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DETECTION OF TRACES OF OXYGEN IN GASES – METHYLENE BLUE METHOD.

by

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Summary

A simple method for the detection of traces of oxygen in gas streams is described.

The method is based on the colour change which occurs when leuco–methylene blue is oxidised to methylene blue. Suggested uses of the method are in argon–arc welding and glove–box work where oxygen must be excluded.

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CONTENTS

1. INTRODUCTION

While such instruments as the Hersch Galvanic Oxygen Meter(1) and the Mass Spectrometer(2) are used for the accurate determination of traces of oxygen in gases, there is a need for a simple, inexpensive monitoring device which can indicate the presence of oxygen in a gas.

The instrument described below was developed to meet a need in the argon-arc welding of stainless steel pipes where the presence of even small amounts of oxygen will result in imperfect welds. It may also be suitable for use as a monitoring device on glove-boxes when oxygen must be excluded.

The apparatus consists of a glass tube containing reduced methylene blue reagent, through which is bubbled the gas being tested. When the oxygen concentration of the gas rises above 100 p.p.m. v/v the liquid develops a blue colour.

2. APPARATUS

The apparatus (figure 1) consists of a pyrex test-tube 15 cm. long, fitted with a B40 standard ground socket. Inlet and outlet tubes are sealed into a B40 cone as shown. A three-way tap is included in the inlet side and a standard tap on the outlet. The incoming gas is broken into fine bubbles by passage through a sintered glass disc.

3. REAGENTS

Stock Solutions

(i) 0.3% Aqueous methylene blue.

(ii) 1.0% Lactose solution (to which is added a small quantity of thymol as preservative.)

(iii) 0.1M. NaOH

All concentrations are approximate.

Indicator Solution

It has been found advisable to prepare the indicator solution daily.
To 100 ml. of distilled water or tap water are added 1 ml of each of the three stock solutions.

4. METHOD

100 ml. of the bright blue, freshly prepared indicator solution are placed in the test-tube and the apparatus is assembled with the taps open. The test-tube is heated by means of a bunsen burner and the contents are boiled until the methylene blue is reduced and the solution becomes colourless (about 3 mins.) The heater is then removed, both taps are closed and the apparatus is cooled to room temperature. If the apparatus is air-tight no air will leak in during cooling and the indicator solution will remain colourless. The apparatus is now ready for use.

The gas stream to be tested is connected to the inlet tube A figure I and the three-way tap is turned so that the gas flows out through the by-pass. When the inlet tube has been flushed out, the tap B figure I is then turned so that the gas flows directly into the bubbler. When bubbles start to appear the tap C may be opened.

Gas containing less than 100 p.p.m. O_2 v/v may be passed through indefinitely and the indicator solution will remain colourless.

When the oxygen concentration of the incoming gas reaches 100 p.p.m. v/v the indicator solution will develop a faint but definite blue-green colour. As the oxygen concentration further increases, the blue colour becomes more intense.

5. EXPERIMENTAL

The calibration procedures were carried out using electrolytically generated oxygen, known amounts of which were added to "oxygen-free" nitrogen. The amount of oxygen in the nitrogen was measured independently by use of the Hersch Galvanic oxygen meter and was found to be 14 p.p.m. v/v. Details of the electrolyser and oxygen meter are given by Hersch[1].

Gas flow rates were measured by a Venturi flow-meter.

(i) Effect of varying oxygen concentrations on indicator.

"Oxygen-free" nitrogen was bubbled through the prepared indicator solution at the rate of 100 mls./min. The oxygen content of the gas was increased step-wise and the effect on the indicator was noted.

O_2 Conc. in N_2 p.p.m. v/v	Effect on Indicator
14	No colour developed.
50	" " "
80	" " "
100	Faint, persistent greenish-blue
200	Faint blue
500	Increased intensity of blue colour
1,000	Deep blue colour (Not as intense in colour as original indicator.)

(ii) Effect of passage of oxygen free gas through oxidised indicator.

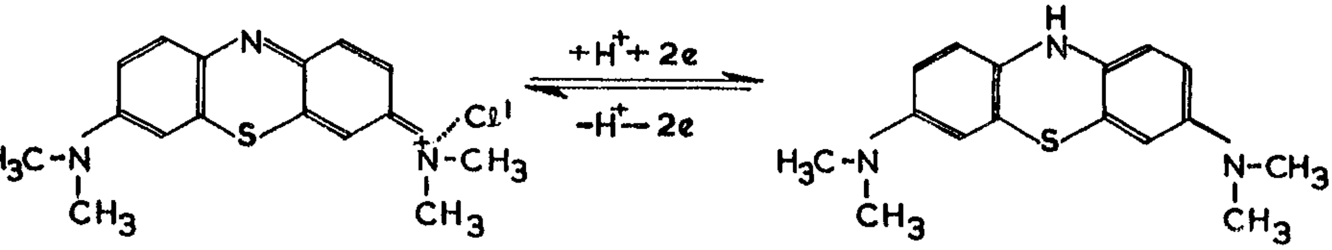
Oxygen free nitrogen ($<$ 20 p.p.m. v/v O_2) was bubbled through the oxidised (blue) indicator solution, kept at room temperature, at the rate of 100 ml./min. for 18 hrs. The solution was not decolouri

(iii) Effect of passage of oxygen free gas through reduced indicator.

Oxygen free nitrogen ($<$ 20 p.p.m.v/v O_2) was bubbled through the reduced (colourless) indicator solution, kept at room temperature, at the rate of 100 mls./min. for 18 hours. The solution remained colourless.

6. DISCUSSION

Methylene blue is widely used as a redox indicator in biological studies. The reaction is:-



Methylene Blue　　　　　　　　　　　　Leuco Methylene Blue

Its use by Thunberg in demonstrating the presence of dehydrogengases in tissues is discussed by Baldwin(3). Methylene blue has also been used as the basis of other tests for the presence of oxygen in gases (4) and the determination of oxygen in gases (5).

The test described here is based on the fact that in mildly alkaline solution, reducing sugars such as lactose are readily enolised at elevated temperatures, so that in the concentration range used, methylene blue will be reduced by the lactose when boiled, but not in the cold.

It is evident from the experimental findings, that the device described above is suitable for the detection of oxygen in pure nitrogen in amounts of 100 p.p.m.$^{v}/_{v}$ or greater. Where interfering gases such as H_2S may be present a second gas bubbler containing oxidised indicator may be included in the circuit. Where interfering gases are present the oxidised indicator will be reduced in the cold.

REFERENCES

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2. A.J.Robertson (1954) "Mass Spectrometry" p.84 (Methuen).
3. E. Baldwin (1948) "Dynamic Aspects of Biochemistry" Cambridge University Press.
4. Mvan Riemiskijk (1922), Nederlands Tijdschr. Geneeskunder 66, I.1423–7.
5. A.Kling and M.Claraz (1936) Compt. rend. 203, 319–321.

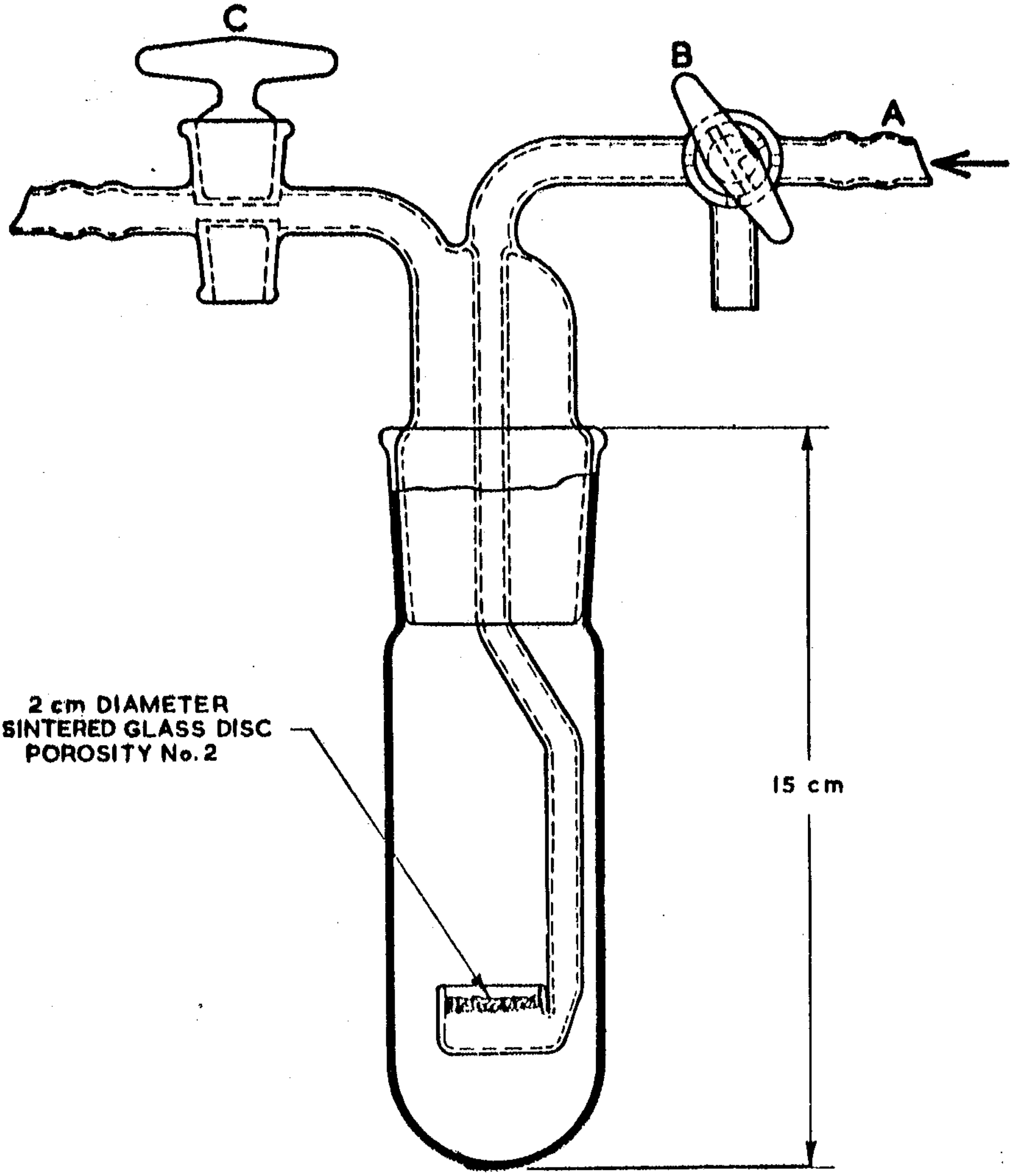

Fig. 1