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Ultraviolet Spectrophotometric Determination of Sulfur Dioxide in Sulfuric Acid

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It was found that a specific ultraviolet absorption band is shown in the concentrated sulfuric acid solution and that this absorption is due to the sulfur dioxide dissolved in the sulfuric acid.

After the effects of the acid concentration on the spectrum of sulfur dioxide were investigated, a method for spectrophotometric determination of sulfur dioxide was studied. Beer's law is obeyed up to about 100 p.p.m. of sulfur dioxide.

Good results were obtained for the known sample and this method was then applied to the determination of sulfur dioxide which was accompanied with commercial sulfuric acid.

The proposed method is simple in procedure, and may be applied not only to the simple test for the purity of the sulfuric acid but also to the direct determination of sulfur dioxide dissolved in the sulfuric acid.

INTRODUCTION

The present paper deals with the study on the ultraviolet spectrophotometric determination of sulfur dioxide in the sulfuric acid. The specific absorption spectrum in the ultraviolet region has been observed in some of the sulfuric acid used in the laboratory, and it has been found that this absorption is due to the sulfur dioxide dissolved in the sulfuric acid. The absorption spectra of sulfur dioxide in various concentrations of sulfuric acid were measured and the various factors for quantitative determination, such as acidity, time of standing and diverse ions, were then studied. A calibration curve was made and Beer's law is obeyed up to 100 p.p.m. of sulfur dioxide in the sulfuric acid.

The proposed method was applied to the determination of sulfur dioxide which was contained in the commercial sulfuric acid. The method is simple in procedure and is advantageous in that it requires no coloring reagents.

EXPERIMENTAL AND RESULTS

Apparatus and Materials

Spectrophotometric measurements were made with a Beckman quartz spectrophotometer, model DU, with 1 cm silica transmission cells with stoppered
cover. The stock solution of sulfur dioxide was prepared as follows. The
gaseous sulfur dioxide, obtained by the addition of sulfuric acid to the metallic
copper, was absorbed into distilled water after washing through sulfuric acid.
The concentration of the sulfur dioxide in the solution was determined by the
titrimetric measurement using the standard potassium bromate solution. As the
factors may be changed during the standing of several days, the determination
of factor of the stock solution was conducted just before the each use for the
investigation.

Absorption Spectra

Some of the absorption spectra obtained are shown in Fig. 1. Curve 1 is a
spectrum of first grade reagent of sulfuric acid for chemical research and curve

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectrum.png}
\caption{Absorption spectra.}
\label{fig:spectrum}
\end{figure}

1: Ist grade reagent of sulfuric acid for chemical research.
2: Special grade reagent of sulfuric acid for chemical research.
3: SO$_2$ in concentrated sulfuric acid.
4: SO$_2$ in distilled water.
5: The solution which was obtained by heating the sulfuric acid
corresponding to Curve 1.

2 is that of special grade one. Both sulfuric acid solutions were used for absorp-
tion measurements without any dilution. Curve 3 is a spectrum of the solution
which was prepared by addition of sulfur dioxide solution to the concentrated
sulfuric acid (corresponding to Curve 2) according to the procedure described
later. Curve 4 is a spectrum of aqueous sulfur dioxide solution. The absorption
band in Curve 1 disappered after the solution was heated to fume, as seen in
curve 5. All of the five curves were obtained against distilled water. From
these spectra it can be said that the absorption spectrum of 1st grade reagent of
sulfuric acid is due to the sulfur dioxide dissolved in the sulfuric acid, beacuse
of the coincidence of the wave length of the maximum absorption (280 m$\mu$)
between Curves 1 and 2, and to the resemblance of the shape of both absorption
curves.

In order to investigate the effects of changes in the concentration of sulfuric
acid on the spectrum, a series of spectra was measured for the solution containing
the known amounts of sulfur dioxide with various concentrations of sulfuric acid.
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The sample solutions for the measurements of absorption spectra were prepared by the addition of known volumes of the stock solution of sulfur dioxide to the sulfuric acid. To prevent the evolution of heat, the addition of sulfur dioxide solution to the sulfuric acid of required concentration was carefully done, drop by drop, cooling the flask in water. The resulting solution was diluted to the volume by distilled water under the same care.

Several curves obtained are shown in Fig. 2 and bathochromic effects were observed when the concentration of the sulfuric acid is increased. The wavelength of maximum absorption shifts from 275 m\(\mu\) to 280 m\(\mu\) as the acid concentration is changed from 1 N to 36 N. The absorbance rises with the sulfuric acid concentration up to about 7 N, but then begins to decrease. The correlation of the absorbance to the acid concentration was further investigated in detail, as shown in Fig. 3. The absorbance is at its maximum when the concentration of the sulfuric acid is about 10 N. The reason for the changes of absorption may be attributed to the difference of dissolved state of sulfur dioxide by the variation of the sulfuric acid concentration.

**Calibration Curve**

The calibration curves were made at appropriate wave lengths such as 220, 278 and 290 m\(\mu\), according to the above procedure on samples containing known amounts of sulfur dioxide with the constant concentration of sulfuric acid, respectively. Results shown in Fig. 4 gave a straight line over the range of 20 to 100 p. p. m. in the case of 9 or 19 N of sulfuric acid, but when the acid concentration was held so high as 26 N, Beer’s law was obeyed up to about 80 p. p. m. of sulfur dioxide.
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Fig. 4. Calibration curve 1. Fig. 4. Calibration curve 2. Fig. 4. Calibration curve 3.
Concentration of H$_2$SO$_4$ : 
9.18N.

Concentration of H$_2$SO$_4$ : 
14.68N.

Concentration of H$_2$SO$_4$ : 
25.69N.

Time of Standing

The effects of time of standing to the absorbance were examined for the solution containing known amounts of sulfur dioxide and of sulfuric acid. The absorbance measurements were done at appropriate wave lengths. It is observed, as shown in Table 1, that the absorbance remains practically constant for 2 days or for several hours, in both cases, when the solution was kept in the stoppered

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Time</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>220 m$\mu$</td>
</tr>
<tr>
<td>SO$_2$ : 81.6 (p.p.m.)</td>
<td>0 hr.</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>4 hr.</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>48 hr.</td>
<td>1.002</td>
</tr>
<tr>
<td>H$_2$SO$_4$ : 14.68 N</td>
<td>With stoppered</td>
<td>96 min.</td>
</tr>
<tr>
<td></td>
<td>5 min.</td>
<td>0.410</td>
</tr>
<tr>
<td></td>
<td>4 min.</td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td>14 min.</td>
<td>0.366</td>
</tr>
<tr>
<td></td>
<td>30 min.</td>
<td>0.348</td>
</tr>
<tr>
<td></td>
<td>58 min.</td>
<td>0.306</td>
</tr>
<tr>
<td></td>
<td>96 min.</td>
<td>0.256</td>
</tr>
<tr>
<td></td>
<td>136 min.</td>
<td>0.215</td>
</tr>
<tr>
<td>SO$_2$ : 47.3 (p.p.m.)</td>
<td>0 min.</td>
<td>0.406</td>
</tr>
<tr>
<td></td>
<td>5 min.</td>
<td>0.407</td>
</tr>
<tr>
<td></td>
<td>10 min.</td>
<td>0.399</td>
</tr>
<tr>
<td>H$_2$SO$_4$ : 14.68 N</td>
<td>Without stoppered</td>
<td>28 min.</td>
</tr>
<tr>
<td></td>
<td>28 min.</td>
<td>0.397</td>
</tr>
<tr>
<td></td>
<td>45 min.</td>
<td>0.392</td>
</tr>
<tr>
<td></td>
<td>60 min.</td>
<td>0.394</td>
</tr>
<tr>
<td></td>
<td>120 min.</td>
<td>0.395</td>
</tr>
</tbody>
</table>
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flask, or one without stopper, if the acid concentration is so high as 15 N. If the solution containing more dilute acid was kept standing without stopper, the absorbance considerably decreases during the several hours, probably due to the liberation of sulfur dioxide.

Diverse ion

The effects of some diverse ions, which are often accompanied with the sulfuric acid, were investigated. The absorption spectra of arsenic (III), selenium, iron (II), iron (III), nitrate, nitrite and chloride in the concentrated sulfuric acid solution were obtained, as shown in Fig. 5. Absorbance measure-

![Absorption spectra of diverse ion in 9.18N sulfuric acid.](image)

ments were also made for the solution containing proper amounts of some of the above elements, with known quantity of sulfur dioxide. Chloride ion was present in solution as natrium salt, and arsenic (III), iron (II), and iron (III) were added as arsenious acid, Mohr’s salt and ferric alum, respectively. It is found that the presences of the above salts do not interfere the determination of sulfur dioxide. Even when small amount of iron (III) is present, which is seemed to interfere seriously because of intense absorption in a given region, a considerable good result was obtained by correction as follows. As previously reported by us,\(^1\) Beer’s law was obeyed for iron (III) when its amounts were as small as several parts per million in the considerable concentrated sulfuric acid solution, being the acid concentration kept constant. The absorbance corresponding to iron (III) present with sulfur dioxide can be calculated at respective wave lengths as below.

\[
A = B \times \frac{C}{D}
\]

where A, the Absorbance corresponding to iron (III) at 220 m\(\mu\); B, the Absorbance obtained for mixed solution at 320 m\(\mu\); C, the Absorbance of 10 p.p.m. of iron (III) at 220 m\(\mu\) (Fig. 5); D, the Absorbance of 10 p.p.m. of iron (III) at 320 m\(\mu\) (Fig. 5). At other wave lengths, such as 278 m\(\mu\), and 290 m\(\mu\) the absorbances corresponding to iron (III) can be calculated by the samy way. The absorbance corresponding to sulfur dioxide is obtained by substructing the value of the absorbance of iron (III) (A) from that of mixed solution measured, and the concentration of sulfur dioxide is determined according to the calibration.
curve.

This calculation was, however, done based on the assumption that any interaction do not occur between iron (III) and sulfur dioxide, although iron (III) is usually reduced by sulfur dioxide when their concentrations are considerably high. The determination of sulfur dioxide was attempted according to the above calculation when 5 p.p.m. of iron (III) was present with 36.1 p.p.m. of sulfur dioxide. The results are shown in Table 2. The amounts of sulfur dioxide found approximately accord with that of the present ones, indicating the reasonability of the assumption above mentioned.

<table>
<thead>
<tr>
<th>Diverse ions</th>
<th>Concentration of H$_2$SO$_4$ (p.p.m.)</th>
<th>SO$_2$ Taken (p.p.m.)</th>
<th>Wave length (m$\mu$)</th>
<th>Absorbance</th>
<th>SO$_2$ Found (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$ (500 p.p.m.)</td>
<td>9.18 N</td>
<td>36.1</td>
<td>278</td>
<td>0.345</td>
<td>36.1</td>
</tr>
<tr>
<td>As$^{3+}$ (50 p.p.m.)</td>
<td>290</td>
<td>28.9</td>
<td>278</td>
<td>0.250</td>
<td>29.2</td>
</tr>
<tr>
<td>Fe$^{2+}$ (10 p.p.m.)</td>
<td>14.68 N</td>
<td>36.1</td>
<td>278</td>
<td>0.196</td>
<td>30.8</td>
</tr>
</tbody>
</table>

Analysis of the Sample

Standard procedure

Five ml of the sample of sulfuric acid (concentrated) are pipetted into a 20 ml of volumetric flask containing about 10 ml of distilled water, drop by drop, and then diluted to the volume with water. To prevent the evolution of heat, the above procedure was conducted by cooling the flask in water. After

<table>
<thead>
<tr>
<th>No. of Sample</th>
<th>Wave length (m$\mu$)</th>
<th>Absorbance</th>
<th>SO$_2$ Found (p.p.m.) (in the Conc. H$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>278</td>
<td>0.198</td>
<td>84.0</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.136</td>
<td>82.0</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>0.280</td>
<td>81.8*</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.203</td>
<td>81.8*</td>
</tr>
<tr>
<td>2</td>
<td>278</td>
<td>0.011</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.008</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>0.022</td>
<td>1.0*</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.019</td>
<td>1.0*</td>
</tr>
<tr>
<td>3</td>
<td>278</td>
<td>0.002</td>
<td>Absent*</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.002</td>
<td>Absent*</td>
</tr>
<tr>
<td>4</td>
<td>278</td>
<td>0.000</td>
<td>Absent*</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.000</td>
<td>Absent*</td>
</tr>
</tbody>
</table>

* When 8 ml of sample was taken.
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being mixed thoroughly, the absorbance of the solution are measured at 278 m\(\mu\) (or at 220, 290 m\(\mu\)) against water. The amount of sulfur dioxide is obtained according to the calibration curve in Fig. 4.

Applying the method to some of the commercial sulfuric acid, the amount of sulfur dioxide contained in the sample was determined, and the results are shown in Table 3. It resulted in that the first grade reagent of sulfuric acid often contained considerable amounts of sulfur dioxide, but for the special grade one the presence of it was not identified.

SUMMARY

A new spectrophotometric determination of sulfur dioxide is presented. The method is based on the measurements of absorption due to the sulfur dioxide dissolved in the sulfuric acid.

Some of the results obtained are as follows.
1. Sulfur dioxide has shown a specific absorption band with the maximum of 280 m\(\mu\) when it is dissolved in the considerably concentrated sulfuric acid.
2. Bathochromic effects were observed as the acid concentration increased, that is, the wave length of maximum shifts from 275 m\(\mu\) to 280 m\(\mu\) when the acid concentrations are changed over the range of 1 N to 36 N.
3. The absorbance at appropriate wave lengths has shown maximum value when the acid concentration was held in about 10 N.
4. Beer's law is followed up to about 100 p.p.m. of sulfur dioxide when the acid concentration was kept constant.
5. Some elements such as arsenic (III), selenium and iron (II) which are often contained in the sulfuric acid, do not interfere the determination. Iron (III) interferes seriously, but even when it was present as little as several parts per million, the determination of sulfur dioxide could be done by suitable correction.
6. The method was applied to the analysis of commercial sulfuric acid.

REFERENCE