AN IMPROVED METHOD OF COLORIMETRIC DETERMINATION OF HYDROGEN SULFIDE IN AIR

Haruhiko SAKURAI* and Toshio TOYAMA*

比較法による空気中硫化水素測定改良法
桜井治彦，外山敏夫

環境空気中硫化水素の簡便且つ正確な測定法を開発する目的で，既存のモリブデン酸アンモン法を検討し，鉱敏度及び再現性を犠牲にすることなく，モリブデン酸アンモン法の簡便性を生かし得る条件を知り，作業現場及び大気汚染監視に有用な改良法を得た。

Since hydrogen sulfide is emitted as a waste product in various industries such as the manufacture of viscose rayons and dyes, and the vulcanization of rubber, a suitable method of analysis is practically required by the industrial health workers. In order to monitor ambient air in a plant, it is necessary to take many samples and to analyze them accurately and rapidly. The analytical method, therefore, must be simple and reproducible without much sacrifice of sensitivity and accuracy.

Although vast literatures exist concerning the determination of sulfur or sulfides, relatively few of them have reported the method of determination of hydrogen sulfide in air. These are mainly iodometric methods, methylene blue methods, lead acetate paper methods, and molybdenum blue methods.

Since 1960, Research Committee on Occupational Health in Japan Chemical Fibres Association has been examining several methods which were used independently in many laboratories. The purpose of the examination has been to select the most suitable method from the standpoint of industrial hygienists.

In 1961, the molybdenum blue method was selected as the most satisfactory. The method employs colorimetric determination of the blue colour, which develops when hydrogen sulfide is passed through the ammonium molybdate reagent. The merit of the method as has been found in the examination is in its simplicity and high reproducibility, because it needs only one process to develop the colour. However, it is not sufficiently sensitive, requiring over 400 ml of the sample air to determine gas concentration around 20 ppm. And, in addition to it, the complete development of the colour takes as long as four hours at the room temperature. Later, it was, moreover, found that the method had not yet been sufficiently exploited to yield the maximum sensitivity.

The purpose of this paper is: (1) to describe the data which may contribute to the improvement of the method, and (2) to present an improved method which may be used satisfactorily in industrial hygiene laboratories.

*from the Department of Preventive Medicine and Public Health, Keio University School of Medicine, Tokyo
*慶応大学医学部衛生学教室衛生学教室
昭和38年8月23日受付，普通授業
Sensitivity

Following three factors should be considered to determine the sensitivity of the molybdenum blue method when the same amount of air is sampled:
(1) concentration of ammonium molybdate,
(2) acidity of the reagent,
(3) kinds of acid which is used to adjust the acidity.

In this paper test results are presented as regards various combinations of ammonium molybdate concentrations and sulfuric and hydrochloric acidities.

(a) Sulfuric acidity

The same amounts of sodium sulfide solution were added to forty-eight combinations of ammonium molybdate and sulfuric acid concentrations. After four hours, absorbances were determined at each peak wave length.

As shown in Table 1 and Figure 1, two kinds of colour developed. For greenish blue, the peak wave length was 700-720 mμ, and for violet 580 mμ. The absorbance was distinctly higher when the violet colour developed, and was the highest at a combination of 3.2% ammonium molybdate and 0.666 N sulfuric acid.

(b) Hydrochloric acidity

To thirty combinations of ammonium molybdate and hydrochloric acid concentrations, the same amounts of sodium sulfide as in the case of sulfuric acid were added. After four hours, the absorbances were read at each peak wave length.

![Graph showing absorption spectra](image)

**Fig. 1 Two kinds of absorption spectrum in the case of H₂SO₄**

*(obtained by Beckman Type 3 Spectrophotometer)*

<table>
<thead>
<tr>
<th>H₂SO₄</th>
<th>Concentration of Ammonium Molybdate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
</tr>
<tr>
<td>0.042N</td>
<td>0.225 (700 mμ)</td>
</tr>
<tr>
<td>0.083N</td>
<td>0.154 (720 mμ)</td>
</tr>
<tr>
<td>0.167N</td>
<td>no colour</td>
</tr>
<tr>
<td>0.333N</td>
<td>no colour</td>
</tr>
<tr>
<td>0.666N</td>
<td>no colour</td>
</tr>
<tr>
<td>1.332N</td>
<td>no colour</td>
</tr>
</tbody>
</table>

As shown in Table 2, the peak wave lengths were in a range between 700 and 720 mμ. The highest absorbance was gained at the concentration of 1.6% ammonium molybdate and 0.2 N hydrochloric acid.

(c) Comparison of sulfuric acidity with
Tab 2. Sensitivity Test (2) HCl
(Absorbances at Peak Wave Length)

<table>
<thead>
<tr>
<th>HCl</th>
<th>Concentration of Ammonium Molybdate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
</tr>
<tr>
<td>0.05 N</td>
<td>0.245 (700 μm)</td>
</tr>
<tr>
<td>0.1 N</td>
<td>0.178 (720 μm)</td>
</tr>
<tr>
<td>0.2 N</td>
<td>no colour</td>
</tr>
<tr>
<td>0.4 N</td>
<td>no colour</td>
</tr>
<tr>
<td>0.8 N</td>
<td>no colour</td>
</tr>
</tbody>
</table>

hydrochloric acidity.

From Table 1 and 2, it is clear that higher absorbance is achieved in the case where sulfuric acid is used. The peak wave length was 580 μm for sulfuric acid, and 710 μm for hydrochloric acid at the combination showing the highest absorbance respectively. When the capacities of usual spectrophotometer or the characteristics of filters are taken into consideration, 580 μm is more convenient than 710 μm for quantitative analysis. By these reasons, it comes to a conclusion that the sulfuric acidity is preferable to the hydrochloric acidity.

(d) Choice of the most sensitive condition in case of the sulfuric acidity

In order to decide the most sensitive condition from the practical point of view, detailed examinations were made over narrower range of the concentration.

Table 3 shows that the highest absorbance is obtained when ammonium molybdate is 2.5% and sulfuric acid is 0.4 N in concentration.

Standing Time for the Colour Development

Before the improvement of this method it took as long as four hours to develop the colour at 25°C. However, the improved method with 2.5% ammonium molybdate and 0.4 N sulfuric acid was found to finish the colour development within fifteen minutes at 21°C (Figure 2).

![Graph showing absorbance over time](Fig. 2 Colour development at 21°C)

Absorption Efficiency

Another fault of the molybdenum blue method is its rather low absorption efficiency. Varying the concentration of ammonium...
molybdate and acid caused no effect on the absorption efficiency. In each case it was about 80% at a sampling rate of 100 ml per 50 seconds. Sampling rate had also little effect. Even when the rate was reduced to 100 ml per 5 minutes, the efficiency scarcely reached 90%.

When two bubbler were connected in series, however, the efficiency reached 95% at a sampling rate of 100 ml per 50 sec. This fact was also proved when the bubbled air was passed again through the same reagent in the same bubbler as before. To improve the absorption efficiency this twice-bubbling method is recommended for industrial hygiene laboratories, because it does not cause much trouble as compared with any other methods.

**Improved Method**

(a) Reagent

Dissolve 25.0 gm of ammonium molybdate in ca. 700 ml of distilled water, add 11.3 ml of 95% sulfuric acid and dilute to 1 liter with distilled water.

(b) Procedure

Transfer 4 ml of ammonium molybdate reagent to a midget bubbler which is designed to operate with reagent of an amount 10 ml or less. Care should be taken not to wet ground glass joint with the reagent, because the colour development may occur with silicate in the glass. Draw 200 ml of air sample at a sampling rate of 200 ml per 100 sec with 200 ml glass cylinder, and make this bubbled air in the cylinder pass again into the same reagent at the rate of 200 ml per 100 sec. Allow to stand for fifteen minutes. Then transfer the coloured reagent to a cuvette of 10 mm light path length and read absorbance at 580 mμ.

(c) Standard curve

Instead of hydrogen sulfide, standard sodium sulfide solution can be used. Dissolve ca. 2 gm of sodium sulfide in 1 liter of dis-
tilled water and measure the concentration of sulfur by iodometry. Prepare aliquots containing 1 to 10 μg of sulfur in 0.1 ml water, add 3.9 ml of the ammonium molybdate reagent, allow to stand for 15 minutes and determine absorbance at 580 μm.

The concentration as ppm by volume of hydrogen sulfide in air is calculated by the following equation when 200 ml of air is sampled:

\[
\text{ppm hydrogen sulfide} = 3.81 \times S
\]

where: S is expressed in micrograms of sulfur.

Plot the absorbance versus ppm of hydrogen sulfide. Typical standard curve is shown in Figure 3.

Summary

An improved colorimetric method for the determination of hydrogen sulfide in air is described.

Air sample is bubbled through ammonium molybdate reagent, and after fifteen minutes, the absorbance of molybdenum blue is read at 580 μm. This method is applicable to the estimation of hydrogen sulfide in a range of 5 to 50 ppm using 200 ml air sample. It is exceedingly suited for industrial hygiene laboratory work as well as air pollution monitoring because of its simplicity and reproducibility without any sacrifice of accuracy or sensitivity.

Reference