essential. Nitric oxide is oxidized to nitrogen dioxide by ozone, permanganate, or chlorine dioxide, and determined along with preformed nitrogen dioxide in a duplicate absorber and colorimeter system. Nitric oxide can then be found by difference. The method is highly specific for compounds that can yield nitrite in solution. The only likely interfering substances are alkyl or other organic nitrites. Care must be taken to avoid oxidation of nitrogen peroxide by an excess of ozone. The other oxidants appear to be less critical in this respect.

Comparison with other methods gave satisfactory agreement on Los Angeles air samples to which known amounts of nitrogen dioxide were added.

LITERATURE CITED

- (1) Bratton, A. C., Marshall, E. K., Jr., Babbitt, D., Hendrickson, A. R., J. Biol. Chem. 128, 537-50 (1939).
- Cadle, R. D., Johnston, H. S., Proc. Natl. Air Pollution Symposium, Second Symposium, pp. 28-34, Stanford Research Institute, Menlo Park, Calif., 1952.

- (3) Chambers, L. A., Foter, M. J., Cholak, J., Ibid., Third Symposium, pp. 24-32, 1955.
- Greiss, P., Ber. 12, 427 (1879)
- (5) Haagen-Smit, A. J., Fox, M. M., Ind. Eng. Chem. 48, 1484-7 (1956).
- (6) Hollings, H., Inst. Gas Engrs., Commun. No. 154, 6 pp. (1937).
 (7) Jacobs, M. B., "The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," pp. 355-9, Interscience, New York, 1949.
- (8) Morriss, F. V., Bolze, C., King, F., Division of Analytical Chemistry, Symposium on Air Pollution, 130th Meeting, ACS, Atlantic City, N. J., September 1956.
- (9) Saltzman, B. E., ANAL. CHEM. 26, 1949-55 (1954)
- (10) Shaw, J. A., IND. ENG. CHEM., ANAL. ED. 8, 162-7 (1936).
- (11) Shinn, M. B., Ibid. 13, 33-5 (1941).
- (12) Thomas, M. D., Hill, G. R., "Photosynthesis in Plants," J. Franck, W. E. Loomis, eds., pp. 20-25, Iowa State College Press, Ames, Iowa, 1949.

RECEIVED for review June 11, 1956. Accepted October 5, 1956. Supported by the Air Pollution Foundation, Los Angeles, Calif., the American Petroleum Institute, and Stanford Research Institute. Presented in part, Division of Analytical Chemistry, Symposium on Air Pollution, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

Ninth Annual Summer Symposium–Analysis of Industrial Wastes

Fixation of Sulfur Dioxide as Disulfitomercurate(11) and Subsequent Colorimetric Estimation

PHILIP W. WEST and G. C. GAEKE

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

Sulfur dioxide in the atmosphere is removed and concentrated by scrubbing through 0.1M sodium tetrachloromercurate(II). Stable, nonvolatile disulfitomercurate(II) is formed. The subsequent determination of the isolated sulfur dioxide is based on the redviolet color produced when p-rosaniline hydrochloridehydrochloric acid mixture (0.04% dye-6% concentrated acid) and formaldehyde (0.2%) are added to the sampling solution. The absorption maximum is at 560 $m\mu$ and the color is temperature-independent and stable for several hours. The method is sensitive (0.005 to 0.2 p.p.m. with a 38.2-liter air sample scrubbed through 10.0 ml. of sampling solution) and should be useful in the absolute determination of sulfur dioxide in air pollution surveys. Nitrogen dioxide is the only common interference.

QULFUR dioxide is almost without question the most impor-D tant of all air pollutants. It is an irritant gas that affects the upper respiratory tract, causing physical discomfort and even death. Four parts per million can readily be detected by odor; but as the nose becomes accustomed to it, the concentration necessary to produce a response increases. Eight to 12 p.p.m. will cause coughing and 20 p.p.m. will lead to eye irritation (4).

The toxicity of sulfur dioxide to man varies, apparently depending on the physical condition of the individual and on other factors. It has been considered a contributory cause of death in disasters such as those at London and Donora, Pa. The maximum allowable concentration is generally accepted as 10 p.p.m. However, sulfur dioxide may be toxic to vegetation in concentrations in the order of 2 or 3 p.p.m. and it is corrosive to metallic construction materials in concentrations of less than 1 p.p.m. Therefore, concentrations smaller than the stated maximum

allowable concentration may be highly objectionable and, under some circumstances, even dangerous.

The occurrence of sulfur dioxide in air is general. This results from its uses in bleaching, fumigation, refrigeration, manufacture of sulfuric acid, etc. Of special significance is the release of this gas as a by-product in the burning of sulfur-containing coals and oils and in the smelting of many ores. It is also released during the manufacture of paper by the sulfite process and in such chemical operations as the synthesis of phenol.

In spite of its significance, methods for the determination of sulfur dioxide in air are generally not too satisfactory, especially if complex industrial atmospheres are to be analyzed. The methods used may be divided into two main groups: based on its reducing properties, or on its acidic character or the acidic nature of its oxidation product.

One of the methods used in early pollution surveys was that of the Selby Smelter Smoke Commission (4). A sample of the atmosphere was drawn into a partially evacuated 20-liter bottle containing a few milliliters of a standard solution of iodine. The sulfur dioxide in the sample was absorbed by the iodine when the bottle was shaken vigorously. The excess iodine was determined by thiosulfate titration. The main method in use today is based on a similar procedure, in which the air sample is scrubbed through a standard solution of iodine and potassium iodide; and the excess iodine is determined by titration with standard this sulfate (3, 5). Many variations of this method have been proposed. However, there are several disadvantages in the use of iodine as an absorber. During the collection of the sample some iodine may volatilize; other reducing agents present in the air, such as hydrogen sulfide, react with iodine, and some iodide is oxidized to iodine by the air bubbling through the solution or by oxidants that may be present in the atmosphere.

Hydrogen peroxide has also been suggested as an absorber for sulfur dioxide (7). The reaction produces sulfate and hydrogen ions, and several methods are available for the determination of either of these ions. Again there are obviously a number of interferences, if a complex atmosphere is being sampled.

Aqueous solutions of alkali have also been used as absorbers. Nonvolatile sulfite ion is formed in this system and may be determined by several methods. Sulfite solutions, however, are unstable. The presence of alkali increases the instability, and when air is bubbled through such solutions, there is substantial loss due to increased contact with oxygen during the scrubbing operation.

The instability of sulfite solutions may be decreased by the addition of certain alcohols. Atkin (1) has used a solution containing 5% glycerol and 10% sodium hydroxide as a sulfur dioxide-absorbing solution and reports that oxidation is decreased. Urone and Boggs (8) have used a solution of 5% glycerol in 0.1N sodium hydroxide as the absorbing solution in their spectrophotometric determination of sulfur dioxide in air. These alcoholic alkali solutions have a tendency to froth and foam, because of their lowered surface tension, and, therefore, very low sampling rates must be used.

The sulfite content of these solutions is usually determined by a colorimetric procedure. The most common colorimetric reagent in use today is based on a sulfuric acid-bleached fuchsin reagent developed by Steigmann (θ). Both Atkin and Urone and Boggs have modified this reagent for work on air pollution.

In the present investigation, an attempt has been made to find an absorbing system which is efficient and, equally important, which forms a stable compound. At the same time, it was thought that an improvement in the sulfuric acid-bleached fuchsin reagent could also be made. A simple, rapid and reliable procedure was needed, that would allow the preservation of field samples for later analysis in the laboratory.

Feigl (2) mentions that disulfitomercurate(II) ion, $[Hg-(SO_3)_2]^{--}$, which is formed when sulfite is added to mercury(II) solutions, is very stable. In fact, even permanganate fails to oxidize the complex, except at a very slow rate. Complete information was not available, but this remarkable stability prompted further investigation, in the hope that an efficient method of isolation and determination of sulfur dioxide could be evolved.

EXPERIMENTAL

Reagents and Solutions. Sodium tetrachloromercurate(II), 0.1*M*. Reagent grade mercury(II) chloride (0.1 mole, 27.2 grams) and 0.2 mole (11.7 grams) of reagent grade sodium chloride are dissolved in water and diluted to 1 liter.

Hydrochloric acid-bleached p-rosaniline, 0.04%. Four milliliters of a 1% aqueous solution of p-rosaniline hydrochloride and 6 ml. of concentrated hydrochloric acid are mixed and diluted to 100 ml.

Formaldehyde, 0.2%. Five milliliters of 40% formaldehyde are diluted to 1000 ml. with distilled water.

Apparatus. Beckman Model DK-1 recording spectrophotometer.

Beckman Model B spectrophotometer.

Micro gas buret and gas dilution apparatus as described by Urone and Boggs (8).

Because complete information on the disulfitomercurate complex was not available, a thorough investigation was initiated into the use of solutions of mercury(II) salts as absorbers for sulfur dioxide. The compounds selected for the initial tests were mercury(II) chloride (a pseudo salt) and mercury(II) nitrate (a normal salt). It was found that with the chloride solution the complex is formed; but with nitrate, reduction to mercury(I) occurs. High concentrations of sulfur dioxide (in the order of 0.1% aqueous solutions) also tend to reduce small amounts of mercury(II) chloride. It is believed that the small concentration of free mercury(II) ion existing in the chloride solution accounts for the fact that complexation rather than reduction occurs. Because mercury(II) forms complexes easily with chloride, it was decided to determine the stability of the complex in solutions of various chloride strengths. A series of solutions (10.0 ml.) was prepared which were 0.1M with respect to mercury(II) chloride and contained various amounts of sodium chloride. One hundred micrograms of sulfur dioxide as sodium bisulfite and 0.1 ml. of an approximately 1% potassium permanganate solution containing a small amount of sulfuric acid were added and mixed. The solutions were allowed to stand for 1 hour and the absorbance of the remaining permanganate was determined at 520 m μ (solutions containing only sulfur dioxide and permanganate were almost completely decolorized instantly).



Figure 1. Effect of chloride concentration on stability of disulfitomercurate(II) complex



Figure 2. Rate of air oxidation of sulfur dioxide absorbed in sodium tetrachloromercurate(II) and in sodium hydroxide plus glycerol

The results of this experiment are shown in Figure 1, where absorbance is plotted against the molar ratio of sodium chloride to mercury(II) chloride. From this curve it can be seen that disulfitomercurate(II) ion is most stable in a solution corresponding to the composition of sodium tetrachloromercurate(II). Therefore, a 0.1M solution of sodium tetrachloromercurate(II) was chosen as the absorbing solution. The reaction involved in the absorption is thought to be an exchange reaction as shown by the equation

 $[\mathrm{HgCl}_4]^{--} + 2\mathrm{SO}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow [\mathrm{Hg(SO}_3)_2]^{--} + 4\mathrm{Cl}^- + 4\mathrm{H}^+$

The study of absorption efficiency was undertaken next.

Two scrubbers, each containing 10 ml. of 0.1M sodium tetrachloromercurate(II), were connected in series to the gas dilution apparatus. Air, containing various concentrations of sulfur dioxide, was passed through the scrubbers at different rates of flow. Fifty-liter samples were collected. The sample in the second scrubber was analyzed for sulfur dioxide. From the data shown in Table I it can be seen that tetrachloromercurate(II) is a very efficient scrubber for sulfur dioxide even at high flow rates, as shown by the fact that no sulfur dioxide escapes the first scrubber.

The effect of air oxidation on the disulfitomercurate(II) complex was next studied. For comparison purposes, the effect of air oxidation on sulfites in 0.1N sodium hydroxide containing 5% glycerol was also determined. Between 250 and 300 γ of sulfur dioxide were absorbed in 200 ml. of the appropriate solution. A 10-ml. sample was withdrawn for analysis and then a



Figure 3. Influence of formaldehyde concentration on absorbance



Figure 4. Sensitivities of various dye-acid mixtures

slow current of air (about 2 liters per minute) was bubbled through the solutions. At various times, 10-ml. samples were withdrawn and analyzed. As can be seen from Figure 2, there was no oxidation of the disulfitomercurate(II) complex. This is important when large volumes of air containing small amounts of sulfur dioxide must be sampled.

Investigation of the red-violet color, developed when fuchsin, sulfuric acid, and formaldehyde are mixed with alkali sulfite solutions (8), showed that the reaction also occurs with disulfito-mercurate(II). As the reagent is difficult to prepare, is stable for only a few hours, and produces some color in the absence of sulfite, it seemed advisable to seek a more satisfactory color-producing agent. It was decided to use *p*-rosaniline hydro-

chloride as the dyestuff instead of basic fuchsin, which is an impure mixture of rosaniline and *p*-rosaniline hydrochlorides. It was found that hydrochloric acid will bleach *p*-rosaniline, giving solutions that are pale yellow to colorless. When this reagent and formaldehyde are added to solutions containing sulfite or disulfitomercurate(II), the characteristic red-violet color is produced.

Table I.	Efficiency of Absorption Tetrachloromercurate	iency of Absorption in Sodium achloromercurate(II)			
Concn. of SO ₂ , P.P.M.	Rate of Flow, Liters/Min.	$\begin{array}{c} \mathrm{SO}_2 \ \mathrm{in} \\ \mathrm{Second} \\ \mathrm{Scrubber}, \ \gamma \end{array}$			
5	$2 \\ 5 \\ 10 \\ 15$	$\begin{array}{c} 0 . 0 \\ 0 . 0 \\ 0 . 0 \\ 0 . 0 \\ 0 . 0 \end{array}$			
.10	$\begin{array}{c} 10\\ 15 \end{array}$	$\begin{array}{c} 0.0\\ 0.0\end{array}$			

To determine the optimum conditions of dye, acid, and aldehyde concentration, a series of solutions was prepared. The dye-acid solutions covered the range from 0.02 to 0.1% prosaniline hydrochloride and 6 to 12% concentrated hydrochloric acid, while the aldehyde solutions ranged from 0.1 to 1% formaldehyde. It was found that for any given dye-acid solution the absorbance of the test solution (containing 5 γ of sulfur dioxide) and the blank increased with formaldehyde concentration (Figure 3). The absorbance maximum is at 560 m μ . The dye-acid concentrations in these solutions were 0.04% dye and 6% acid. All curves were obtained with a Beckman Model DK-1 recording spectrophotometer.

After all of the curves for the various solutions had been plotted, the sensitivities were calculated (absorbance of sample minus absorbance of blank) and plotted against dye concentration. These data for 0.2% formaldehyde are shown graphically in Figure 4. The reagent containing 0.04% dye and 6% acid with the addition of 0.2% formaldehyde was found to give the greatest sensitivity with the least blank correction (blanks are approximately 0.02 absorbance unit). In all cases, 1 ml. of dye-acid and 1 ml. of formaldehyde solution were added to 10 ml. of 0.1M sodium tetrachloromercurate(II) containing 5 γ of sulfur dioxide. Color development was found to be reasonably rapid, being complete in about 20 minutes and stable for 2 to 3 hours.

Table II. Effect of Temperature on Color Development

	(Time, 30 minutes)							
SO ₂		Temperature, ° C.						
Conen., $\gamma/10$ Ml.	11	15	20 Absort	22 pancies	26	30		
$\begin{array}{c} 0.5\\ 1.0\\ 2.0\\ 4.0\\ 6.0\\ 8.0\\ 10.0 \end{array}$	$\begin{array}{c} 0.015\\ 0.041\\ 0.082\\ 0.144\\ 0.216\\ 0.280\\ 0.343 \end{array}$	$\begin{array}{c} 0.017\\ 0.038\\ 0.078\\ 0.148\\ 0.219\\ 0.282\\ 0.342 \end{array}$	$\begin{array}{c} 0.015\\ 0.040\\ 0.079\\ 0.145\\ 0.215\\ 0.280\\ 0.340 \end{array}$	$\begin{array}{c} 0,016\\ 0,037\\ 0,081\\ 0,145\\ 0,219\\ 0,280\\ 0,342 \end{array}$	$\begin{array}{c} 0.016 \\ 0.041 \\ 0.082 \\ 0.146 \\ 0.218 \\ 0.281 \\ 0.341 \end{array}$	$\begin{array}{c} 0,014\\ 0,036\\ 0,078\\ 0,144\\ 0,217\\ 0,278\\ 0,339 \end{array}$		

The effect of temperature was determined by taking solutions containing various amounts of sulfur dioxide, adding the colordeveloping reagents, and thermostating for 30 minutes. At the end of the standing time the absorbance was read at 560 m μ . The results are shown in Table II.

The reagent described has been found to be about 20% more sensitive than the sulfuric acid-bleached fuchsin reagent under

VOLUME 28, NO. 12, DECEMBER 1956

the same conditions. The system obeys Beer's law up to approximately 25 γ of sulfur dioxide per 10 ml. Nitrogen dioxide interferes if present in concentrations above 2 p.p.m. Higher levels decrease the color intensity and nitrogen dioxide concentrations over 8 p.p.m. prevent color development completely. The only other common interference, usually associated with the reagent, is sulfide. In the presence of the mercury-absorbing solution, this ion precipitates and may be removed by filtration or centrifugation. Sulfur trioxide, chlorine, ammonia, and halogen acids do not interfere.

RECOMMENDED PROCEDURE FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE

Collect 38.2 liters (1.35 cubic feet) of sample in 10.0 ml. of sodium tetrachloromercurate(II) solution in a small fritted The sampling rate may be as high as 0.2 cu. foot per bubbler. minute with no loss due to decreased efficiency of absorption. To the 10.0-ml. sample add 1.0 ml. of acidic p-rosaniline solution and 1.0 ml. of formaldehyde solution. Treat a blank of 10 ml. of sodium tetrachloromercurate(II) in the same manner. Allow to stand 20 to 30 minutes for full color development. Determine the absorbancy of the test solution compared to the blank at 560 m_{μ} . Read the concentration of sulfur dioxide from a standard curve prepared by using standard solutions of sodium bisulfite in sodium tetrachloromercurate(II). If the sample size is 38.2 liters, then each microgram of sulfur dioxide represents 0.01 p.p.m. of sulfur dioxide in the air.

Nitrogen dioxide is the only interference with this method, and it can be tolerated in concentrations up to 2 p.p.m. (if sulfides are present, the precipitate formed must be removed by filtration or centrifugation). Samples may be collected in the field and analyzed at any later time with no loss of sulfur dioxide due to either oxidation of volatilization.

SUMMARY

A procedure for the fixation of sulfur dioxide is based on the formation of stable, nonvolatile disulfitomercurate(II) ion. The determination is based on the red-violet color developed when ${\it sulfur\ dioxide\ or\ disulfitomercurate (II),\ p{\it -rosaniline,\ hydrochloric}}$ acid, and formaldehyde are mixed. The method is sensitive, reproducible, and accurate.

ACKNOWLEDGMENT

The authors wish to express their thanks to the Mine Safety Appliances Co. for financial assistance during part of this investigation.

LITERATURE CITED

- Atkin, S., ANAL. CHEM. 22, 947 (1950).
 Feigl, F., "Chemistry of Specific, Selective and Sensitive Reactions," p. 75, Academic Press, New York, 1949.
 Fieldner, A. C., Oberfell, C. G., Teague, M. C., Lawrence, J. N.,
- J. Ind. Eng. Chem. 11, 523 (1919).
- (4) Holmes, J. A., Franklin, E. C., Gould, R. A., U. S. Bur. Mines Bull. 98 (1915). (5) Jacobs, M. B., "Analytical Chemistry of Industrial Poisons,
- Hazards, and Solvents," 2nd ed., pp. 758-9, Interscience, New York. 1949.
- (6)
- Steigmann, A. J. Soc. Chem. Ind. 61, 18 (1942). Thomas, M. D., IND. ENG. CHEM., ANAL. ED. 4, 253 (1932). (7)
- (8) Urone, P. F., Boggs, W. E., ANAL. CHEM. 23, 1517 (1951).

RECEIVED for review June 20, 1956. Accepted October 2, 1956.

Ninth Annual Summer Symposium—Analysis of Industrial Wastes

Recent Trends in the Analysis of Industrial Wastes

W. ALLAN MOORE and M. B. ETTINGER

Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio

Surface waters are becoming progressively scarcer, and their use for disposing of liquid industrial waste should be continually re-examined. Intelligent control of waste discharge must be based on analytical methodology, which does not appear to be keeping pace with the problem that confronts it. Requirements for discharge of wastes to surface waters will become increasingly critical.

 ${
m E}^{
m STIMATES}$ based on "population equivalents" (28) rate industrial wastes as responsible for more than twice as much stream pollution as municipal sewage discharges. It has been further estimated that between 1950 and 1975 population will increase by about one third and industrial production will double. Estimates by chemical industry (17) of future expansion make these statements on industrial growth seem highly conservative. Production increase will obviously be accompanied by increasing use of water.

The future growth of water use is likely to occur in a framework of shrinking availability of surface water. The existing water shortages in the arid areas of the country are well understood. Supplementary irrigation in humid areas is increasing rapidly. This consumption of water occurs during dry summer periods, when most streams have their lowest flow of the year, and it has been estimated (31) that it can use the entire flow of

many streams, even if only a small fraction of 1% of the land in a watershed is irrigated.

Municipal use of water is increasing faster than population. Thus, the average urban dweller uses 150 gallons of water today, whereas 30 years ago he used only 20 gallons (11). Recreational use of water is harder to assess, but both increased leisure time and increased income are causing the public to demand more water resources for recreation.

Requirements for discharge of wastes to surface waters will, of necessity, become increasingly critical. Analytical means of gaging the suitability of wastes for discharge must be developed further as implements for protecting an increasingly critical public interest in water quality, without unduly hampering industrial activity.

INSTRUMENTATION

The analytical work in progress does not appear to be adequate in relation to the expanded and critical waste control problem which it must eventually meet. Perhaps the most hopeful sign is the awakening interest in instrumentation as a means of recording waste properties or stream quality. Along with others, the Sanitary Engineering Center (14) is working toward the development of a machine for continuously indicating and recording dissolved oxygen in surface water. Kieselbach (13) of Du Pont has reported on an apparatus for continuous recording