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DETERMINATION OF DISSOLVED OXYGEN IN LUBRICATING FLUIDS

J. C. White
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ABSTRACT

The volume of dissolved or entrained oxygen in some lubricating fluids was determined by displacing the insoluble gases in the fluids with carbon dioxide, following which, the oxygen in the insoluble gases was absorbed in potassium pyrogallate. The oxygen content for the lubricants under consideration ranged from a maximum of 42 μg of oxygen per ml of fluid to a minimum of 15 μg per ml. The coefficient of variation of this method was about 7 per cent.

DETERMINATION OF DISSOLVED OXYGEN IN LUBRICATING FLUIDS

J. C. White, A. S. Meyer, Jr., and B. L. McDowell

In the circulation of alkali metal systems, a knowledge of the volume of dissolved or entrained oxygen in the fluids which are used in lubricating the pump parts appears to be essential. The possibility exists that the helium cover gas displaces the oxygen in the lubricant and thereby increases the oxygen content of the cover gas. Since the cover gas must be as free of oxygen as possible, and much effort is expended to insure this purity, all possible sources of oxygen contamination should be investigated. In this connection, the concentration of dissolved oxygen in lubricating fluids was desired to ascertain the maximum amount of oxygen that would conceivably be added to the cover gas through this media.

EXPERIMENTAL

The determination of dissolved oxygen in lubricating fluids was carried out in a closed system, in which the gases, which are insoluble in potassium hydroxide solution, hereafter referred to as "insoluble gases," in the oil are swept by carbon dioxide into an azotometer which is filled with a solution of potassium hydroxide. The insoluble gases are equilibrated with a solution of potassium pyrogallate, from which the change in volume of gas is attributed to absorption of oxygen in the potassium pyrogallate solution.

Apparatus

The apparatus for this determination is shown in Figure 1.

1. Carbon dioxide generator. A 2-liter Dewar flask filled with crushed solid carbon dioxide. The flask was sealed with a Hershberg[1] valve.

2. Flask "A." A 200-ml, round-bottom flask with a ground-glass joint at the top.

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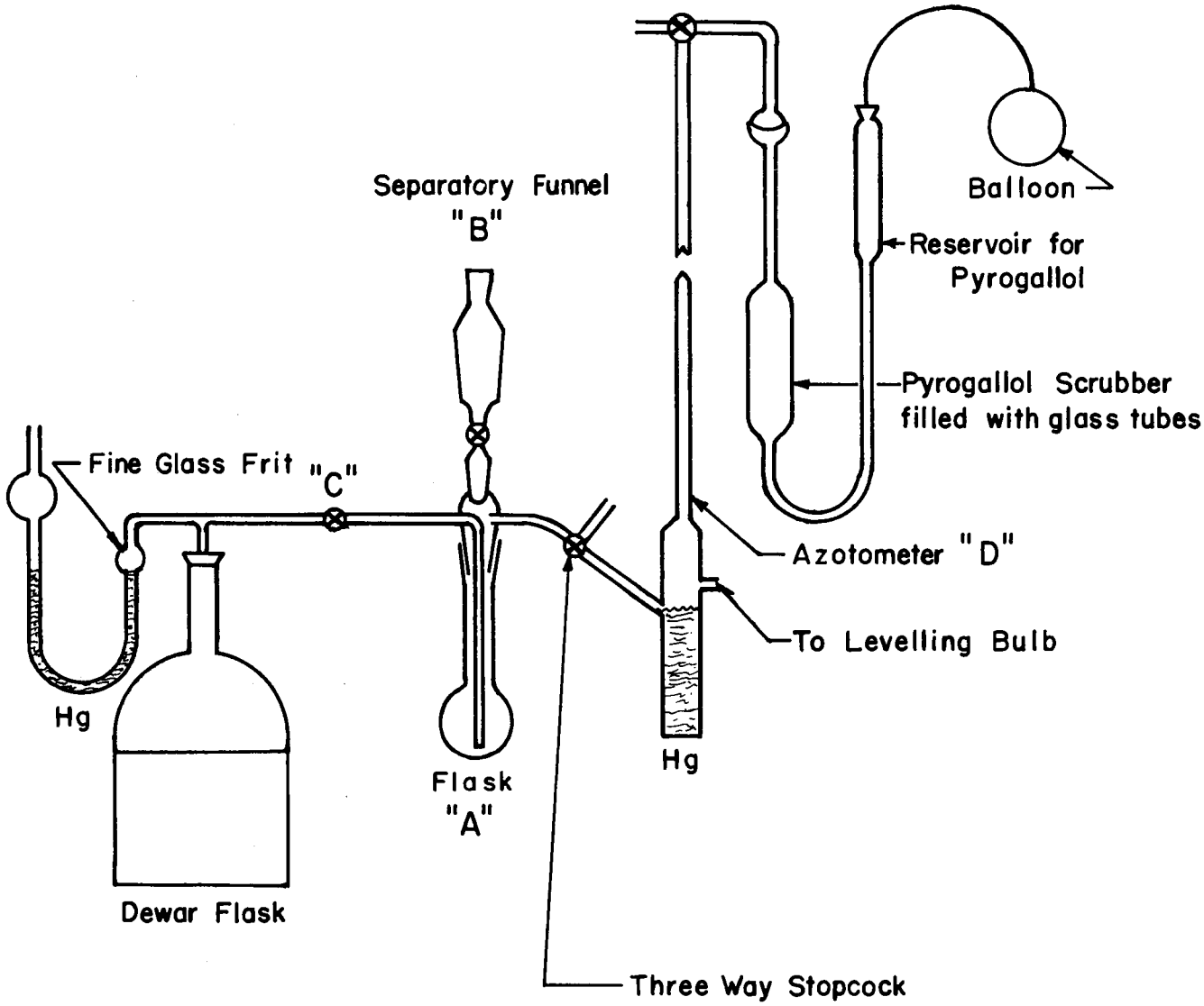

CARBON DIOXIDE GENERATOR

FIGURE 1 - APPARATUS FOR THE DETERMINATION OF DISSOLVED OXYGEN IN LUBRICATING FLUIDS

3. Separatory funnel "B." A 125-ml separatory funnel mounted on top of the round-bottom flask.

4. Azotometer "D." A 25-ml azotometer used to measure the gas which was evolved from the samples.

5. Pyrogallol scrubber and reservoir for pyrogallol. Both the pyrogallol scrubber and the reservoir for pyrogallol were especially fabricated for this apparatus.

Reagents

1. Potassium hydroxide (1:1 w/v). Dissolve 500 g of reagent grade potassium hydroxide in 500 ml of water.

2. Potassium pyrogallate. Dissolve 5 g of reagent grade pyrogallic acid in 100 ml of (1:1) KOH solution.

Procedure

1. Alternately evacuate and purge the round-bottom flask (A) of the apparatus with carbon dioxide three times.

2. Purge the entire apparatus (exclusive of the separatory funnel (B) for adding the oil sample) with carbon dioxide until micro-bubbles appear in the azotometer.

3. Equilibrate the small volume of gas insoluble in the KOH with the pyrogallol until no change in volume is noted. All oxygen is thereby removed from this volume of gas.

4. Place the sample of lubricant in the separatory funnel (B) which is mounted on top of the round-bottom flask (A).

5. With the stopcock (C) on the carbon dioxide generator closed, place crushed, solid carbon dioxide on the surface of the oil in order to create enough pressure to force the oil into the round-bottom flask when the separatory funnel is stoppered.

6. Allow carbon dioxide to bubble through the oil until micro bubbles appear in the azotometer (D). Heat the oil while purging with carbon dioxide.

7. Record the total volume of insoluble gas, the temperature, and barometric pressure.

8. Equilibrate the volume of insoluble gas with the solution of potassium pyrogallate by raising and lowering the leveling bulb (E) on the azotometer until the volume of gas remains unchanged.

9. Record the volume of gas, temperature, and pressure.

10. Calculate the loss in volume, attributed to oxygen, according to equation 1.

Calculations

Let V_1 = total volume of insoluble gas.

V_2 = volume of insoluble gas after equilibration with potassium pyrogallate.

T_1 = temperature, ^{o}C.

T_2 = standard temperature, 273 ^{o}K.

P_1 = pressure of the oxygen, mm.

P_2 = standard pressure, 760 mm.

$V_1 - V_2$ = volume of oxygen

$$V_1 - V_2 \times \frac{T_2}{273 + T_1} \times \frac{P_1}{P_2} = \text{volume of oxygen at STP} = V \qquad (1)$$

$$\frac{V}{22.4} \times 32 = \text{oxygen, mg.} \qquad (2)$$

Results

The dissolved oxygen content of some typical lubricants as determined by this method is shown in Table I. Samples of these fluids were taken directly from the containers in which the fluids were received.

Table I

Dissolved Oxygen Content of Some Lubricating Fluids

Type of Lubricant	Volume of Fluid, ml	Oxygen Volume, STP, ml	Oxygen Total, mg	Oxygen µg/ml Fluid	
Gulf I - A	50	1.20	1.72	34	
B	100	1.97	2.81	28	
C	100	2.21	3.16	32	31
Gulf II- A	100	2.56	3.65	37	
B	100	2.93	4.19	42	
C	100	2.62	3.74	37	39
Ucon I - A	100	2.04	2.91	29	
B	100	2.08	2.98	30	30
Ucon II- A	100	2.26	3.23	32	
B	100	2.13	3.04	30	31
Ucon 65 -A	100	1.77	2.53	25	
B	100	1.67	2.40	24	25
New Diffusion Pump Oil-A	100	1.40	2.00	20	
B	100	1.44	2.05	21	21
Recleaned Diffusion Pump Oil- A	100	1.05	1.50	15	
B	100	1.15	1.63	16	16

Coefficient of Variation, 7 per cent.

The oxygen content is essentially the same for each of the lubricants under consideration, ranging from a maximum of 42 µg of oxygen per ml of fluid to a minimum of 15 µg per ml. These results mean that under the most unfavorable conditions, that is, complete displacement of the oxygen in the fluid into the helium cover gas, approximately 160 mg of oxygen would be thus transferred per gallon of lubricant.

The presence of oxygen in these fluids is probably a consequence of the presence of dissolved air in the fluids. If so, the oxygen concentration should be approximately 20 per cent of the total insoluble gas volume. The oxygen concentrations of insoluble gases from these fluids are shown in Table II.

Table II

Oxygen Concentration Calculated from Insoluble Gases Found in Some Lubricating Fluids

Type of Lubricant	Oxygen, Per Cent
Gulf I	35
Gulf II	45
Ucon I	40
Ucon II	28
Ucon 65	28
Diffusion Pump Oil	30
Diffusion Pump Oil (recleaned)	17

The amount of oxygen in the insoluble gases from these fluids is larger than that which is ordinarily present in air. It is of interest to observe that the oxygen content of the insoluble gases from the recleaned diffusion pump oil most closely approximates that of air. It is possible to speculate that the oxygen is preferentially absorbed in these fluids with respect to nitrogen or, conversely, that nitrogen diffuses more rapidly than oxygen from the fluids.

In this connection, 100 ml of Ucon II (30 $\mu g\ O_2/ml$) was purged with helium for 4 hours, after which the oxygen concentration was redetermined. Only 4 $\mu g\ O_2/ml$ was found after this treatment. The total insoluble gas content was 19 $\mu g/ml$, which is less by a factor of approximately ten, than normally found for the fluids which were tested. This would indicate that degassing the lubricant with helium would be beneficial in removing dissolved oxygen from these lubricants.

DISCUSSION

No particular experimental difficulties were encountered in the use of this method for determining dissolved oxygen.

The evolution of gas from these fluids was fairly slow; however, five determinations can be carried out in an eight-hour period by means of a single apparatus.

PRECISION AND ACCURACY

Since the content of dissolved oxygen of the lubricants was not known, there is no way to evaluate the accuracy of the method. On the basis of duplicate determinations from the same sample, the coefficient of variation of the method is about 7 per cent, which is adequate for this purpose.

CONCLUSIONS

The procedure for the displacement of the insoluble gases in lubricants with carbon dioxide followed by equilibration of the insoluble gases with a solution of potassium pyrogallate is satisfactory for the determination of dissolved oxygen in lubricant fluids. Since no standard was available, no conclusion about the accuracy of the procedure can be drawn. The reproducibility was about 7 per cent.

REFERENCE

1. E. B. Hershberg and G. W. Wellwood, Ind. Eng. Chem., Anal. Ed. 9, 303 (1937).