

Colorimetric Determination of Sulfur Dioxide from Malt and Beer by Complexing with Sodium Tetrachloromercurate(II)

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A rapid, sensitive method is presented for the determination of sulfur dioxide in malt and beer which embodies a distillation procedure in conjunction with a pararosaniline hydrochloride-formaldehyde colorimetric determination. A solution of sodium tetrachloromercurate(II) is used as the absorbing medium for sulfur dioxide. This results in the formation of the stable disulfitomercurate (II) ion which does not require an immediate analysis for sulfur dioxide. The method is specific for sulfur dioxide, and no interferences have been found. When the method was applied to the determination of sulfur dioxide in the range of 1 to 75 p.p.m., a maximum error of $\pm 5\%$ was realized.

EXTENSIVE INVESTIGATIONS involving a colorimetric analysis of sulfur dioxide in low concentrations have been carried out by Grant (1), Steigman (4), and Joslyn (2), who successfully used a basic fuchsin-formaldehyde complex as the color reagent. West and Gaeke (6) have reported increased stability and sensitivity of the color reagent by substitution of hydrochloric acid-bleached pararosaniline for the previously used sulfuric acid-bleached fuchsin.

In the present study, preliminary application of a colorimetric procedure to malt and beer was based on the work of Steigman in conjunction with a modified Monier-Williams method (3). Evolved sulfur dioxide was absorbed in a solution of 5% glycerol in 0.1N sodium hydroxide as suggested by Urone and Boggs (5). West and Gaeke have improved upon the absorbing medium through introduction of a sodium tetrachloromercurate(II) solution. Use of this solution as an absorbing medium for sulfur dioxide results in formation of the stable disulfitomercurate(II) ion. The method presented here for determination of sulfur dioxide in malt and beer embodies a distillation procedure together with an adaptation of the colorimetric method for sulfur dioxide developed by West and Gaeke.

Reagents and Apparatus

Pararosaniline Hydrochloride Solution. Dissolve 0.1 gram of pararosaniline hydrochloride (Certified Dye, National Aniline Division, Allied Chemical and Dye Corp.) in distilled water and dilute to 100 ml. Allow it to stand for 1 day to assure complete solution.

Bleached Pararosaniline Hydrochloride Solution. Pipet 20 ml. of pararosaniline hydrochloride solution into approximately 100 ml. of distilled water contained in a 500-ml. volumetric flask. To this add 30 ml. of reagent grade concentrated hydrochloric acid; allow the dye to bleach to a pale yellow-green

color and dilute to 500 ml. with distilled water.

Sodium Tetrachloromercurate(II) Solution. Dissolve 11.7 grams of reagent grade sodium chloride and 27.2 grams of reagent grade mercuric chloride in 1 liter of distilled water.

Formaldehyde Solution. Dilute 5.5 ml. of 36% reagent grade formaldehyde to 100 ml. with distilled water.

Standard Sulfite Solution. Accurately weigh a quantity (approximately 0.2 gram) of reagent grade sodium bisulfite (iodometric assay 58.5% sulfur dioxide) and dissolve in 100 ml. of sodium tetrachloromercurate(II) solution. Dilute to 500 ml. with distilled water. Transfer a 10-ml. aliquot to a 100-ml. volumetric flask and dilute to volume with distilled water.

Alkaline Pyrogallol Solution. Dissolve 5 grams of pyrogallol in 25 ml. of hot distilled water. Cool this solution and mix with 100 ml. of an 80% potassium hydroxide solution.

Spectrophotometer. A Beckman Model DU spectrophotometer with 1-cm. borosilicate glass cells.

Distillation Apparatus. The assembled distillation apparatus is illustrated in Figure 1.

Analytical Procedure

Preparation of Standard Curve. Aliquots of 1 to 10 ml. of the standard sulfite solution were pipetted into 100-ml. volumetric flasks containing 25 ml. of bleached pararosaniline hydrochloride solution and 2 ml. of formaldehyde solution. The color was developed for 7 minutes at room temperature, followed by dilution to volume. The absorbance was immediately determined at a wave length of 560 $m\mu$ using matched 1-cm. borosilicate glass cells. The color was stable for 5 minutes and then faded slowly. Absorbance readings can be expected to decrease by about 2% over a period of 60 minutes. The standard curve was linear in the concentration

range of 0 to 0.2 mg. of sulfur dioxide per 100 ml.—effective for malt and beer.

Experimental. Three hundred grams of beer were weighed into the 1-liter distillation flask and degassed for 5 minutes with nitrogen, which had been purged of oxygen by passage through the alkaline pyrogallol trap. Twenty milliliters of reagent grade concentrated hydrochloric acid were added via the aspirator bottle and connecting tube. In this manner, air was not introduced into the distillation system.

The distillation flask was heated for 45 minutes with continuous nitrogen flushing at the rate of about 75 ml. of nitrogen per minute. Sulfur dioxide was distilled into 100 ml. of sodium tetrachloromercurate(II) solution contained in a 125-ml. gas absorption tower, the gas dispersion tube of which was fitted with a medium porosity fritted disk. After completion of the distillation, a 5-ml. aliquot was withdrawn from the gas absorption tower and transferred to a 100-ml. volumetric flask containing 25 ml. of bleached pararosaniline hydrochloride solution and 2 ml. of formaldehyde solution. The color was developed

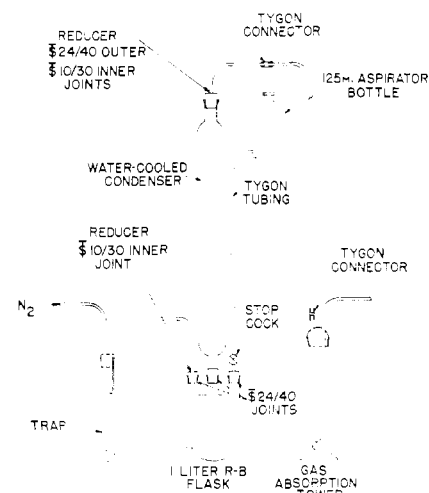


Figure 1. Assembled distillation apparatus

Table I. Recovery of Sulfur Dioxide from Synthetic Solutions

Added, Mg.	Recovered, Mg.	Recovery, %
1.40	1.42	101.6
3.50	3.43	98.0
7.66	7.55	98.6
11.71	11.85	100.5
14.00	14.30	102.1
18.90	19.10	101.6
23.70	24.60	103.6

Table II. Precision of Method on a Commercial Beer Sample

Sample	Sulfur Dioxide, P.P.M.	Sample	Sulfur Dioxide, P.P.M.
1	9.20	7	8.83
2	8.80	8	9.20
3	8.73	9	9.17
4	9.33	10	9.26
5	9.40	11	9.20
6	9.38	12	9.23
		Mean	9.14
		S.D.	0.23

Table III. Comparative Analysis of Commercial Beers

Beer	Sulfur Dioxide, P.P.M.	
	Colorimetric	Gravimetric
A	0.81	0.90
B	3.00	2.93
C	3.23	3.33
D	4.83	4.77
E	8.16	8.87
F	9.83	9.33

Table IV. Comparison of Colorimetric and Gravimetric Determinations of Sulfur Dioxide in Malt

Malt	Sulfur Dioxide, P.P.M.	
	Colorimetric	Gravimetric
A	19.0	19.2
	17.2	17.6
	18.4	22.5
	18.6	18.1
B	39.0	43.3
	39.6	43.9
	39.6	38.4
	38.4	42.1
C	70.0	71.9
	69.9	73.0
	70.0	65.5
	70.0	72.5

as for preparation of the standard curve. The sulfur dioxide concentration was obtained from the standard curve.

For the determination of sulfur dioxide in malt, experimental conditions outlined for beer were adhered to with the exception of the following modifications: Three hundred milliliters of distilled water were added to the distillation flask, and the sample consisted of 50 grams of well-mixed whole malt.

Results and Discussion

Efficiency of the distillation apparatus was ascertained by carrying out distilla-

tions, as outlined for the experimental procedure, with known amounts of sodium hydrogen sulfite. Results of these experiments are tabulated in Table I. The data indicate that the distillation apparatus, time of distillation, and a single absorption tower give satisfactory recoveries. A number of initial experiments were conducted using two absorption towers; in every case, no detectable quantities of sulfur dioxide were found in the second absorption tower. These observations corroborate the findings of West and Gaeke relative to the efficiency of sodium tetrachloromercurate(II) as a sulfur dioxide absorption medium when used with a single absorption tower.

Precision of the method was ascertained on a commercial beer sample (Table II). The data indicate that reproducibility is within the desired range of $\pm 5\%$ maximum error.

A comparative analysis of commercial beers and malts was conducted utilizing both the currently accepted Monier-Williams gravimetric and the colorimetric procedure presented in this investigation. Results of these analyses are presented in Tables III and IV, respectively. According to the data of both tables, satisfactory agreement exists between results of the two methods. In general, gravimetric results for malt are slightly higher than similar colorimetric results.

Attempts to apply the 1.0% pararosaniline hydrochloride concentration proposed by West and Gaeke to the present study were prohibitive, as it would have necessitated a reduction of the malt sample size and subsequently introduce sampling errors. A 0.1% pararosaniline hydrochloride solution was, therefore, substituted for the 1.0% solution of pararosaniline hydrochloride used by West and Gaeke. This change yielded the degree of desired sensitivity for the method.

Although, as previously indicated, the standard curve showed conformity to Beer's law to a concentration of 0.2 mg. of sulfur dioxide per 100 ml., the curve continued to be linear to a concentration of 0.3 mg. of sulfur dioxide per 100 ml. Concentrations of sulfur dioxide are limited in application to a precision spectrophotometer such as the Beckman DU. Attempts to adapt the method to a filter instrument were successful to a limited degree. Instrument response was such that the standard curve obtained conformed to Beer's law only at low concentrations of sulfur dioxide. Therefore, if usage of a filter instrument is contemplated, the limiting concentration range corresponding to sensitivity of the particular instrument must be ascertained.

During malt analyses, an occasional sample was encountered containing as much as 200 p.p.m. of sulfur dioxide. A 5-ml. aliquot of the sodium tetrachloro-

mercurate(II) trapping solution resulted in high absorbance readings. This condition was satisfactorily overcome by using a smaller (2- or 3-ml.) aliquot without loss of sensitivity.

In the course of the present investigation, attention was given to stability of the reagents. Of reagents used, bleached pararosaniline hydrochloride exhibited a minor stability problem. After standing for 1 week, the bleached pararosaniline hydrochloride yielded results which were slightly higher than those realized for a freshly prepared solution; therefore, bleached pararosaniline hydrochloride solution should be used for a maximum of 3 days.

In addition to the possible interferences studied by West and Gaeke, distillable substances from malt and beer were investigated. Color development was not affected by volatile substances produced in reflux distillation.

Conclusions

The Monier-Williams method was modified to the extent that sodium tetrachloromercurate(II) was used as the absorbing medium for sulfur dioxide in malt and beer. This solution has the advantage over the usual alkali solutions generally employed as sulfur dioxide absorbing media in that very stable disulfitomercurate(II) ion is formed. Determination of sulfur dioxide was based on the color produced when pararosaniline hydrochloride and formaldehyde were added to the absorbing medium. The method proved to be sensitive and much less time-consuming than the usual gravimetric procedure.

The ability to use 50 grams of dry material eliminates many sampling difficulties. This suggests possible application of the analysis to other food products containing low levels of sulfur dioxide.

In the malting industry, sulfur dioxide is at times applied to malt during the kilning cycle just prior to drying. Recent application of the colorimetric procedure to analysis of kiln air containing high levels of sulfur dioxide has presented very encouraging results, although the study is incomplete at this time.

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