

Development of a Coulometric Method for Assessing the Concentration of Ambient Levels of CO₂/Air in Compressed Gas Mixtures

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**G. D. Mitchell and
A. A. Bell**

National Institute of Standards
and Technology,
Gaithersburg, MD 20899

The coulometric method presented here is a reliable method for the direct analysis of CO₂/air cylinder gas mixtures. It is based on Faraday's laws of electrolysis and therefore no external standardization is required. A series of CO₂/air cylinder gas mixtures ranging in concentration from 300 to 375 $\mu\text{mol/mol}$ (ppm) were analyzed and the results compared to those results obtained by non-dispersive infrared (NDIR) analysis with traceability to gravimetric stan-

dards. The coulometric method is rapid, sensitive, precise, and with the proper experimental controls, will yield accurate results.

Key words: carbon dioxide; coulometry; current efficiency; cylinder gases; monoethanolamine; N,N-dimethylformamide.

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1. Introduction

The understanding of global "greenhouse" issues as they relate to CO₂ in the atmosphere is a current environmental concern [1,2]. To assess changes in the levels of CO₂ in the atmosphere, three considerations are important: 1) a substantial history of the global levels of CO₂ over an extended period of time, 2) the fidelity of standards upon which the analyses are based, and 3) accuracy and reproducibility of methods used. At the National Institute of Standards and Technology there is a continuous search for methods of analysis that yield results that are traceable to fundamental quantities. The present method used for the certification of CO₂/air cylinder gas mixtures as Standard Reference Materials is nondispersive infrared analysis which is calibrated with CO₂ in air standards prepared by gravimetry [3]. In this work we present an analytical technique based on coulometry that provides accurate CO₂ analysis for ambient-air standards having negligible quantities of other acid components. This technique can be used to assist

in the validation of CO₂/air SRMs.

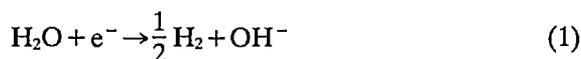
In our companion paper [4] we described the design, construction, and use of an apparatus for the determination of SO₂ in gas cylinder mixtures at the $\mu\text{mol/mol}$ level. Here, the apparatus has been modified to demonstrate the potential utility of coulometry as an accurate and reliable method for assessing the concentration of CO₂ at the 300 to 375 $\mu\text{mol/mol}$ level in cylinder gas mixtures.

2. Experimental Methods

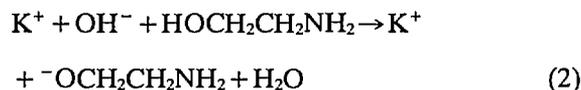
The apparatus and experimental details have been previously described [4] and will not be discussed fully here. However, because the analytical technique is being applied to CO₂/air and not SO₂/N₂, the experimental differences will be delineated. The experimental method is based on acid-base coulometric titration with photometric end-point detection. The experimental objectives are to: (a) select a reaction scheme; (b) develop an accurate

and precise sample delivery and absorption system; and (c) determine the current efficiency independently. The absorption system selected is designed to meet the two major criteria for coulometric titration, i.e., complete absorption of the CO₂ analyte gas and near 100% current efficiency [5,6,7].

The absorbing solution consists of 78 mL N,N-dimethylformamide [HCON-(CH₂)₂], 2 mL 0.1% thymolphthalein (5',5''-diisopropyl-2',2''-dimethylphenolphthalein) dissolved in dimethylformamide, 3 g potassium iodide dissolved in 3 mL water, and 3 mL monoethanolamine (HOCH₂CH₂NH₂). The solution is prepared in a 100 mL flask. The pH indicator, thymolphthalein, operates over the pH range from 9.3 to 10.5 and has an absorption maximum at 598 nm. All chemicals are reagent grade and are used without further purification. A possible reaction scheme involves the reduction of H₂O at the cathode,



then



Alternative schemes are presented in Ref. [5].

2.1 Procedure

The apparatus for CO₂ analysis uses a narrow band interference filter (599 ± 10 nm) and a titration cell, filled with the absorbing solution described above. Light passing through the clear gas-absorbing solution causes the photodiode detector to generate a titration current that is fed back to the cathode, thus causing reaction [1] to occur. The pH indicator thymolphthalein is activated by the production of the base and the absorbing solution turns blue, which decreases the output of the photodiode. When the color of the absorbing solution reaches a selected level of intensity, the feedback circuit is adjusted to give a zero current output for the cell. The CO₂/air mixture is introduced, metered by a mass flow controller calibrated to 0.1 mL/min. When the feedback circuit is adjusted to zero and the CO₂/air mixture is introduced into the cell, the analytical procedure and data analysis are identical to those discussed in Ref. [4].

The critical measurement parameters are cell current (A) and flow rate (mL/min). The current is measured using a calibrated digital current meter

and the flow rate is monitored using a calibrated mass flow controller. The relationship of cell current and flow rate of CO₂ is linear over the experimental range. Equation (3) gives the relationship of cell current and flow rate as it is used to determine CO₂ concentration in μmol/mol.

$$\text{CO}_2 \left(\frac{\mu\text{mol CO}_2}{\text{mol air}} \right) = \frac{C_{\text{cell}} \cdot K'}{Q} \quad (3)$$

where C_{cell} = Cell current (A)
 Q = Flow rate of sample (mL/min)
 and

$$K' = \frac{6 \cdot 10^7 \cdot MV_T}{n \cdot F} \quad (4)$$

MV_T = Molar volume of air (corrected for temperature) mL/mol
 ($MV_T = 24475.59$ @ 298 K)

n = Number of electron change (e⁻)
 ($n = 1$)

F = The Faraday constant (96485.38 A s/mol)

$6 \cdot 10^7$ is a unit conversion factor

$$\left(\frac{\text{s} \cdot \mu\text{mol}}{\text{min} \cdot \text{mol}} \right)$$

3. Results and Discussion

Ten compressed gas cylinders with CO₂ concentrations from 300 to 375 μmol/mol were previously analyzed by a non-dispersive infrared (NDIR) analyzer calibrated with gravimetrically prepared standards [3]. A cylinder representing the mid-range of the set of 10 cylinders was selected as a control (cylinder 4, Table 1) to be used throughout this study to evaluate the overall uncertainty associated with the coulometric method and the day to day imprecision of the analysis. The control was studied over a variety of experimental conditions and for an extended period of time. The control cylinder was analyzed by the coulometric method on 17 separate occasions. Figure 1 shows the uncorrected data for the control cylinder as they were obtained chronologically over a 11 month period. The mean and the 95% confidence interval are indicated by the horizontal solid and dashed lines, respectively. The best estimate of the true mean concentration

Table 1. Comparison of CO₂ coulometric^a and NDIR data

Cylinder number	Direct coulometric concentration μmol/mol	Corrected ^b concentrations μmol/mol	NDIR concentration ^c μmol/mol	Ratio Coul/NDIR
1	307.3	303.3	303.8	0.998
2	337.5	333.1	335.9	0.992
3	338.1	333.7	335.9	0.993
4*	346.4	341.9	341.7	1.001
5	344.8	340.3	342.8	0.993
6	348.2	343.7	343.2	1.001
7	349.8	345.2	347.6	0.993
8	352.7	348.1	351.5	0.990
9	380.2	375.3	375.2	1.000
10	380.7	375.8	375.3	1.001

^a Uncertainty ± 4.2 μmol/mol.^b Direct coulometric data corrected for current efficiency.

$$\text{Current efficiency} = \frac{\text{Coulometric current (mA)}}{\text{Theoretical current (mA)}} \times 100.$$

^c Uncertainty ± 0.4 μmol/mol.

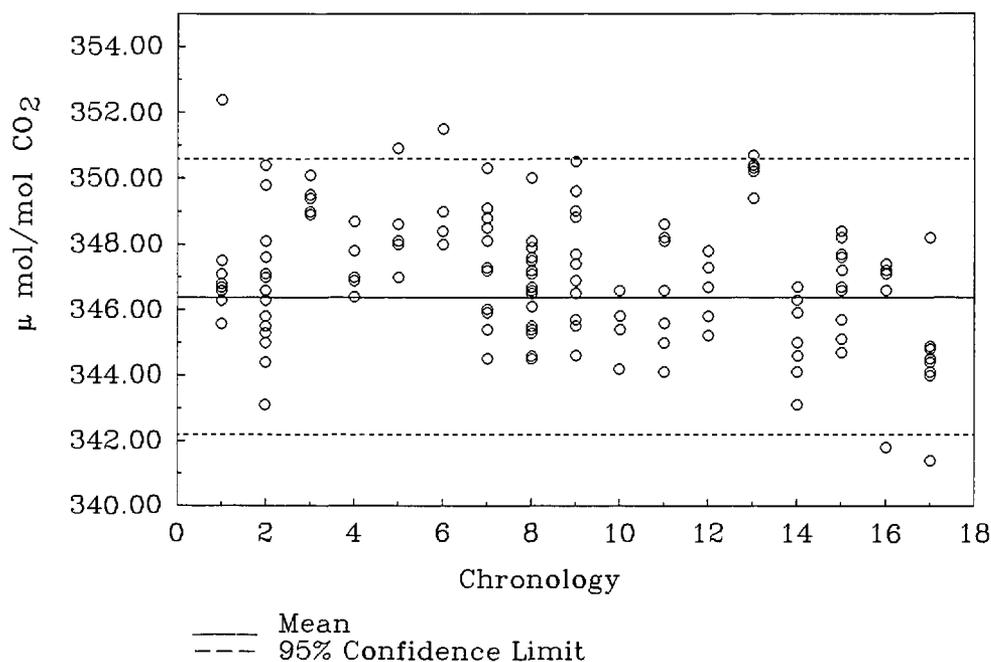
and its uncertainty at the 95% level of confidence is 346.4 ± 4.2 μmol/mol. For any given day, the standard deviation of a single measurement for the concentration range from 300 to 375 μmol/mol CO₂/air is 2.1 μmol/mol. The reported NDIR concentration of the control cylinder was 341.7 ± 0.4 μmol/mol. The comparison of this value to the coulometrically determined value is a measure of the current effi-

ciency. At the 95% level of confidence, the current efficiency is calculated to be $101.3 \pm 1.0\%$. This value represents a systematic bias in the measurement system and gives the factor by which the experimental data should be corrected.

Results for the coulometric analysis of the 10 CO₂/air gas cylinders mixtures as well as those obtained by NDIR are given in Table 1. The difference between the NDIR and corrected coulometric analytical values range from 0.003 to 1.1%. These results, however, show that at the present stage of development the method is capable of producing results that are comparable to those of the reference method. Figure 1 shows that the resulting analysis of the control cylinder is biased by 1.3%. No explanation for the bias is being offered at the present, however, future work is planned to improve both the precision and accuracy of the method.

4. Conclusion

A coulometric method for the direct analyses of reference cylinder gas mixtures has been demonstrated. It has been shown to be sensitive, potentially precise and accurate for determining CO₂ in air at atmospheric concentrations, as well as a viable method of assessing the concentration of CO₂

**Figure 1.** Chronological study.

cylinder gas mixtures. The system presented here provides rapid analyses, and is capable of being independent in the determination of CO₂ at ambient air levels. The upper and lower limits of detection have not yet been fully explored. However, on the upper end, the limiting critical component of this approach is the ability of the absorbing solution to handle higher concentrations of CO₂. On the low end, preliminary tests have provided detection limits of approximately 1 μmol/mol CO₂/air. This method of analysis is traceable to the Faraday constant and therefore no standardization against analyzed samples or pure materials is required. At the present state of development, the imprecision of a single analysis by the coulometric method is approximately 1.3%.

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About the authors: Gerald D. Mitchell is an analytical chemist in the Organic Analytical Research Division and Adville A. Bell is a computer analyst with the Surface Microanalysis Science Division, both of which are in the Chemical Science and Technology Laboratory of NIST.