Alternating Current Polarographic Determination of Dissolved Oxygen in Gasoline

By

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Introduction

In view of the well known fact that dissolved oxygen plays a very important role in petroleum refinery\textsuperscript{1)}, the present investigation was undertaken to establish a rapid and accurate method for the determination of dissolved oxygen in gasoline.

In 1924 Heyrovsky\textsuperscript{2)} first reported that dissolved oxygen is reduced at the dropping mercury electrode to produce two waves\textsuperscript{3)}. The first wave results from reduction to hydrogen peroxide:

\[ \text{O}_2 + 2\text{H}^+ + 2e \rightarrow \text{H}_2\text{O}_2 \] (acid medium)

\[ \text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow \text{HO}_2^- + \text{OH}^- \] (neutral or alkaline medium).

The second wave corresponds to the reduction of the hydrogen peroxide either to water or hydroxyl ion, depending on the pH:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightarrow 2\text{H}_2\text{O} \] (acid medium)

\[ \text{HO}_2^- + 2e + \text{H}_2\text{O} \rightarrow 3\text{OH}^- \] (alkaline medium).

The diffusion currents are normally well-defined and show a linear dependence on oxygen concentration. However, three main difficulties are encountered in the application of a.c. polarography to the determination of oxygen in gasoline: the limited solubility of gasoline in aqueous or semi-aqueous electrolyte system, the exclusion of atmospheric oxygen in handling sample and the accurate calibration of calibration curve. The first difficulty was resolved by adopting a supporting electrolyte of sodium hydroxide in absolute alcohol and the second by the design of a special polarographic cell. Two ways of accurate calibration were investigated: by using water of known dissolved oxygen content directly as a calibration standard, and by using air-saturated alcoholic electrolyte as a secondary standard, the dissolved oxygen content being determined polarographically using water as a primary standard.

Experimental Part

Reagents. 1F sodium hydroxide: Prepare a 1F ethanolic solution of sodium hydroxide by dissolving 42.4 g of sodium hydroxide in absolute alcohol and diluting to 1 liter with this solvent. Air-saturated water of known oxygen content: For most purposes a published value can be assumed for the oxygen content\textsuperscript{4)}, but for more accurate work the dissolved oxygen should be determined by the Winkler method\textsuperscript{5)}. Air-saturated
water may be prepared by shaking a flask with water for several minutes, recording the temperature at which this is done. All other reagents were of extra-pure grade.

Apparatus. Polarograph: Polarograph used was the apparatus constructed by Yanagimoto Co. according to the Takahashi-Niki circuitry. The capillary used had an m value of 1.45 mg/sec and drop time of 5.40 sec/drop at -0.5 V vs. Hg.pool. When measured in an air-free 0.1 F sodium hydroxide solution containing ethanol at 64.5 cm of effective height of mercury \( (m^{2/3} t^{1/2} = 1.70 \text{ mg}^{2/3} \text{ sec}^{1/2}) \). All experiments were carried out in a thermostatic bath of 25 ± 0.1°C.

Sampling tube: A sampling tube connected to the polarographic cell is shown in Fig. 1. It comprises a tube of about 5-ml capacity with two 3-way taps C and D, so arranged that the sample is delivered through tap C to the polarographic cell. The volume of the sampling tube is determined by filling it with water and weighing.

Polarographic cell: This is also illustrated in Fig. 1. A specially designed cell is so arranged that the dropping electrode, sample inlet tube and stirrer are inserted through a tight-fitting stopper into the cell. It contains two taps A and B, A being a 3-way tap, the inlet of which is connected to an nitrogen supply and arranged so that the electrolyte can be deaerated. Tap A can also be connected to tap D of the sampling tube through
a teflon tubing and nitrogen is used to gently transfer the gasoline through taps A and B into the cell, the latter being connected by means of teflon tubing. A side arm is also provided for the anode connection.

Selection of medium. One has to select a solvent mixture of high oxygen solubility and low electric resistance. Many media proposed for the oxygen determination in a number of materials are listed in Table I.

As well known the a.c. peak height strikingly depends on the reversibility of electrode process and choice of the solvent is very important in a.c. polarography.

In Table II are listed the a.c. peak heights in various media, from which it is seen that the supporting electrolyte of ethanol-sodium hydroxide system proposed is most suited.

Removal of oxygen dissolved in electrolyte-solvent. Only 15 to 20 min. bubbling of dry nitrogen through the solution was sufficient to eliminate the dissolved oxygen as shown in Fig. 2.

Effect of sodium hydroxide. The composition of this electrolyte-solvent was further

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1F LiCl in MeOH : Benzene</td>
<td>Hal17)</td>
</tr>
<tr>
<td>2</td>
<td>0.1F LiCl in MeOH</td>
<td>Woodruff18)</td>
</tr>
<tr>
<td>3</td>
<td>0.1F TEAI in EtOH</td>
<td>Usam19)</td>
</tr>
<tr>
<td>4</td>
<td>0.1F NaClO4 in EtOH</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.1F LiClO4 in EtOH</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1F NaOH in EtOH</td>
<td></td>
</tr>
</tbody>
</table>

Oxygen concentration : 10 ppm

<table>
<thead>
<tr>
<th>Electrolyte-solvent (No.)</th>
<th>A.C. peak height (μU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.0</td>
</tr>
<tr>
<td>2</td>
<td>60.1</td>
</tr>
<tr>
<td>3</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>25.5</td>
</tr>
<tr>
<td>5</td>
<td>70.0</td>
</tr>
<tr>
<td>6</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Oxygen concentration : 10 ppm

Fig. 2. Alternating current polarograms of oxygen
modified by increasing the sodium hydroxide content, since the a.c. polarography requires a high conductivity of the basal solution. Reduction waves of oxygen were recorded at various concentrations of sodium hydroxide from 0.05 F to 0.5 F in the solutions containing ethanol and 10 ppm oxygen. The a.c. peak height of oxygen varied with concentrations of sodium hydroxide as shown in Fig. 3.

As shown in Fig. 3, in the range of concentration of sodium hydroxide from 0.2 F to 0.5 F the a.c. peak height has a constant value, and the optimum concentration of sodium hydroxide was found to be 0.5 F sodium hydroxide.

Influence of cell resistance. Let $Z_F$ be the faradaic impedance of the dropping mercury electrode due to oxygen, and $R$ the cell resistance. Then,

$$
\frac{1}{I_{Ac}} = Z_F + R
$$

It is evident from Fig. 4 that the a.c. peak heights are independent of electrode distance and the above electrolyte-solvent has a sufficiently high electric conductance.

Calibration curve. Take 40 ml of 0.5 F sodium hydroxide and 5 ml of gasoline into the polarographic cell. Fit the stopper to the cell, close tap B and degas the solution by turning tap A and bubbling nitrogen through the electrolyte for 10 min. Close tap A. Introduce 5 ml of air-saturated distilled water at a known temperature by means of a microburette through the tap B, close the tap B, and then stir the solution rapidly by a motor-driver stirrer. When a homogeneous solution is obtained, polarographed
in the region of applied potential from 0.0 to -2.0 volt against the mercury pool anode. Empty the all after the measurement.

Take 40 ml of 0.5 F sodium hydroxide, 5 ml of gasoline and 1 ml of water into the polarographic cell and degas with nitrogen via tap A for 10 min. Close the tap A measure the wave height due to any residual oxygen. Introduce 4 ml of air-saturated water by means of a microburette through tap B, stir and record the wave height of the resulting polarogram.

Repeat this procedure with 40 ml of 0.5 F sodium hydroxide/5 ml of gasoline/2 ml of water, with 40 ml of 0.5 F sodium hydroxide/5 ml of gasoline/3 ml of water and with 40 ml of 0.5 F sodium hydroxide/5 ml of gasoline/4 ml of water, degas, then add 3 ml, 2 ml and 1 ml of water, respectively. The calibration curve is shown in Fig. 5.

![Calibration curve for oxygen](image)

**Fig. 5. Calibration curve for oxygen**

**Temperature**: 25 ± 0.1°C  
**Atmosphere**: 776.3 mmHg

**Results and Discussion**

The procedure for the determination of dissolved oxygen in gasoline is as follows.

1. Connect the sample tube and tubing to the sampling point with teflon tubing (Notes 1 and 2) and rinse the inside of the tubs. Close tapes C and D so that the tube is completely filled with gasoline.

2. Take 40 ml of 0.5 F sodium hydroxide solution and 5 ml of water into the polarographic cell. Fit the rubber stopper to the cell and close tap B. Degas the system by passing nitrogen through tap A and the solution for 10 min. Close tap A and record the a.c. polarogram of the solution in the region of applied potential from 0.0 to -2.0 volt.

3. Connect the sampling tube to the cell with teflon tubing between tap B and C and between taps A and D. Turn tap A so that nitrogen passes through tap D into the atmosphere for about 1 min, then close tap D and open taps B and C and purge with nitrogen for the same period. Close taps B and C. Close tap A to the cell and turn it to the teflon connection between A and D, opening taps D and C in that order and then open tap B in such a manner that the sample is very slowly added to the cell. Close tap B after the addition of sample.
Record the a.c. polarogram in the range from 0.0 to −2.0 volt at a sensitivity to give a maximum wave and read the concentration of oxygen by consulting the calibration graph shown in Fig. 5.

Calculation

Let \( a \) be the mg of oxygen from the graph and \( v \) be the volume of sample. Hence

\[
\text{ppm w/v} = \frac{a \times 10}{v}
\]

Notes

1. Avoid the use of rubber tubing and silicone tap grease because this interferes with the polarographic determination.
2. The length of teflon tubing should be kept to a minimum because it is permeable to oxygen.
3. A. C. polarogram must be record within 40 min

Finally, a comparison of the a.c. polarographic and chemical methods\(^{11}\) was made. In the latter, oxygen dissolved in the sample gasoline was displaced into an acid solution of 0.01 \( F \) chromous chloride by a stream of nitrogen.

The chromous chloride solution was added to a solution of iron (III) alum and the resulting ferrous iron, was titrated with a standard solution of carium (IV) sulphate using ferroin as an indicator. The change in the chromous ion concentration before and after the oxygen absorption is equivalent to the amount of the oxygen contained in the sample solution. Comparison of the two methods is shown in Table III.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Volume of sample gasoline taken at 15°C* (ml)</th>
<th>Oxygen content determined (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>By polarography</td>
</tr>
<tr>
<td>24.0</td>
<td>4.947</td>
<td>25.65</td>
</tr>
<tr>
<td>25.0</td>
<td>4.941</td>
<td>25.63</td>
</tr>
<tr>
<td>24.3</td>
<td>4.945</td>
<td>25.65</td>
</tr>
<tr>
<td>25.0</td>
<td>4.941</td>
<td>25.63</td>
</tr>
<tr>
<td>24.3</td>
<td>4.945</td>
<td>25.64</td>
</tr>
</tbody>
</table>

Average 25.64
Coeff. of var. 2.01%

* The temperature of the sample gasoline is measured and its volume at 15°C is calculated by the equation,\(^{14,15}\)

\[
V_t = V_{15} [1 + 0.0012(t - 15)]
\]

These results show a fairly good agreement, but the speed at which determinations can be completed by polarography is comparable to the chemical method. One determination can be carried out within an hour

Acknowledgement

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交流ポーラログラフ法によるガソリン中の溶存酸素の定量

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Heyrovsky によってはじめて酸素の還元波が発見されて以来、その還元機構については多数の研究者によって検討されて来たが、しかし交流ポーラログラフ法によるガソリン中の溶存酸素の定量は行なわれていない。そこで著者らは、市販ガソリンを適当な溶媒を用いて溶液化し、それをそのまま交流ポーラログラフ法に適用することを検討した。その結果の一例としてガソリン中に含まれる溶存酸素の定量分析について以下に詳細を報告する。

装置；酸素の加圧装置（AP-20 型）に同社製ガルベレーター143 型を接続して使用。実験条件；水銀柱の高さ65.4cm、滴下時間が4.0±0.2秒、温度；
25±0.1°C，Span 電圧；2.0 Volt である。電解ビンおよび試料管はFig.1 に示す特別なデザインのものを
使用した。溶液；精製したエチルアルコールを使用。支持電解質；水酸化ナトリウムの特級品のものを使用した。

基礎波の検討；過去の文献を参考にし、特にガソリ
ンと混和性のある溶媒を選ぶように心がけ、アスピ
レーターにて空気を温度既知の蒸留水に吸引しながら
溶解した空気飽和水溶液を作り、ウィンクル法にて
濃度を決定した。50 mlメスフラスコに空気飽和水溶液
を5 ml 採取し、Table I に示すおおよその溶媒で標
線まで希釈して、それぞれの交流ポーラログラムを記
録した (Fig.2)。その結果として、希釈剤す支持電解
質として、エチルアルコール・水酸化ナトリウムを得
た (Table II)。

電極間の距離が交流波高におよぼす影響；電極間距
離を 2 から24mm まで変化させ交流波高を観察した。
横軸に電極間距離をとり、縦軸を交流波高の逆数をプロ
ットした。その結果、余り変化がないので以下5 mm
で一連の実験を行なった。

検量線によるガソリン中の溶存酸素の定量；50 ml
メスフラスコを使用し、ガソリンを便利ビペットで5
ml 採取し、上記の基礎波で標線まで希釈して、電解
供試液を調製した。この電解液をよく混合したのち、
電解ビンに移し、溶存酸素は窒素ガスを20分間通して
除去し、交流ポーラログラムを記録した。さらに精度
既知の空気飽和水溶液を適当量添加して検量線を作成
した。最後に、窒素通気を行なった基礎波 40 ml と
蒸留水 5 ml に、酸素除去を行なっていない試料ガソ
リンを別の試料管 (容積 5 ml) に採取した電解供試
液の交流ポーラログラムを記録して検量した (Table
III)。

以上の結果、本定量法は次の諸点において旧来の定
量法に比較して特徴をもつことを明らかにした。 (1) 従
来の定量法に比べ、操作が簡単である。 (2) 本法の分析
所要時間は、1 試料 1 回 1 時間以内で、かつ再現性よ
く定量できる利点がある。

（日本分析化学会，第20年会において発表）