.3	815.1±0.6	813.6±1
Van der Waals corrected	816.1±0.3	815.9±0.3	815.1±0.6	816.8±1

^a The last row lists the final value after correction for the non-ideal gas behavior of CO₂.

^b In this determination the volume of the needles is irrelevant.

^c Here not applicable.

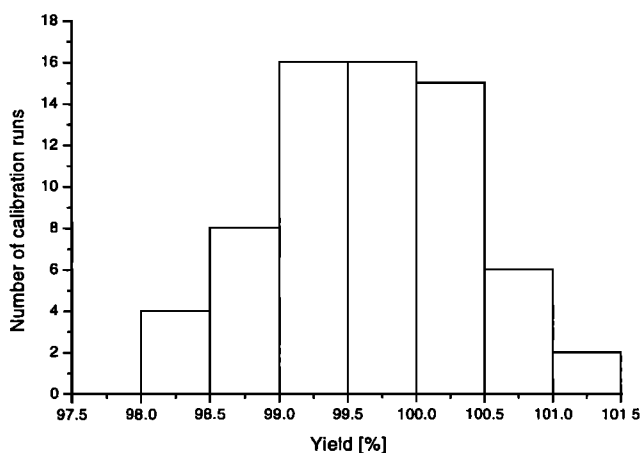


Figure 2. Frequency distribution for 67 calibration runs performed over 1 year.

$\mu\text{mole/mole}$. On the basis of calibrations using this mixture, the yield of the extraction system is 99.8%, with a standard deviation for an individual run of 0.7%. These numbers are based on 67 determinations for September 1998 to October 1999. No calibration result has been omitted. Two persons have operated the system without this causing systematic differences. The frequency distribution obtained is symmetrical (Figure 2). The near 100% yield and 0.7% standard deviation prove independently that the CO can be determined with a precision and accuracy of about 1%. This overall test involves conversion, trapping, releasing, and transferring.

2.6. Tests of the Overall Efficiency

In total efficiency the conversion of CO to CO_2 is also critical. If this step is not quantitative, inserting a second Schütze reactor into the system and thus doubling the reaction time for CO will increase the yield. If, for instance, the yield is only 90%, the addition of a second reactor boosts it to 99%. A less cumbersome and effective alternative is the reduction of the pressure in the Schütze reactor during sample processing. Accordingly, by using two processing pumps in parallel the system pressure was reduced from the standard 180 hPa to 50 hPa. This reduces the residence time of a CO molecule in the reactor from about 2 s to 0.5 s. It can be shown that when the yield during the normal 180 hPa conditions is 99%, the yield should drop substantially to a mere 70%. In contrast, during these experiments a drop in efficiency of less than 1% was observed from which it is calculated that the efficiency is over 99.9999%. During these tests the pressure in the entire system was lowered, from which it is inferred that also the trapping of CO_2 in the collection trap is nearly 100% efficient. That the yield would drop in the Schütze reactor, and that this would coin-

identally be compensated by a concurrent increase in trapping efficiency of the collection trap, is unlikely. No change in isotopic composition was observed. Independently, the effect of lower levels of liquid nitrogen around the sample collection Russian doll trap has been investigated earlier [Brenninkmeijer and Röckmann, 1996]. Altogether these tests corroborate that the values of the main operating parameters are not in a critical range.

Despite the a priori linearity of the system, evidence for a small systematic deviation was obtained by analysis of data for duplicates. For a total of 22 cylinders with air samples collected at Spitsbergen [Röckmann and Brenninkmeijer, 1997], two subsamples of nominally 400 and 700 L were processed. It turns out that the mixing ratios established for the 700 L samples are systematically lower by 1.3%. This is a puzzling effect because there is no obvious mechanism by which less CO_2 would result for larger samples, or an error in the amount of air processed would be made. The cause of the effect is traced back to the efficiency of the Russian doll collection trap. Apparently, when the trap is cooled for a longer period of time, its efficiency drops. Because nearly all samples and calibrations are over a period of less than 80 min, during which 350 to 400 L is processed, this effect had escaped observation during normal operating conditions. To determine the effect, normal calibrations were followed by delayed calibrations during which no calibration mixture was injected into the zero-air flow during the first hour. Under these conditions there was a drop of $2 \pm 0.5\%$ in efficiency. These tests confirm the existence of a loss of efficiency when samples are processed over a longer period of time. The value of $2 \pm 0.5\%$ will not be used to correct for the loss of efficiency. The 22 sample pairs of 400 and 700 L give the more accurate value of 1.3%.

The cause for the abstruse loss in efficiency when sample air is processed over longer periods is not fully understood. The amount of CO_2 seems too small to affect the properties of the large surface area of glass available for trapping it. Analysis of the composition of the air passing through the system did not show unexpected delays in one of the main components. A recent improvement to the procedure is to heat the collection trap to about 50°C during back flushing. After correcting the results for the 700 L samples for loss in efficiency, the duplicates can be used to assess the reproducibility of the system. A standard deviation for a single determination of only 0.5% is obtained. Thus, for routine operation, a random error of 0.5% can be guaranteed. This error is even smaller than that obtained for the calibration runs.

2.7. Linearity Tests

Deviations in linearity are investigated using two different linearity tests. Test one is based on injecting the calibration gas mixture at different rates. With the range of the mass flow controller being 0 to 10 mL min^{-1} there is a practical lower limit of about 1 mL min^{-1} . Below this the uncertainty in the injected quantity becomes too large. The results are shown in Table 2. For each

Table 2. Linearity Test 1

Run ^a	Injection Flow, mL min^{-1}	Mixing Ratio ^b	Injected Quantity, μL	Recovered Quantity, μL	Yield, %
1600	1.0510	58	23.19	23.32	100.56
1601	1.0510	58	23.27	23.34	100.30
1602	2.0441	113	45.16	45.35	100.42
1609	2.0448	113	45.20	45.54	100.75
1603	3.0409	169	67.99	68.12	100.19
1608	3.0280	169	66.81	66.75	99.91
1599	3.9974	223	88.41	88.52	100.12
1604	4.0205	223	89.95	89.63	99.64
1605	6.3471	349	139.71	139.92	100.15
1606	8.0916	446	178.42	178.05	99.79
1607	9.8738	544	217.58	215.76	99.16

^a October 1998.

^b Nominal mixing ratios in nmole/mole related to 400 L sample air.

setting of the calibration gas mass flow controller it was calibrated against a gas burette with a piston sealed by a mercury ring. At a flow rate of 5 L min^{-1} STP zero air, and a total of 400 L air, the equivalent mixing ratio varied from about 60 to 550 nmole/mole. The yield obtained was 100.1% with a standard deviation for an individual measurement over the entire range of 0.45%. The four duplicate determinations agree well within 0.4%. A linear least squares fit to the data give for the recovered quantity gives $y = 0.9927x + 0.52 \text{ nmole/mole}$ ($r^2 = 0.99996$). The data suggest a small drop in efficiency. At 544 nmole/mole the yield is 1% below that obtained for the lower concentrations. Furthermore the yield is higher than that obtained for the calibration runs (99.8%). The calibration runs are performed at nominally 200 nmole/mole, for which the linear regression gives 99.5%. There are no significant discrepancies between the results.

Linearity test 2 is based solely on the duration of the injection period at a constant setting of 2.0 mL min^{-1} . This test checks the linearity in the low nmole/mole range up to 300 nmole/mole. Calibration gas was passed through a three-way valve into the zero-air flow allowing a rapid switching between waste and injection position. Injections at a flow of $2.0 \text{ cm}^3 \text{ min}^{-1}$ were performed for 5 min (with increments of 10 min) to a maximum period of 120 min. The minimum equivalent effective concentration was therefore only approximately 6.5 nmole/mole for the equivalent of 400 L of air processed. Figure 3 shows a good linearity for up to about 60 hPa, and a very small random error. Applying a linear regression, excluding the upper two data points gives $y = 1.0871x + 0.2214 \text{ hPa}$. The standard deviation for a single determination is 0.4%. Using this formula, the deviations for the two highest concentrations are 0.4 and 1.4% respectively. The test suggests a small drop in efficiency when air is processed over long periods of time. This is equivalent to the effect noted for the processing of the 400 and 700 L subsamples of the air cylinders and for the extended calibration run. The effect is not of relevance for the routine conditions. Test number 2 is not the exact equivalent of the injection of, for instance, 7 nmole/mole over the full period of sample processing. It does however establish the linearity of the system in the important low concentration range.

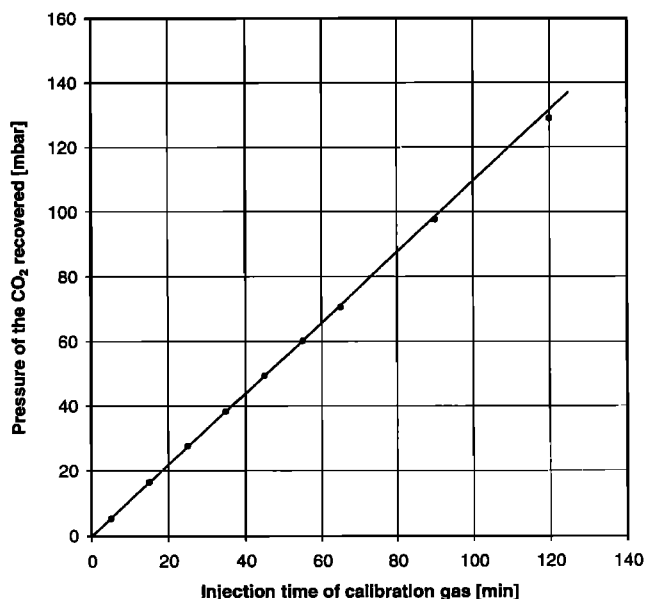


Figure 3. Linearity test 2 showing the pressure recorded in the manometer against the duration of the calibration gas injection at a flow rate of $2 \text{ cm}^3 \text{ min}^{-1}$. The nominal equivalent concentration range is approximately 7 to 260 nmole/mole.

Because Russian doll traps are efficient to a degree that can cause a gas chromatographic delay for CO passing through [Brennkmeijer and Röckmann, 1996], and because the 1 L Schütze reactor itself in effect is a gas chromatography column, the speed with which a pulse of CO passes through the system was measured. CO at $8 \text{ cm}^3 \text{ min}^{-1}$ was injected only during the very last 5 min of a run. The corresponding yield was 99% which assures that there is no significant delay or retention of CO. The tests consistently confirm the high linearity, quantitative yields, and high reproducibility. One remaining question is whether it is pure CO₂ that is collected. Mass spectra recorded at high amplification confirm purity of the sample collected.

A source of interference could be the oxidation of trace gases other than CO to CO₂ in the Schütze reactor. This was tested by Stevens and Krout [1972] and is a negligible source of interference for normal air samples. Generally for the lower CO mixing ratios in remote air, concurrent nonmethane hydrocarbon mixing ratios are also lower. Tests based on the injection of C₂H₄ into calibration or zero air has no effect. Injection of 100 $\mu\text{mole/mole}$ CH₄ does not change the amount of CO₂ recovered, or its isotopic composition. Higher hydrocarbons (>C₃) are effectively trapped by the Russian doll traps and are present at very low concentrations only.

2.8. Accuracy and Precision

Estimated and measured random errors for the 50 nmole/mole level and processing 350 L of air are as follows: blank correction 0.2%, pressure reading 0.3%, temperature of CO₂ sample in the manometer 0.3%, and quantity of air 0.1%.

The combined random error therefore is approximately 0.5%. This can be compared with the independently determined value for the measured standard deviation of 0.5% which is based on duplicates. The precision obtained therefore is 0.5%. For 200 nmole/mole this value improves to about 0.4%.

Estimated values for the maximum systematic error are as follows: Quantity of air 0.2% and quantity of sample CO₂ 0.3%. The maximum deviation is thus 0.5%. This can be compared with the independently determined value using the calibration runs of $0.2 \pm 1\%$ deviation.

3. Laboratory Intercomparison Tests

3.1. Analysis and Evaluation of the 1993-1995 Laboratory Intercomparison

Over more than 10 years thorough work has been carried out to continuously improve the quality of CO measurements [Novelli et al., 1994]. Ring tests which are laboratory intercomparisons in which laboratories analyze subsamples of air from the same suite of cylinders help to compare data [Novelli et al., 1998a]. It is important not only to compare scales but also to understand the differences. A predecessor of the present system [Brennkmeijer, 1993] was used in the 1994-1995 ring test [Novelli et al., 1998a]. Four cylinders with nominally 50, 100, 150 and 200 nmole/mole were analyzed at the National Institute of Water and Atmospheric Research (NIWA), New Zealand in 1994. Because it was considered that by withdrawing as much as 350 L of air from the cylinders the CO concentration might be somehow affected, thus possibly spoiling the results of other laboratories later in the test sequence, it was decided to use the NIWA gas chromatograph (GC) system equipped with a reducing gas analyzer. Therefore the results could not be as precise as they would have been with direct analysis by extraction.

The GC was calibrated using the extraction system and a set of 10 cylinders with CO values from 50 to over 200 nmole/mole. The response of the GC system with reducing gas analyzer was not

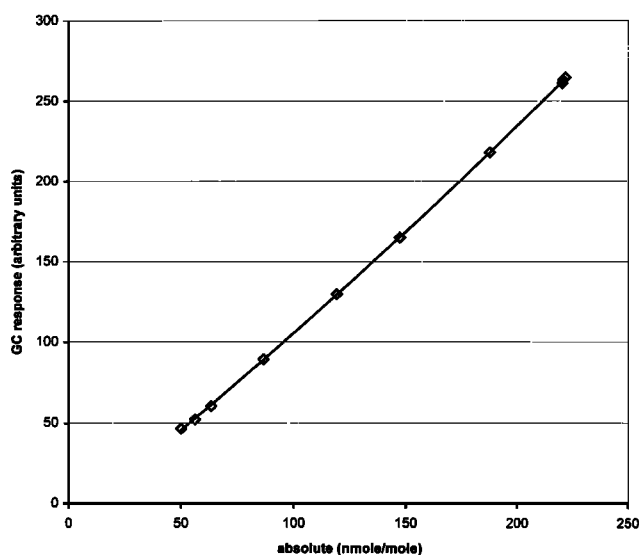


Figure 4. The calibration with quadratic least squares fit of the NIWA CO gas chromatograph in 1994 using 10 cylinders assayed by the absolute method.

linear. Furthermore, an air sample with a CO mixing ratio of 3.7 nmole/mole did not give a chromatography peak that could be integrated. The response of the GC systems with reducing gas analyzers is not always linear and may vary depending on the operating conditions. The results are shown in Figure 4. The scatter of the individual data points relative to the quadratic least squares fit is less than 1%.

Table 3 shows the ring test results [Novelli *et al.*, 1998a]. The mixing ratios relative to the NOAA-CMDL scale differ by 3% at the high end to 8% at the 50 nmole/mole level. In Figure 5 all results except those from INPE and HKP which showed rather large deviations (for acronyms, see Novelli *et al.* [1998a]) are plotted against the NIWA data as percentage deviation.

Several inferences that may improve the understanding of the differences will be made. CMDL, the Common Wealth Scientific and Industrial Research Organization (CSIRO), and NASA used the GC technique and the CMDL scale. NASA agrees fairly well with the NIWA values, but CMDL and CSIRO do not. The latter two are mutually consistent, and their results suggest that the NIWA values have an increasingly positive bias with decreasing concentration, for brevity referred to here as "the trend". IFU and CSIR, both using a mutual scale, and the GC technique, closely confirm the trend. Therefore one almost cannot escape but one conclusion. The NIWA values must be wrong, and this explains the trend. But is this correct? Not necessarily, because this also depends on whether the IFU scale used was independent of the CMDL scale. Both scales have a history of intercomparisons. Consequently, there may be no independent proof that the NIWA values are wrong.

What seems to cast some doubt on the NIWA data is that AL using the gas filter correlation technique (GFC) and National Institute of Standards and Technology (NIST) standards, seems to confirm the trend. Indeed, if the AL values are based on an independent scale and technique, the trend is confirmed independently, and the NIWA values must be in error. However, the UMD results, which also used GFC and NIST standards contradict the existence of the trend. Actually, both NASA and UMD do have very similar results, despite the use of different techniques and different standards. Admittedly their agreement at the 50 nmole/mole level is not as close as for the other three values, but with the GFC technique larger errors occur in the lower reaches, and these are also given. However, because UMD and NASA use independent scales and independent techniques, their results give support for the NIWA data showing an opposing trend.

From the available information it is not possible to retrospectively assess which values are correct. The results of the absolute method do not necessarily appear more correct. For better understanding the causes for the observed deviations a model based on the applied metrology is used. The NIWA data are used as reference; this is a working hypothesis. Consider the GC and GFC techniques. The GC technique suffers from two deficiencies. One is that the detector response is not always linear. This effect will not be considered here. The second problem is that the detection limit is not zero. When air containing only a few nmole/mole is injected, there may be no chromatography peak that can be integrated for determining a signal. The gas filter correlation (GFC) technique is intrinsically linear, but suffers from a worse signal-to-noise ratio. Several laboratories have improved these instruments, yet even then, air containing a few nmole/mole CO cannot be assayed accurately. Thus both techniques cannot directly determine whether an air sample is free from CO at the nmole/mole level. The other problem is the familiar one that both techniques are indirect, and depend on the comparison of the system response with that for standards.

The errors introduced by offset and calibration errors in systems based on standards can be calculated. It is assumed for the present discussion that the assumed or measured mixing ratio " a " is related to true or real value " r " and the offset of the detector " z " via $a = cr + z$. The relative error is $\Delta = a/r - 1 = (c - 1) + z/r$. In the next case the effect of errors in standards is addressed. Standards can be produced with great accuracy, based on gravimetric procedures. In these, uncertainties in the degree of dilution can be minimal. Another option is dynamic dilution, where the dilution errors may be larger, but often still acceptable. For reaching the low mixing ratios dilution with zero air or gas is applied. The point is that a large amount of air is added to lower the mixing ratio. Therefore the CO content of the dilution gas must be in the sub-nmole/mole range. If a high degree of dilution is needed, a residual CO level of 0.5 nmole/mole will lead to approximately the same bias of the diluted concentration produced. At the 50 nmole/mole level this would induce an error of 1%. It is assumed for the present discussion that a standard is available with an actual mixing ratio " s ". The assumed mixing ratio is, however, cs

Table 3. Results for Two Laboratory Intercomparisons^a

1993–1995 Ring Test		1998–1999 Ring Test		
NIWA gas chromatography/absolute	NOAA-CMDL	MPI-C absolute	MPI-C gas chromatography	NOAA-CMDL 1999 ^b
56.1	51.5	51.8	52.1 (0.5) ^c	45.0 (0.9) ^c
102.7	97.6	98.8	98.9 (1)	91.6 (0.9)
154.1	147.7	151.4	149.5 (1.5)	147.1 (1.4)
204.5	198.0	183.4	182.3 (2)	183.6 (1.8)
		350.7	351.4 (7)	355.7 (6)

^a Units are nmole/mole.

^b P. Novelli (personal communication, 1999).

^c Uncertainty.

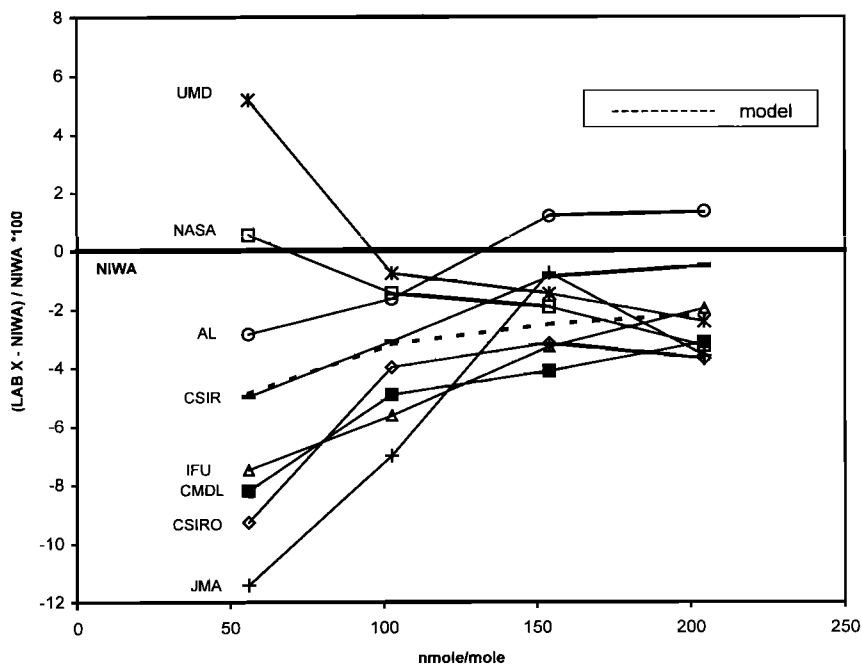


Figure 5. The results of the 1994-1995 ring test, plotted as the percent deviation relative to the NIWA data. The curve shown is based on $c = 0.989$ and $z = -2.2$ nmole/mole (see text). For the laboratory identifiers, see *Novelli et al., 1998a*.

nmole/mole. Further, it is assumed that the air for dilution is assumed to have 0 nmole/mole although it actually contains “ z ” nmole/mole. This leads, for the standard made by dilution of a factor “ f ”, to the assumption $a = fcs$. The real mixing ratio is, however, $r = fs + (1-f)z$. The resulting error is $\Delta = a/r - 1 = (c - 1) + z/r$. This error in the standards causes the same error for sample values. A third possibility for introducing systematic errors is that CO is gradually produced in a set of standards stored in cylinders. This is a common problem, and in the simplest case CO would grow at constant and identical rates in all cylinders irrespective of the CO concentration. This leads to a similar expression as for the two cases considered.

What becomes apparent from inspection of Figure 5 is that nearly all curves exhibit the hyperbolic characteristic of the expression derived above. The differences between the laboratories can be expressed in terms of offsets and calibration differences. At low values the offset becomes a dominant source of error. These deviations between the laboratories can also be gleaned from the tabulation by *Novelli et al., [1998a]* based on quadratic equations comparing all institutes to the NOAA scale. In Figure 5, NASA and UMD have curves that show an increasing positive deviation. CMDL, CSIRO, AL, JMA, and IFU together with CSIR show an increasing negative relative deviation towards the low concentrations. The curves most probably represent either the effect of bias in calibration and the existence of an offset, or the use of a nonzero dilution gas and a deviating value for the gas that was diluted, or the growth of CO in cylinders with standard mixtures.

The results from NIWA will now be compared with the average values of the other laboratories. At the nominal value of 200 nmole/mole the deviation between NIWA and the average is 4.4 nmole/mole, or 2.2%. For calculating the averages, the values in Table 3 [*Novelli et al., 1998a*] are used without weighting the individual errors. Only the last CMDL value and one of the values submitted by CSIRO were used. HKP and INPE results were omitted. Because some scales are linked, this average is biased. Despite this, the most probable conclusion would be that the NIWA data at nominally 200 nmole/mole were 2.2% too high. At the lowest mixing ratio near 50 nmole/mole, the average value is 53.3 nmole/mole, which is 5.0% below the NIWA value. For cal-

culating the average value, the second value submitted by CSIRO has been used, otherwise the same criteria apply as before. Using the equations derived above gives $z = -2.2$ nmole/mole and $c = 0.989$ as offset and calibration error, respectively, for the average compared to NIWA.

Without further information no further conclusions can be drawn. On the basis of the previous sections on the absolute method, it would seem that a plausible scenario is that NIWA had an error in the 200 nmole/mole range of about 2%. This for instance could be the result of a wrong calibration of the gas meter. If this applies, it still does not explain the higher values in the 50 nmole/mole range. In view of the low detection limit of the absolute method, and the high linearity, a conclusion would be that the average of the other laboratories is too low by a several nmole/mole. For a direct comparison between NIWA and the NOAA scale, this would mean that in the 50 nmole/mole range, the NOAA value was 3.5 nmole/mole too low in 1995.

3.2. The 1998-1999 Laboratory Intercomparison

The second ring test involved two circuits of laboratories and two sets of cylinders. One set of cylinders with nominal values from 50 to 350 nmole/mole was made available to the Max Planck Institute for Chemistry. This time, in contrast to the first comparison in New Zealand, the mixing ratio for each cylinder was directly determined by processing 400 L of air from each cylinder with the system described. This volume of air was less than 10% of the cylinder's content.

It was also decided to additionally perform gas chromatographic determinations with a reducing gas analyzer (type RGA 3). The gas chromatograph was calibrated independently from the extraction system results by using a single cylinder that was calibrated by NOAA-CMDL in 1996 to have 172 ± 3 nmole/mole, and applying dynamic dilution downward using zero air. During this calibration by dynamic dilution, two further cylinders with air were fixed in their mixing ratio relative to the dilution line. The three cylinders were then used to assay the five unknown NOAA-CMDL test standards. Extrapolation was used for the higher concentrations. The results listed in Table 3 show good agreement. There is a discrepancy with the values of NOAA/CMDL obtained

in 1999, which indicates a problem with the standards. Such problems were acknowledged (P. Novelli personal communication, 1999) and are treated in a paper in press (K.A. Masarie et al., The NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements derived from independent laboratories, submitted to *Journal of Geophysical Research*, 2000).

4. Conclusions

1. The extraction system has well defined characteristics. The linearity (better than 1%), the low detection limit (< 0.2 nmole/mole), and the quantitative conversion and trapping of the CO_2 formed, even in the smallest quantities equivalent to 7 nmole/mole, support the contention that CO mixing ratios can be determined with an error of less than 1%.

2. The gas chromatography results provide independent evidence for conclusion 1, assuming that the standard once assayed by NOAA as having 172 nmole/mole indeed had this value at the moment of the test. This assumption is not unreasonable, but the agreement is possibly coincidental because the standard is a few years old and may have drifted.

3. The intercomparison results for the 1993-1995 ring test systematically reflect the effect of offsets at low mixing ratios. The results from the different laboratories do not allow a conclusion to be made as to which values were correct. There is no independent evidence that the absolute method as used in 1994 produced better results. However, the results of the 1998-1999 ring test show an even stronger trend effect. With the refinement in the absolute method, the test for linearity, and the confirmation by means of gas chromatography, this strongly suggests that the lower end of the NOAA scale has dropped.

4. The results from the absolute method in 1994 and 1999 together suggest that the lowest range NOAA standards actually were already low in 1994 by about 5%.

5. It is recommended that in publications of laboratory inter-comparisons of CO standardization the laboratories involved supply information about zero gas, offsets, standards, and linearity.

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