

## A Differential Oxygen Analyser

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For the determination of very small differences in oxygen content of air samples, a method based on the well known absorption of oxygen by pyrogallol was developed.

*Principle:* Two vessels, connected through a manometer, are filled with the two samples to be compared; the pressure difference is adjusted to zero. The oxygen is absorbed by the pyrogallol and the pressures are again compared, the pressure difference being proportional to the difference in oxygen content.

*Apparatus:* Fig. 1 shows a diagram of the apparatus used: The manometer M is connected on each side to a ground joint socket. The vessels carry ground joint cones that fit into the sockets. The vessels have only a 1 cm hole which gives free passage between the vessel and the manometer connection when the vessel is turned to the appropriate position. Opposite the manometer connection another glass tube is fitted to the socket. When the vessels are turned through 180°, the air samples may be introduced through these tubes (B' and B''). The manometer liquid is silicone oil (DC 200/10,  $d$  0.94). The reading is carried out with a cathetometer. In this way pressure differences of up to ca. 1 cm silicone oil ( $\approx$  1 mm Hg) can be read with an accuracy of 0.01 mm silicone oil ( $\approx$  10<sup>-3</sup> mm Hg), *i.e.* 10<sup>-4</sup> % of the total pressure (1 atm.).

The volume of each vessel is approximately 200 ml.

*Procedure:* Small double walled paper bags are made from lens paper (*ca.* 5 cm long and 0.8 cm diameter); each is filled with 1 g of ground pyrogallol. They are closed at both ends by twisting the paper and attached to a small polyethylene covered magnet (stirrer) by means of a cotton thread.

The cones are greased with Apiezon L. A magnet (stirrer) is placed in the larger section (a) of the vessel. The bag with pyrogallol is placed in the front section (b) of the vessel; ca. 15 ml 50 % (w/w) potassium hydroxide are added through a suitably bent pipette to the a-section of the vessels (see Fig. 1). These are then fitted into the sockets and the whole assembly is lowered into a temperature controlled bath.

The air samples are introduced through the outer tubes B' and B'' after evacuation of the vessels.

The vessels are turned through 180° and connected through the valves A' and A''. In order to remove carbon dioxide and to reach water vapour equilibrium the air in the vessels is stirred now and again during one hour by means of the magnet from section a of the vessel, care being taken that no drops of potassium hydroxide touch the pyrogallol bag.

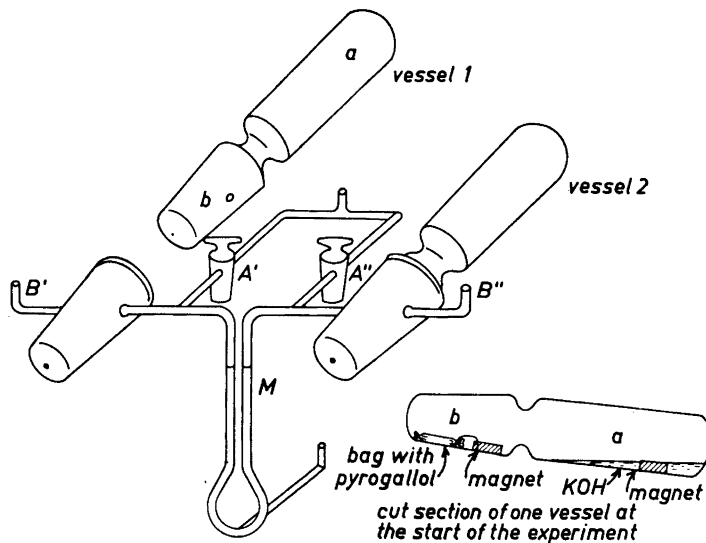


Fig. 1.

A' and A'' are closed and the apparatus is left for at least half an hour during which a small change in manometer reading usually 0—0.05 mm silicone oil may take place.

The vessels are cautiously closed by rotating them until the holes are at the top (tongs are used in order not to heat the samples).

The pyrogallol bags are pulled into the potassium hydroxide solution by the magnet attached; after a couple of minutes of magnetic stirring the bags disintegrate and the pyrogallol dissolves.

Mechanical stirring is effectuated by rocking the apparatus about a horizontal axis until the system approaches equilibrium.

In the meantime the air in the manometer tubes above the silicone oil has been replaced by nitrogen at  $0.79 \times$  atmospheric pressure by evacuating and filling through the valves A' and A''. Some time must elapse before the nitrogen is in sufficient equilibrium with the silicone oil in the manometer (after one hour the change may be about 0.01 mm silicone oil per hour). The equilibrium pressure difference is recorded.

The vessels are then opened towards the manometer. Reading and stirring are continued until the manometer is stable, usually after 20 min.

The bulk of each sample is sucked out of the vessel and passed through a carbon monoxide tester under standard conditions. The difference in percentage carbon monoxide is recorded.

Although the principle is very simple, the procedure is never the less a fairly lengthy one. At present only one set of samples can be analysed in a full working day the actual performance of the determination taking 4 h but many improvements can be envisaged which will reduce the labour and shorten the time required to make one determination.

In view of the accuracy obtained this may not compare unfavourably with the best Orsat gas analysis methods.

*Calculations:* A first approximation: The mole fractions of oxygen in the samples are called  $(1-a_1)$  and  $(1-a_2)$ ; total number of gram molecules are  $n_1^\circ$  and  $n_2^\circ$ . The volumes  $v_1$  and  $v_2$  are assumed to be constant.  $p_1^\circ$  and  $p_2^\circ$  are the initial pressures,  $p_1'$  and  $p_2'$  are the final pressures.

According to the gas laws we have at the start of the experiment

$$p_1^\circ v_1 = n_1^\circ RT \quad \text{and} \quad p_2^\circ v_2 = n_2^\circ RT$$

At the end

$$p_1' v_1 = a_1 n_1^\circ RT \quad \text{and} \quad p_2' v_2 = a_2 n_2^\circ RT$$

or

$$\frac{p_1'}{p_1^\circ} = a_1 \quad \frac{p_2'}{p_2^\circ} = a_2$$

By subtraction

$$a_1 - a_2 = \frac{p_1'}{p_1^\circ} - \frac{p_2'}{p_2^\circ} = (p_1' - p_2') \frac{1}{p_1^\circ} + (p_2^\circ - p_1^\circ) \frac{p_2'}{p_1^\circ p_2^\circ}$$

$$\frac{1}{p^\circ} (p_1' - p_2' - \frac{p'}{p^\circ} (p_1^\circ - p_2^\circ)) \quad [(p_1^\circ - p_2^\circ) \text{ is kept as low as possible};$$

where, when air is tested,

$$p^\circ = 1 \text{ atm and } \frac{p'}{p^\circ} = \frac{4}{5} \text{ (with sufficient accuracy).}$$

For an accurate calculation it is necessary to take the following factors into account:

1. The volumes change when the manometer reading changes.
2. The nitrogen atmosphere that replaces the air in the manometer does not have pressures exactly equal to the pressures inside the vessels after absorption of oxygen.
3. The temperature of the system may change and so may the temperature difference between the vessels.
4. A volume change may take place when potassium hydroxide solution and pyrogallol is mixed.
5. The water vapour pressure will change a) when potassium hydroxide solution and pyrogallol is mixed, b) when the temperature changes.
6. The volumes may change if grease is forced into the vessels from the ground joints.
7. The pyrogallol powder and the bag should have a vapour pressure equivalent to that of the potassium hydroxide solution. In order to obtain this the bags are dried at 80°C and stored in a desiccator over a 50 % potassium hydroxide solution.
8. Deviations from the ideal gas laws may effect the results.
9. Carbon monoxide is produced.

If the conditions listed below are fulfilled then it can be shown by fairly

simple, but rather lengthy, calculations \* that the only factors of any importance (*i.e.* factors which give a contribution to the result which approaches the value of the standard deviation) are 1 and 9:

List of conditions:

$$a. \frac{\varphi_1}{v_1} - \frac{\varphi_2}{v_2} < 10^{-3} \text{ and } \frac{p_1}{v_1} - \frac{p_2}{v_2} < 10^{-2}$$

where  $\varphi_1$  and  $\varphi_2$  are the volumes of the manometer tubing above the silicone oil.

b.  $p_1 - p_2 < 3$  cm silicone oil and  $(p_1 - p_2) - p_1^* - p_2^* < 0.1$  cm silicone oil.  $p_1^*$  and  $p_2^*$  are the pressures in the manometer after it has been filled with nitrogen but before the vessels are opened (*cf.* p. 1032).  $p_1$  and  $p_2$  are the pressures at the end of the experiment.

c. The one gramme of pyrogallol should be weighed out with an accuracy of a few mg.

d. The 15 ml potassium hydroxide should be measured accurately with a pipette.

e. Variations of bath temperature at any particular point should be less than 0.01°C.

f. The difference between the temperature of vessel 1 and vessel 2 should be less than 0.01°C.

g. The variation of this difference should be less than 0.001°C.

The result of the calculations can be shown to be

$$a_1 - a_2 = \frac{1}{p^0} [(p_1 - p_2) - \frac{4}{5} (p_1^0 - p_2^0) + \left(\frac{p_1}{v_1} + \frac{p_2}{v_2}\right) \frac{A}{2} ((p_1 - p_2) - (p_1^* - p_2^*))] - (co_1 - co_2).$$

Here  $p_1^0 - p_2^0$  is the initial pressure difference in cm silicone oil;

$p_1 - p_2$  is the final pressure difference in cm silicone oil;

$p_1^* - p_2^*$  is the pressure difference in cm silicone oil between the manometer tubes after they have been filled with nitrogen but before the vessels are opened;

$A$  is the area (in cm<sup>2</sup>) of the cross section of the manometer tubing;

$v_1$  and  $v_2$  are in cm<sup>3</sup>;

$co_1$  and  $co_2$  are the mole fractions of carbon monoxide in the vessels after the experiment.

$A$  has been found to be 0.048 cm<sup>2</sup>.  $v_1 \approx v_2 \approx 200$  cm<sup>3</sup>,

$$p_1 - p_2 \approx \frac{4}{5} p^0 \approx \frac{4}{5} \times 1.1 \times 10^3 \text{ cm silicone oil,}$$

$$i.e. a_1 - a_2 \approx \frac{1}{p^0} ((p_1 - p_2) - \frac{4}{5} (p_1^0 - p_2^0) + 0.20 ((p_1 - p_2) - (p_1^* - p_2^*))) - (co_1 - co_2)$$

\* These calculations are available, to anyone interested, by contacting the author.

Table 1. Difference in mole fraction of oxygen in the two vessels:  
 $(1-a_2)-(1-a_1) = a_1-a_2$ .

	Series 1		Series 2	
			A	B
	$a_1-a_2$		$a_1-a_2$	
	No.	mole fraction	No.	mole fraction
	1	$2.0 \times 10^{-5}$	1	$-2.5 \times 10^{-5}$
	2	$0.0 \times 10^{-5}$	4	$-1.5 \times 10^{-5}$
	3	$2.5 \times 10^{-5}$	6	$-2.0 \times 10^{-5}$
	4	$0.0 \times 10^{-5}$	7	$-2.5 \times 10^{-5}$
	5	$1.0 \times 10^{-5}$	10	$-2.0 \times 10^{-5}$
	6	$1.0 \times 10^{-5}$	12	$-2.5 \times 10^{-5}$
	7	$2.0 \times 10^{-5}$		
	8	$2.0 \times 10^{-5}$		
	9	$0.5 \times 10^{-5}$		
	10	$1.0 W 10^{-5}$		
Average	$(1.2 \pm 0.3) \times 10^{-5}$		$(-2.2 \pm 0.2) \times 10^{-5}$	
Standard deviation	$1 \times 10^{-5}$		$0.4 \times 10^{-5}$	
Average standard deviation	$1 \times 10^{-5}$			
Zero of apparatus	$(1.2 \pm 0.3) \times 10^{-5}$		$\frac{-2.2 + 3.3}{2} \times 10^{-5} = (0.6 \pm 0.3) \times 10^{-5}$	
Average zero	$1 \times 10^{-5}$			
Difference in oxygen content (mole fraction) of the two samples			$\frac{3.3 + 2.2}{2} \times 10^{-5} = (2.8 \pm 0.3) \times 10^{-5}$ i. e. $(1.4 \pm 0.15) \times 10^{-2}$ % of the oxygen content	

Table 2. The difference in carbon monoxide production in relation to order of mixing (in cm silicone oil).

Series 1				Series 2			
No.	Vessel 1 first	No.	Vessel 2 first	No.	Vessel 1 first	No.	Vessel 2 first
1	$+1.5 \times 10^{-2}$	6	$+0.5 \times 10^{-2}$	1	—	4	$-1.0 \times 10^{-2}$
2	$+1.0 \times 10^{-2}$	7	$-1.0 \times 10^{-2}$	2	$+1.5 \times 10^{-2}$	5	$-0.5 \times 10^{-2}$
3	$+1.0 \times 10^{-2}$	8	$-1.0 \times 10^{-2}$	3	$+1.5 \times 10^{-2}$	7	$-1.0 \times 10^{-2}$
4	$+1.5 \times 10^{-2}$	9	$-1.0 \times 10^{-2}$	6	$+1.5 \times 10^{-2}$	8	$-0.5 \times 10^{-2}$
5	$+1.0 \times 10^{-2}$	10	$0.0 \times 10^{-2}$	9	$+1.0 \times 10^{-2}$	12	$-1.5 \times 10^{-2}$
				10	$+1.0 \times 10^{-2}$	13	$0.0 \times 10^{-2}$
				11	$+1.0 \times 10^{-2}$		

*Carbon monoxide determination:* It was found that using the procedure described on p. 1032 for preparing a pyrogallol solution the amount of carbon monoxide liberated is about 0.008 to 0.01 % of total pressure, which agrees well with Kilday's findings<sup>1</sup>.

A Carbon Monoxide Gas Detector, Mines Safety Appliances Co., Ltd. (Glasgow) was used for the determination of carbon monoxide. Small differences can be estimated with an accuracy of about 50 % of the difference. Most differences found were about  $0.001 \pm 0.0005$  %.

*Difficulties with the grease* add to the fairly high standard deviation found in the actual experiment. For instance when the pressure inside the vessel is changed from 1 atm to 0.8 atm the vessels will be pressed against the wall where the hole is and some grease (an uncontrollable amount) may be forced into the vessels. This is an established source of error but its magnitude is difficult to assess. Its importance can of course be diminished by reducing the amount of grease in the ground joint to a minimum.

*Results:* Two series of experiments have been performed (Table 1): In the first series the samples were known to be identical and in the second there was a constant well defined difference between the two samples. The oxygen content was close to that of normal air (mole fraction 0.209).

In series 2 the results can be divided into two groups:

A. sample I in vessel 2 and sample II in vessel 1 and

B. » I » » 1 » » II » » 2.

*Discussion:* It is not quite certain why series 2 in general seems better than 1, nor is it known why No. 2 ser. 2 is out. It is in fact a borderline case and could have been left out.

It may seem rather surprising that the zero of the apparatus lies at + 0.01 cm silicone oil and the reason is in fact not known but a fairly plausible explanation seems to be that due to differences in the quality of the ground joints of the vessels the difference between the volumes of grease forced out during the experiment will on an average show a definite value ( $10^{-2}$  cm silicone oil is equivalent to 2  $\mu$ l).

*Conclusion:* Small differences in the oxygen content ( $< 0.1$  % of total pressure) of air can be determined with a standard deviation of 0.01 cm silicone oil =  $10^{-3}$  % of total pressure (1 atm) or 0.005 % of the oxygen content.

For comparison it should be noted that the very best Orsat gas analysis apparatus may give results reproducible within 0.003 % of total volume or 0.015 % of the oxygen content.

*The value of the carbon monoxide correction:* It was found impracticable to mix pyrogallol and potassium hydroxide solution in both vessels simultaneously and it turned out that the vessel which is mixed first would always show the highest carbon monoxide value, see Table 2. This finding is in agreement with that of Kilday<sup>1</sup>, who states that contact between a fairly high oxygen concentration and pyrogallol with no proper agitation is unfavourable.

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#### REFERENCE

1. Kilday, M. V. *J. Research, NBS* **45** (1950) RP 2112.

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