

SHORT COMMUNICATION

A SIMPLE ANALYSER FOR GASES IN MIXED SAMPLES

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It is often necessary to measure the concentration of a single gas in a sample of mixed gases. Dalton's Law of Partial Pressures indicates that this may be done by measuring the volume of a sample before and after absorption of the gas of interest; the ratio of the difference between the two volumes to the original volume stating exactly the concentration of the absorbed gas.

Several simple analysers have been described that perform such an analysis by employing an indexed chamber of fixed size to measure the volume of a sample (Scholander & Roughton, 1942; Berg, 1946; Scholander, Van Dam, Lloyd Claff & Kanwisher, 1955). This paper describes a simple analyser which employs a chamber of variable size to measure the volume of a sample. As a result of its design this instrument accepts a larger range of sample sizes and demonstrates higher accuracy in volume determination (and hence overall accuracy) than previously described instruments.

The analyser is drawn in Fig. 1. In operation the glass tube is filled with approximately 400 μl of an inert solution, after which 50–150 μl of sample is placed inside the outer reservoir (OR) with a syringe. The bubble of sample gas is then drawn through the capillary towards the inner reservoir (IR) by using the micrometer to increase the volume of the IR. Readings are taken from the micrometer as the bubble first and then last touches the reference mark on the capillary as it is pulled towards the IR. The difference between the two readings indicates the volume of the sample. Once the volume of the sample has been determined it is moved completely into the IR and the inert solution in the OR is replaced with approximately 300 μl of a reagent which absorbs the gas of interest. The volume of the IR is then increased to draw the new reagent through the capillary into the IR where it encounters the sample. The sample is then moved back to the OR by decreasing the volume of the IR. The several seconds this movement takes are sufficient for the new reagent to absorb completely the gas of interest. The sample is then remeasured as above and the change in volume is compared with the original volume of the sample, giving the concentration of the absorbed gas. Following this,

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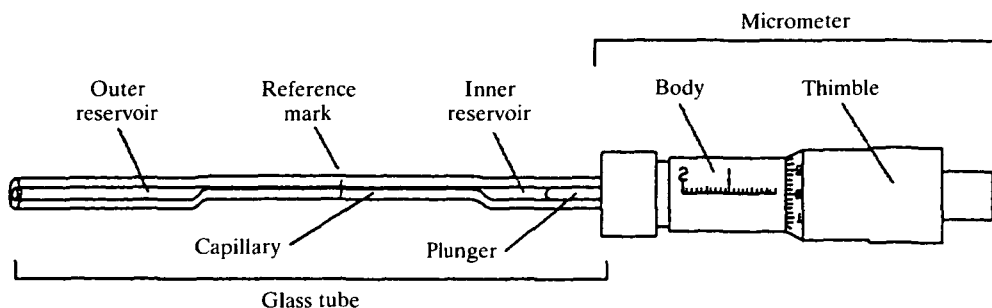


Fig. 1. Illustration of the analyser. The instrument consists of a tubular glass section attached to a micrometer head (Gilmont Instruments, Inc., 401 Great Neck Road, Great Neck, NY 11021, USA). The glass section consists of a length of capillary tubing joined to two sections of larger diameter tubing termed the outer and inner reservoirs (OR and IR, respectively). The capillary bears a reference mark and is offset parallel to the OR and IR. Dimensions of the glass section are given below. A solid plunger connects directly to the micrometer thimble and fits inside the IR. Internally, the micrometer body and the end of the IR trap an 'O' ring which surrounds the plunger, forming a seal between the plunger and IR through which the plunger may move. This seal is maintained in compression by a fitting on the micrometer body. The OR is open to the atmosphere. Changes in the volume of the IR are produced by rotating the thimble and are measured by indices on the micrometer body and thimble. A water jacket (not shown) surrounds the glass section, serving to prevent any measurable temperature changes. Glass dimensions: capillary, length = 80 mm, i.d. = 0.5 mm; outer reservoir, length = 45 mm, i.d. = 3.203 mm; inner reservoir, length = 34 mm, i.d. = 3.203 mm.

the sample may again be moved completely into the IR and the process repeated to determine the concentration of another constituent of the sample.

The results of the analyses of three samples of N_2 containing CO_2 and O_2 , in physiological ranges, and ambient air are given in Table 1. All samples were approximately 100 μ l in volume. In each analysis the volume of the sample was measured first in acid-citrate to determine total volume, second in KOH to absorb CO_2 , and third in pyrogallol to absorb O_2 (all solutions as per Scholander *et al.* 1955). The gas concentrations in each sample were calculated as:

$$\%CO_2 = [(V_{AC} - V_{KOH})/V_{AC}] \times 100,$$

$$\%O_2 = [(V_{KOH} - V_{Pyrog.})/V_{AC}] \times 100,$$

where V_{AC} = volume of sample measured in acid-citrate; V_{KOH} = volume of sample measured in KOH; $V_{Pyrog.}$ = volume of sample measured in pyrogallol.

The average of the standard deviations across all samples indicates that the precision of the analyser, as ± 1 s.d., is approximately $\pm 0.2\%$. The average of the discrepancies for each gas across all samples indicates an error in accuracy of -0.11% for CO_2 and -0.23% for O_2 . These two discrepancies are representative of only three samples each, taken from a reference standard which varied by $\pm 0.015\%$. Therefore they may not be representative of the true accuracy of the instrument.

Table 1. *Records of analyses*

	Sample 1		Sample 2		Sample 3		Air
	CO ₂	O ₂	CO ₂	O ₂	CO ₂	O ₂	O ₂
Expected:							
reference	2.949 %	16.418 %	4.208 %	10.397 %	8.618 %	21.115 %	20.95 %
Observed:							
<i>N</i>	15	15	10	10	10	10	10
Mean	2.83 %	16.12 %	3.90 %	10.46 %	8.72 %	20.59 %	20.81 %
Discrepancy	-0.12 %	-0.30 %	-0.30 %	+0.06 %	+0.098 %	-0.52 %	-0.14 %
s.d.	0.1499	0.2191	0.1870	0.1123	0.2819	0.2152	0.1902

Reference values indicate concentrations of gas in each sample analysed to 0.015 %*.

N value indicates number of analyses performed for each gas.

Mean indicates the observed average percentage concentration for *N* trials.

Discrepancy equals reference value minus mean value.

s.d. is the standard deviation of the mean in units of percent concentration.

* Samples 1-3 consisted of CO₂ and O₂ in N₂ and were obtained from cylinders of gas previously analysed using a Scholander 0.5 ml gas analyser (Scholander, 1947). Analysed samples were generously provided by the Hall Laboratory for Environmental Research, Duke University, Durham, NC 27706, USA.

Nonetheless, these latter averages indicate the presence of a small systematic error in the determination of the percentage concentration of CO₂ and O₂ by this analyser.

With this instrument, the size of a sample is directly related to the precision with which its volume may be measured. The micrometer head is advertised by the manufacturer as having an accuracy in *delivery* of $\pm 0.2 \mu\text{l}$, so a 100 μl sample should show a maximum precision of $\pm 0.2 \%$ (as shown by the data), a 50 μl sample a maximum of $\pm 0.4 \%$, a 25 μl sample a maximum of $\pm 0.8 \%$, and so on. However, this instrument does not constrain the use of a particular sample size within a 1-150 μl range in order to resolve $\pm 0.2 \mu\text{l}$ (cf. the maximum volumes of Scholander *et al.* 1955, of 28.3 μl or Berg, 1946, of 0.46 μl). With the substitution of a more accurate micrometer head, the precision of the instrument would increase.

The factor capable of producing the greatest error is temperature change. A change of 0.1 °C will cause a volume change of just under 0.4 μl in a 100 μl sample. The water jacket fitted to the instrument makes this error small. CO₂ is very soluble in water, so a high-salt acidic formula is used for the initial solution in order to prevent CO₂ dissolution. Although no inaccuracy due to CO₂ solubility is shown in the data, samples with CO₂ concentrations of 15 % or more could be expected to show some loss into the initial solution in spite of its composition. Oxygen is much less soluble by comparison and should show little solubility at higher concentrations. There is some problem predicting these solubilities because, although calculations will show that a significant proportion of a sample should go into solution, this does not occur in practice. It is thought that there is insufficient mixing during an analysis to produce the expected amount of gas dissolution.

The accuracy and simplicity of use of this instrument, coupled with its ability to analyse for O₂ and CO₂ in the same sample, may make it suitable for instructional as well as research applications. This instrument is available from the author in limited quantity.

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