A PARAMAGNETIC METHOD FOR MEASURING THE CARBON DIOXIDE CONCENTRATION OF A GAS

F. MEADE AND J. B. OWEN-THOMAS

SUMMARY

A paramagnetic method of carbon dioxide analysis enables the simultaneous analysis of carbon dioxide and oxygen to be made at 2-min intervals. The method depends upon observing the change of oxygen concentration in a gas mixture before and after absorbing the carbon dioxide component. The carrier-gas in the experiments reported was nitrogen. The output of the paramagnetic meter was measured both by a digital voltmeter and by a chart recorder and the carbon dioxide concentrations calculated from these observations ($Y_1$% and $Y_2$% respectively) were compared with those obtained by Lloyd-Haldane ($x$%) gas analysis, for carbon dioxide concentration of 2–20% in a range of oxygen concentrations of about 9–90%. The agreement between paramagnetic and Lloyd-Haldane carbon dioxide analysis is shown in the following linear regression equations: $Y_1 = 0.996x - 0.001 (r = 0.9999 \pm 0.04$ SEM of estimate; $P < 0.001$); $Y_2 = 0.997x - 0.006 (r = 0.9999 \pm 0.06$ SEM of estimate; $P < 0.001$). Carbon dioxide in nitrogen was measured by the prior addition of an arbitrary concentration of oxygen, to a gas sample. The method is applicable to the measurement of carbon dioxide and oxygen, when the carrier-gas may have characteristics which preclude the use of katharometer, infra-red or Haldane analysis.

Since the introduction of the classical chemical method of carbon dioxide and oxygen gas analysis by Haldane (1898), its simplification by Lloyd (1958), and its clinical modification by Campbell (1960) for the rapid analysis of respiratory gas, it has remained the reference whereby calibration gases used in physical methods of gas analysis, such as infra-red absorption, thermal conductivity, magnetic susceptibility, carbon dioxide and polarographic electrodes, are standardized. However, chemical methods of gas analysis require experience and technical skill and, lacking these, show considerable observer error (Cotes and Woolmer, 1962; Sykes, McNicol and Campbell, 1969; Benadé, Strydom and Van der Walt, 1970).

The method described below is based upon the use of a paramagnetic oxygen analyser to observe the change in oxygen concentration in a gas sample following the absorption of the carbon dioxide component by soda-lime. Both oxygen and carbon dioxide can be measured simultaneously over a range of concentrations which exceeds that of the Haldane apparatus. A number of workers have evaluated carefully both the accuracy and the stability of the paramagnetic oxygen analyser (Nunn et al., 1964; Ellis and Nunn, 1968), and also its physiological application (Machta and Hughes, 1970; Kappagoda and Linden, 1972; Stoker et al., 1973).

METHODS

Apparatus. The diagram (fig. 1) shows the method whereby the gas sample is directed through one or other of two glass absorption tubes (A and B) before entering the paramagnetic analyser. One tube (A) contained soda-lime and a final column of calcium chloride, and the other tube (B) calcium chloride only. Thus after passing through absorber A, the gas was freed of carbon dioxide and dried, but absorber B only dried the sample, leaving the carbon dioxide sample unaffected. The glass columns were 1.2 cm i.d. and 7 cm long, containing approximately 7 g of reagent (Indicarb 8–14 mesh, Hopkin and Williams, Essex. Calcium chloride: fused granular 8–16 mesh, British Drug House, Dorset). Each tube incorporated also a sintered filter (Porosity 1), to replace the filter supplied by the manufacturer to protect the analyser cell. The gas flow was switched from one tube to the other at 1-min intervals by means of an electromagnetic valve (Type KV 7/11, G.E.C. for readers.
Elliott Ltd, Kent) controlled by a timing device (Sealectro Ltd, Hants). The sample flow from the electromagnetic valve passed to a paramagnetic oxygen analyser (Type OA272, Servomex Ltd, Sussex), the electrical output of which was recorded by a digital voltmeter (A.200 Solartron, Hants) and a chart recorder (Bryans 27000, Baird and Tatlock, Essex). The oxygen analyser had three ranges of sensitivity giving a full scale deflection for either 5, 25 or 100 % oxygen.

_Calibration._ In all experiments the sample gas flow through the analyser was standardized at 60 ml/min. The instrument was set to zero electrical output with nitrogen, the carrier-gas in all experiments. The span was adjusted on the 25 % range, using room air (20.95 % oxygen).

_Absorption of carbon dioxide._ The absorption capacity of soda-lime for carbon dioxide was demonstrated as follows. A gas sample containing 8 % carbon dioxide was passed through 7 g of soda-lime at the standard flow, and its oxygen concentration was measured by the paramagnetic analyser and recorded continuously on chart paper. The soda-lime continued to absorb carbon dioxide for approximately 4 hr until an abrupt decline in recording of the analyser output indicated exhaustion of the soda-lime.

The completeness of absorption of carbon dioxide by soda-lime was compared with caustic potash by using the apparatus described above (fig. 1). One absorber tube contained soda-lime only and the other caustic potash. The final common pathway leading into the oxygen analyser was a small tube of calcium chloride to dry the gas. A mixture containing 8 % carbon dioxide in oxygen was passed through this arrangement so that any difference in the power of either reagent to absorb carbon dioxide would be shown as a difference of oxygen concentration. For maximum discrimination the oxygen analyser was set on the 0–5 % scale using offset zero facilities and the output recorded with a digital voltmeter and printer capable of discriminating to 1 μV. In such a mixture, change in oxygen concentration resulting from carbon dioxide removal would be equal to the change of carbon dioxide concentration. If, as has been reported, the analyser and recording system can detect a change of 0.0005 % oxygen (Ellis and Nunn, 1968), it can also detect this difference of carbon dioxide concentration between samples which have passed either through soda-lime or caustic potash. A mixture of 20 % carbon dioxide in 33% oxygen was used to test the capacity of the soda-lime to remove a comparatively large concentration of carbon dioxide at two flows (table I).

### Table I. Comparison of carbon dioxide absorption by soda-lime with caustic potash (Mean ± SD).

<table>
<thead>
<tr>
<th>CO₂ (%/o)</th>
<th>Flow (ml/min)</th>
<th>n</th>
<th>Soda-lime deflection (μV)</th>
<th>Caustic potash deflection (μV)</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>60</td>
<td>8</td>
<td>101.762 ± 0.031</td>
<td>101.776 ± 0.017</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>7</td>
<td>101.764 ± 0.031</td>
<td>101.727 ± 0.031</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>12</td>
<td>101.503 ± 0.019</td>
<td>101.493 ± 0.027</td>
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<tr>
<td>8</td>
<td>120</td>
<td>6</td>
<td>101.515 ± 0.014</td>
<td>101.538 ± 0.024</td>
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<tr>
<td>20</td>
<td>60</td>
<td>5</td>
<td>43.780 ± 0.018</td>
<td>43.768 ± 0.011</td>
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<tr>
<td>20</td>
<td>120</td>
<td>9*</td>
<td>43.796 ± 0.031</td>
<td>43.698 ± 0.034</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>5</td>
<td>43.714 ± 0.008</td>
<td>43.709 ± 0.008</td>
</tr>
<tr>
<td>20</td>
<td>120</td>
<td>5</td>
<td>43.738 ± 0.006</td>
<td>43.734 ± 0.008</td>
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</tbody>
</table>

*P<0.001 in these samples; all others = not significant.

_Analysis of samples._ Thirteen cylinders containing 2–20% carbon dioxide in 9–90% oxygen (balance nitrogen) were analysed by the method described above. These cylinders were also analysed for carbon dioxide concentration using a Lloyd-Haldane apparatus with a modified technique described by Owen-
PARAMAGNETIC CO₂ ANALYSER

Thomas and Meade (1975). Ten estimates were made using each method on two separate occasions.

Analysis of carbon dioxide in outdoor air. Outdoor air sampled from the roof of the laboratory was analysed simultaneously for carbon dioxide content by Lloyd-Haldane analysis and by paramagnetic oxygen analyser using the method described above.

Carbon dioxide in nitrogen. Carbon dioxide in nitrogen was estimated by adding an arbitrary volume of oxygen to the sample requiring analysis. In calculating the results, allowance was made for the dilution of oxygen to the sample requiring analysis. In calculating the results, allowance was made for the dilution of oxygen to the sample requiring analysis. In calculating the results, allowance was made for the dilution of oxygen to the sample requiring analysis.

Table I shows the results obtained when 8% and 20% carbon dioxide were passed through the analyser, which may well have been a result of exhaustion of the caustic potash.

<table>
<thead>
<tr>
<th>Table II. Results of carbon dioxide analysis in oxygen and nitrogen mixtures. (Means ± SD of 10 estimates.)</th>
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<tbody>
<tr>
<td>Cylinder</td>
</tr>
<tr>
<td>O₂</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>13</td>
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</table>

Analysis of carbon dioxide in oxygen and nitrogen. The results of analysing the carbon dioxide content of each of 13 cylinders are shown in Table II. The results are also summarized in two regression equations given below in which Y₁ and Y₂ are carbon dioxide concentrations (%) derived from paramagnetic analysis using digital voltmeter or chart recording respectively, and x is the corresponding value resulting from Haldane analysis:

\[ Y_1 = 0.996x - 0.001 \quad (r=0.9999±0.04 \text{ SEM of estimate}) \]  

\[ Y_2 = 0.997x - 0.006 \quad (r=0.9999±0.06 \text{ SEM of estimate}) \]  

Calculation of results

The following symbols were used in the calculation of the results:

\[ \text{Fco}_{2} = \text{CO}_2 \text{ fraction in gas sample} \]

\[ \text{Bm} = \text{O}_2 \text{ fraction in gas sample before removing CO}_2 \]

\[ \text{AFO} = \text{O}_2 \text{ fraction in gas sample after removing CO}_2 \]

then

\[ \text{BHm} = \text{Bm} \text{X (20.95/S)} \text{ X (20.95/R)} \text{ X (Bm/Rm)} \]

so that

\[ \text{Fco}_{2} = \text{BHm} \text{/(1-Fco}_{2}) \]

The effect upon the paramagnetic analyser of the diamagnetic susceptibility of the carrier gas (nitrogen) was eliminated by setting the instrument to electrical zero output with nitrogen.

The calibration span, absolute oxygen concentration in the sample and the change of oxygen concentration caused by carbon dioxide absorption were measured on appropriate analyser ranges which for convenience of reference are called R₀, R₁, and R₂, respectively.

The electrical output of the analyser was recorded in arbitrary units, appropriate to either chart recorder (mm), measured to 0.1 mm or digital voltmeter (mV), measured to 1 µV.

Let

\[ S = \text{units with 20.95% O}_2 \text{ (air) on range R}_0 \]

\[ A\text{R}_1 = \text{units with sample O}_2 \% \text{ after removing CO}_2 \]

\[ B\text{R}_1 = \text{units with sample O}_2 \% \text{ before removing CO}_2 \]

both on range R₁

\[ (A\text{R}_1 - B\text{R}_1) = \text{units with change in the sample O}_2 \% \text{ after removing carbon dioxide, on range R}_2 \]

\[ R_0, R_1 \text{ and } R_2 = \% \text{ concentration for full-scale deflection on each range.} \]

Equation (4) becomes:

\[ \text{Fco}_{2} = [(A\text{R}_1 - B\text{R}_1)/A\text{R}_1] \cdot \text{R}_1/R_2 \]

and sample O₂ %= B₁ × (20.95/S) × R₁/R₀

respectively.

Let

\[ S = \text{units with 20.95% O}_2 \text{ (air) on range R}_0 \]

\[ A\text{R}_1 = \text{units with sample O}_2 \% \text{ after removing CO}_2 \]

\[ B\text{R}_1 = \text{units with sample O}_2 \% \text{ before removing CO}_2 \]

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and sample O₂ %= B₁ × (20.95/S) × R₁/R₀

respectively.
Example. Figure 2 shows chart recordings taken during analysis of cylinder No. 10 (table II) for carbon dioxide and oxygen concentration.

The deflections recorded were as follows:
- \( A_{R_1} = 60 \text{ mm} \)
- \( B_{R_1} = 54 \text{ mm} \)
- \( (A_{R_2} - B_{R_2}) = 118 \text{ mm} \)
- \( S = 140.5 \text{ mm} \)
- \( R_0 = 25\% \text{ range} \)
- \( R_1 = 100\% \text{ range} \)
- \( R_2 = 5\% \text{ range} \)

From equation (5), \( \text{CO}_2\% = 100 \times \frac{118}{60} \times \frac{5}{100} = 9.83\% \)

From equation (6), \( \text{O}_2\% = 54 \times \frac{20.95}{140.5} \times \frac{100}{25} = 32.21\% \)

Carbon dioxide in outdoor air. Fifty estimates of the oxygen concentration in outdoor air, before and after the absorption of carbon dioxide, gave mean values of oxygen of 20.883\% and 20.876\% respectively, recording the analyser's electrical output by digital voltmeter giving a carbon dioxide content in the atmosphere of 0.034\% (equation 4). No attempt was made to adjust the calibration span to 20.95\% oxygen, since this is not necessary for the purpose of carbon dioxide estimation. Ten consecutive estimates by Lloyd-Haldane analysis gave a value of carbon dioxide \( \% = 0.034 \pm 0.0052 \) (Handbook of Chemistry and Physics: 0.033 \pm 0.001).

Carbon dioxide in nitrogen. The contents of a cylinder containing a nominal concentration of 10\% carbon dioxide in nitrogen were analysed by the Lloyd-Haldane method. In a separate experiment the contents of the cylinder were blended with oxygen using rotameters to produce a mixture containing approximately 30\% oxygen. This mixture was analysed by the paramagnetic method described above. Lloyd-Haldane analysis gave a carbon dioxide concentration of 10.09\% ± 0.063 (n=29), and paramagnetic analysis 10.09\% ± 0.032 (n=10). Allowance was made for the dilution caused by the added oxygen, by dividing the result obtained from equation (5) by \( (1 - F_0) \) where \( F_0 \) is the oxygen fraction in the mixture, this fraction being calculated using equation (6).

**DISCUSSION**

The results presented cover a wide range of physiological gas concentrations of oxygen from 9 to 92\% and of carbon dioxide from 0.03 to 20\%. The accuracy of estimating carbon dioxide in a gas sample by paramagnetic analysis approaches that of Haldane standards (table II).

In our hands, Lloyd-Haldane estimates of carbon dioxide concentration show a standard deviation of 10 observations to be \( \pm 0.01\% \) or less, over the entire range of carbon dioxide concentrations studied (table II) and there is evidence from a smaller number of estimations that this level of accuracy is attainable with care (Cormack, 1972). The significance of the standard deviation as a measure of overall accuracy relates to the absolute carbon dioxide concentration being measured, and in this respect all our standard deviations were less than 0.6\% of the mean sample concentration (the coefficient of variation, \%). By comparison, results recorded by paramagnetic analysis had a maximum coefficient of variation of 0.55\% and 1.15\% for digital voltmeter and chart recording respectively.

The regression equations (1) and (2) show a high correlation between Lloyd-Haldane and paramagnetic analysis, whether recorded by digital voltmeter or chart, indicating that the results obtained by paramagnetic analyser are lower than Lloyd-Haldane estimates by a factor of 0.996 and 0.997 for digital voltmeter and chart recording respectively.

It will be noted that the mean value for first and second estimates by paramagnetic analyser of a particular cylinder may differ, but, as a result of the small standard deviation, this difference is statistically significant in more than half of the estimations made. However, the first and second mean estimates do not differ from the mean of the combined 20 estimates of
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that particular cylinder by more than 0.49% for digital voltmeter and 0.62% for chart recording.

Paramagnetic analysis requires little technical expertise and gives a complete analysis of carbon dioxide and oxygen at 2-min intervals and would seem to offer useful advantages to physiologists where simultaneous gas analysis is required, and the use of a chemical method undesirable.

Carrier-gas. Other physical methods of carbon dioxide analysis, such as infra-red absorption, are prone to instability (Cormack and Powell, 1972) and require careful repeated calibration checks with a number of known carbon dioxide concentrations to maintain linearity of response.

Common anaesthetic gases such as nitrous oxide and cyclopropane cause gross discrepancies in the analysis of carbon dioxide because of the collision broadening effect of carrier-gases of similar molecular weight and infra-red absorption band to carbon dioxide (Coggeshall and Saier, 1947; Bergman, Rackow and Frumin, 1958; Ramwell, 1957; Severinghaus, Larson and Eger, 1961). By comparison, the interference of nitrous oxide resulting from its diamagnetic susceptibility is small, and can be either eliminated or allowed for as shown in the Methods section. Similarly, the diamagnetic interference resulting from helium and argon (Ammann and Galvin, 1968) can be eliminated, or allowed for. Therefore, a paramagnetic method would seem to offer advantages when interfering properties of a carrier-gas must be eliminated and multiple, simultaneous estimates of both carbon dioxide and oxygen are required.

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REFERENCES


UNE METHODE PARAMAGNETIQUE D'ANALYSE DE LA CONCENTRATION D'ANHYDRIDE CARBONIQUE D'UN GAZ

RESUME

Une méthode paramagnétique d'analyse de l'anhydride carbonique permet d'effectuer simultanément, à intervalles de 2 minutes, l'analyse de l'anhydride carbonique et de l'oxygène. Cette méthode dépend de l'observation du changement dans la concentration d'oxygène dans un mélange de gaz, avant et après l'absorption d'anhydride carbonique. Dans les expériences qui font l'objet de ce rapport, le gaz porteur était l'azote. La sortie de l'appareil de mesure paramagnétique a été contrôlée par un voltmètre numérique et par un enregistreur à tableau; les concentrations d'anhydride carbonique que l'on a calculées à partir de ces observations respectivement (Yₐ % et Yᵢ %) ont été comparées à celles obtenues par l'analyse du gaz Lloyd-Haldane (x %), pour une concentration d'anhydride carbonique de 2-20 %, sur une plage de concentrations d'oxygène d'environ 9-90 %. L'accord entre l'analyse paramagnétique et l'analyse Lloyd-Haldane de l'anhydride carbonique est indiqué par les équations linéaires à régressions ci-dessous: Yᵢ = 0,996x - 0,001 (r = 0,9999 ± 0,04
Eine paramagnetische Methode zur Untersuchung der Kohlendioxyd-Konzentration eines Gases

Zusammenfassung

Diese Methode ermöglicht die gleichzeitige Analyse von Kohlendioxyd und Sauerstoff in Intervallen von 2 Minuten. Sie hängt ab von der Beobachtung der Veränderungen der Sauerstoffkonzentration einer Gasprobe vor und nach Absorbierung des Kohlendioxydteils. Das Trägergas in den behandelten Experimenten war Stickstoff. Der Ausgang des paramagnetischen Meßgerätes wurde sowohl von einem digitalen Voltmeter als auch durch Aufzeichnung auf einem Streifen gemessen; und die aus diesen Beobachtungen (\(Y_1\%\) und \(Y_2\%\)) errechneten Kohlendioxydkonzentrationen wurden mit denen verglichen, die durch eine Lloyd-Haldane-Analyse (x%) erzielt wurden, und zwar für eine Kohlendioxydverdünnung von 2–20% in einem Bereich von Sauerstoffkonzentrationen von etwa 9–90%. Die Übereinstimmung zwischen diesen beiden Analysemethoden wird in den folgenden linearen Regressionsgleichungen gezeigt: \(Y_1 = 0,996x - 0,001\) (r=0,9999±0,04 SEM des geschätzten; P<0,001); \(Y_2 = 0,997x - 0,006\) (r=0,9999±0,06 SEM des geschätzten; P<0,001). Kohlendioxyd in Stickstoff wurde durch vorherige Zugabe einer beliebigen Konzentration von Sauerstoff zu einer Gasprobe gemessen.

Diese Methode ist für die Messung von Kohlendioxyd und Sauerstoff geeignet, wenn das Träergas Eigenschaften haben kann, die eine Verwendung von Katharometer sowie einer Infrarot- oder Haldaneanalyse verhindern.

Ein Metod paramagnetico para reanudar la concentración de bióxido de carbono de un gas

Sumario

Un método paramagnético de análisis del bióxido de carbono permite realizar, con intervalos de dos minutos, el análisis simultáneo del bióxido de carbono y el oxígeno. El método se basa en la observación del cambio de concentración de oxígeno en una mezcla de gases antes y después de absorber el componente de bióxido de carbono. El gas portador en los experimentos citados fue el nitrógeno. El rendimiento del metro paramagnético se midió con un voltímetro digital y un aparato registrador de diagramas, y las concentraciones del bióxido de carbono extraídas de esas observaciones (\(Y_1\%\) e \(Y_2\%\) respectivamente) se compararon con las que se obtuvieron del análisis del gas Lloyd-Haldane (x%), para una concentración del 2 al 20% en una variedad de concentraciones de oxígeno de más o menos del 9 al 90%. La coincidencia entre el paramagnético y el análisis del bióxido de carbono Lloyd-Haldane se muestra en las siguientes ecuaciones de regresión lineal: \(Y_1 = 0,996x - 0,001\) (r=0,9999±0,04 SEM de cálculo; P<0,001); \(Y_2 = 0,997x - 0,006\) (r=0,9999±0,06 SEM de cálculo; P<0,001). El bióxido de carbono en nitrógeno se midió por un añadido previo de una concentración arbitraria de oxígeno a una muestra de gas. El método es aplicable a la medición del bióxido de carbono y el oxígeno, cuando el gas portador puede tener características que excluyen el uso del catarómetro, infrarrojo o análisis Haldane.