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Appraisal and Modification Of West-Gaeke Method For Sulfur Dioxide Determination

The West-Gaeke method has been shown to be feasible for detecting changes in SO_2 concentration greater than 10%. Reliable results can be obtained if one makes up stock solutions of the pararosaniline dye from the same powder batch at the same time. Gum arabic stabilizes the SO_2-tetrachloromercurate complex at concentrations of $SO_2 > 8$ μg/ml.

Since its inception in 1956, the West-Gaeke method[1] seems to be the one most widely used for the determination of atmospheric sulfur dioxide (SO_2). It is most important for workers in the field to have an exact idea of its accuracy, reproducibility, and limitations; particularly when they are trying to detect small differences in its concentration. Some of the latter considerations have been discussed in the literature.[1–7] Part of the experimental error lies in analytical determination of SO_2, while part is inherent in the method of sampling. This paper will discuss only the analytical portion of the West-Gaeke method. We shall appraise the method and consider certain modifications which minimize its errors.

The West-Gaeke method is applicable to SO_2 in the concentrations range of 0.005 to 5 ppm. SO_2 from an air sample is absorbed, generally by a flow process, in 0.1*M* sodium tetrachloromercurate (Na_2HgCl_4). By this technique, the formation of nonvolatile dichlorosulfitomercurate ion stabilizes SO_2 in solution. Upon the addition of acid-bleached pararosaniline dye and formaldehyde to the above solution, reddish-purple pararosaniline methyl sulfonic acid is formed and determined spectrophotometrically at 560 μ. West and Gaeke maintain that the system obeys Beer's law up to about 10 μl SO_2 per 10 ml absorbing solution. It has been suggested that the West-Gaeke method is more sensitive than the hydrogen peroxide method and is not subject to interference from acidic or basic gases or solids.[5]

Some of the limitations of the West-Gaeke determination relate to:

1. The instability of the SO_2 complex with Na_2HgCl_4
2. The fairly rapid fading of the developed color
3. The purity of dye and lack of reproducibility of the stock dye concentrations and calibration curves
4. The deviation from Beer's law at relatively low absorbances
5. Interference of oxides of nitrogen and ozone—concentrations of interfering oxidants should be less than that of SO_2, i.e., up to about 2 ppm.

Each of these points (emphasizing 1.

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Table I. Data on Precision of West-Gaeke

C_{SO_2}	Identity of Study	Coefficient[8] of Variation	Number of Samples	Number of Participants
0	This laboratory	234.2	10	1
0.25	A.R.S.	17.6	123	40
0.414	This laboratory	2.41	10	1
0.70	A.R.S.	15.8	121	40
0.826	This laboratory	1.75	10	1
1.0	Taft Center	6.55		
1.10	A.R.S.	12.8	115	38
1.107	This laboratory	2.51	10	1
1.686	This laboratory	0.447	10	1

and 2.) will be discussed after an appraisal of the reproducibility and accuracy of our results.

Results

Precision of the Analytical Method

In our laboratory we have made a study of the precision of the West-Gaeke method by the addition of sulfite to Na_2HgCl_4 solutions rather than by air sampling. The results of this study appear in Table I in combination with data from other laboratories. The SO_2 solutions were made up from a 400 μg per ml standard SO_2 solution and determined essentially by the method of Hochheiser[6] which involves iodometric titrations.

Except for the very poor precision around zero, which is understandable, our precision has a coefficient of variation between 0 and 2.5%.

An extensive study of the precision of the West-Gaeke method has also been made by the Analytical Reference Service (A.R.S.),[7] of the Taft Center, Cincinnati, and these data are included in Table I as are some recent data of Scaringelli, Saltzman, and Frey.[9] While our data compare favorably with those of the other investigators, such comparisons are not entirely valid. Our data were obtained at one time by one chemist using identical solutions, while the data from A.R.S. were obtained by many different laboratories, leading to decreased precision. Nevertheless, it seems clear that for the determination itself, excluding the air sampling, it is possible to achieve a precision of 2 to 3% for reasonable absorbances, i.e., 0.2 to 0.8 absorbance units.

Precision of Calibration Curves

Using the West-Gaeke procedure, nine calibration curves were obtained with several different stock dye solutions from a single batch of purified pararosaniline hydrochloride. By the least mean square regression technique, the following regression equation was obtained from the data for all nine runs:

$$A_{560} = 0.001816 + 0.04962 \times \left(\frac{\mu\text{gms } SO_2}{\text{sample}}\right) \quad (1)$$

It may be shown that the standard deviation is 3.53×10^{-3} and that the average slope is $\bar{b} = 0.04962 \pm 0.00288$ within the 95% confidence limits for eight degrees of freedom. The coefficient of variation equals 0.711%, indicating fairly precise data.

Statistical analyses of our data indicates that, for the most part, calibration curves are not substantially affected by the dye solution, providing that it is made up from the same batch of dye, using a standard technique.

Accuracy of Results

In order to determine the accuracy of our results, seven different solutions were made up by dilution from a standardized SO_2 solution. Then West-Gaeke determinations were run on each solution in duplicate and the observed absorbance at 560μ was substituted into eq. (1) to give a corresponding value of μgms SO_2 per sample. These results are tabulated in Table II.

In examining these results, one notes that the error varies from +0.35 to −8.1%. Our results compare favorably with data from the A.R.S.[7]

Clearly the accuracy may be improved by use of a calibration curve including perhaps 50 to 100 runs, rather than nine, over different dye samples from different batches so as to have a more statistically valid sample. Nevertheless, our data does suggest that we can expect, in general, our error will be under 10% and probably under 8% using the experimental system as is and the present calibration curve.

Stability of the SO_2 - Na_2HgCl_4 Complex

Other workers have recommended the addition of gum arabic to SO_2 solutions in order to enhance the stability of the SO_2-tetrachloromercurate complex.[4,7,10]

In order to corroborate this work, the effect of gum arabic on different concentrations of SO_2 was investigated. Various concentrations of SO_2 were made up from bisulfite in 0.1M Na_2HgCl_4 and in 0.1M Na_2HgCl_4 containing 0.5g of gum arabic/100 ml. At various times after preparation, 1 ml aliquots were removed and diluted to 10 ml with the appropriate absorber. The color was developed in each case in the usual way. The results of this experiment are shown in Fig. 1 with data for the concentrations: 17 and 8.5 μgSO_2/ml. A marked loss of the SO_2 occurs with no gum arabic present in the case of 25 (not shown) and 17 μgSO_2/ml and only a slight loss for 8.5 μgSO_2/ml. In the cases where gum arabic was added, a slight loss may possibly occur in the two higher concentrations after about two weeks. Experiments were also performed at concen-

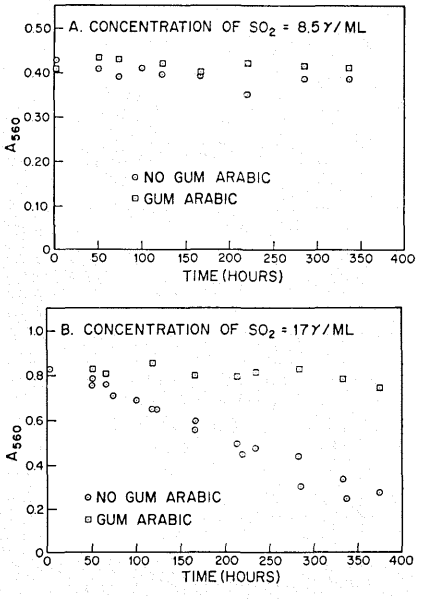

Figure 1. Decompostion of SO_2-Tetrachloromercurate Complex as a function of time. Concentration of Na_2HgCl_4 is 0.1M; concentration of gum arabic is 0.5 g/100 ml 1:10 dilution made in each case before determination.

trations of 2 and 4 μg/ml, but these data are not included, since there was significant scattering at these low levels. The paired "t-test," comparing gum arabic solutions with those containing no gum arabic, showed differences at 8.5 and 17 μg/ml for both 95 and 99% confidence levels. But for 4 μg/ml there was only a difference at the 95% confidence level.

Our data suggests that for a level of 1 to 2 μgSO_2/ml, gum arabic does not appreciably enhance the stability of the SO_2-tetrachloromercurate complex. Only at high concentrations of SO_2 (approximately 8 μg/ml or more) and where the SO_2 solutions must stand for several days before analysis, is the use of gum arabic recommended.

An additional point to consider is that gum arabic, like many proteins, foams as air is drawn through it. Even moderate flow rates may cause the absorber to bubble out of the impinger. For field use with the gum arabic modification, either low flow rates or the use of an added defoamer would be recommended.

Development and Fading of Color

In our experiments, for the most part, a color development period of about 30 minutes was arbitrarily used. However, if at this time the absorbance was still increasing, measurements were continued until a stable value was attained.

Because of the variability of this time for color development from sample to sample, some limited experiments were run to ascertain the effect of age, dye, gum arabic, and concentration of SO_2 on time of color development. Data were obtained for A_{560} as a function of time for SO_2 solutions with final concentrations of 1.6 μg/ml. In each pair one of the solutions contained gum arabic while the other did not, and one pair used freshly-made acid-bleached dye, while in the other it was two weeks old. Also, data were obtained for the corresponding reagent blanks versus distilled water and showed a rising absorbance with time. The maximum absorbance for the solutions was reached in 14 to 15 minutes. Thereafter, there is a decline in the absorbance, although the rate of decline is much less than the rapid rise during the first ten minutes. After 70 minutes have elapsed, the decrease from maximal development for 1.6 μg/ml is 8 to 9%. The results of these experiments show no significant change in behavior due to addition of gum arabic or substitution of old dye for new dye. However, in the solution containing gum arabic there was a more substantial rise in the absorbance of blank versus distilled water than where no gum arabic was present. To eliminate the effect of changing absorbance of reagent blank, the absorbance of the solution can be considered versus distilled water.

Table II. Determinations of Accuracy in West-Gaeke Procedure as a Function of Concentration. (Our Laboratories)

Sample Designation	μgms SO_2 per Sample Actual (by titration)	A_{560}	μgms SO_2 per Sample, West-Gaeke (best calibration curve)	Error (%)
A	1.978	0.101	1.915	−3.185
B	3.957	0.203	3.971	+0.354
C	7.920	0.367	7.280	−8.08
D	9.88	0.466	9.275	−6.13
E	11.86	0.592	11.81	−0.423
F	15.82	0.746	14.91	−5.75
G	19.76	0.928	18.65	−5.62
			(Average error)	−4.22

Error Analyses

A detailed error analysis cannot be included here because of space limitations. However, by the method of Livingston,[12] the probable relative error in the concentration of SO_2 has been determined and found to be ±9.6% by considering all possible errors in the analytical and sampling portions of the method. This is the random error that one can expect after systematic errors, most of which are negative, have been considered.

Conclusions

Reliable results can be obtained by the West-Gaeke method for the determination of SO_2 if stock solutions of dye are made from the same dye batch at the same time.

Gum arabic enhances significantly the stability of the SO_2-tetrachloromercurate complex only at high concentrations of SO_2 (>8 μg/ml).

The rate of color decay is greater than that which has been indicated in the literature. The absorbance of the reagent blank rises with time.

Error analysis showed the probable relative error of SO_2 concentration to be ±9.6%.

Acknowledgment

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