

Estimation of Residual Sulfur Dioxide in Malt

Subcommittee Members: B. Lukes, *Chairman*; D. A. Baker, J. Carver, D. Davidson, P. J. Frohmader, T. H. Hartzell, M. Moll (*EBC*), W. J. Olson, D. Rider, S. Rothenberg, G. P. Skocic, B. Thoet, D. W. Whitney, R. G. Widmaier, and C. W. Hahn (*ex officio*).

Key words: *Colorimetric, Distillation, Methodology, Monier-Williams.*

CONCLUSIONS

1. Data obtained from collaborative study of the distillation-colorimetric procedure for estimation of residual SO₂ in malt (3) showed acceptable within-laboratory error but statistically significant between-laboratory error.
2. Results contributing to between-laboratory error are systematic and appear related to standardization.
3. Insufficient data were collected from the Monier-Williams method (1) for statistical evaluation.

RECOMMENDATIONS

1. Further collaboration on the distillation-colorimetric procedure with emphasis on uniform standardization is warranted.
2. An extraction-colorimetric procedure (4) should be subjected to collaborative testing.

This subcommittee was organized at the 1980 ASBC Annual Meeting when interest was generated in analytical methods for estimating residual SO₂. The effect of sulfuring on nitrosamine levels in malt was the primary cause of this interest. The assignment for the year 1980-81 was to evaluate an improved method (3) presented at the 46th Annual Meeting.

PROCEDURE

Two pairs of commercial malt samples were sent to each collaborator for analysis according to the Youden Block Design (4). One pair consisted of two-row malts processed similarly and containing approximately 10 mg/kg residual SO₂; the other pair consisted of six-row malts processed similarly and containing approximately 35 mg/kg residual SO₂.

Collaborators were previously sent instructions for the distillation-colorimetric procedure, in addition to basic fuchsin and

assayed sodium bisulfite. They were requested to familiarize themselves with the method prior to analyzing test samples.

Because of the limited stability of residual SO₂ in malt, collaborators were instructed to analyze all test samples within sixty days after arrival at their laboratory.

Collaborators were asked to perform a single analysis of each test sample by the distillation-colorimetric procedure. The report form provided for separate inclusion of Monier-Williams data from collaborators using modifications of that method.

RESULTS AND DISCUSSION

Results of the distillation-colorimetric procedure are presented in Table I. No outliers were identified by Dixon's test (2) at ($P=0.05$). Data for collaborators 7 and 8 show systematic errors for both sample pairs, indicating a problem in standardization. All laboratories produced standard curves that were linear, with high coefficients of correlation. Statistical treatment of the results is summarized in Table II. Within-laboratory error is within an acceptable range for an analysis of this nature. Between-laboratory errors are significant and contribute to high F-values and coefficients of variation for the combined errors.

Data from the Monier-Williams method are given in Table III. Results are variable, as are the methods used to obtain them. Statistical evaluation was not attempted with this small collection of data.

Comments by collaborators indicated some dissatisfaction with

TABLE I
Estimation of Residual SO₂ in Malt^a

Collaborator	Sample Pair I		Sample Pair II	
	A	B	C	D
1	20.0	10.5	34.8	40.2
2	9.5	8.3	34.0	36.6
3	9.8	7.5	38.0	39.0
4	10.4	7.2	36.2	42.8
5	12.8	9.3	29.0	33.7
6	11.7	7.2	35.0	40.0
7	16.9	11.6	41.6	46.2
8	8.9	4.9	25.1	27.4
Mean	12.50	8.31	34.21	38.24
Grand mean	10.41		36.23	

^aValues are mg/kg malt.

TABLE II
Estimation of Residual SO₂ in Malt—Statistical Summary

Sample Pair	No. of Labs.	Grand Mean ^a	Error			c.v. ^d (%)	Calculated F ^b	Critical F ^c
			Within-Laboratory ^b	Between-Laboratory ^b	Combined ^c			
A, B	8	10.41	1.76	2.64	3.18	30.5	5.49	4.28
C, D	8	36.23	1.32	5.29	5.45	15.1	33.12	4.28

^aGrand mean = GM = $(\bar{A} + \bar{B})/2$.

^bCalculated per Youden and Steiner (4).

^cCombined error (S_c) calculated from within-laboratory error (S_w) and between-laboratory error (S_b); $S_c = \sqrt{S_w^2 + S_b^2}$.

^dCoefficient of variation of S_c = c.v. = 100 (S_c/GM).

^eCritical F from tables of F distribution (2) at P = 0.05.

TABLE III
Estimation of Residual SO₂ in Malt by Monier-Williams Method

Collaborator	Sample Pair I		Sample Pair II	
	A	B	C	D
1	18.9	18.1	28.4	37.8
5	2.0	2.0	30.0	27.0
7	15.0	11.0	44.0	46.0

the distillation-colorimetric procedure due to the quantity of apparatus required and preparation time involved.

Pararosaniline hydrochloride, the primary component of basic fuchsin, is currently listed with OSHA for study as a possible

carcinogen. Basic fuchsin is widely available due to its use in histology and bacteriology. Manufacture and distribution of basic fuchsin are not restricted at this time. Direct contact with basic fuchsin should be avoided.

LITERATURE CITED

1. Association of Official Agricultural Chemists. Official Methods of Analysis (9th ed.), 27.078. The Association: Washington, DC, 1960.
2. Dixon, W. J. *Biometrics* 9:74, 1953.
3. Lukes, B., O'Brien, T. J., and Scanlan, R. A. *J. Am. Soc. Brew. Chem.* 38:146, 1980.
4. Pitz, W. J., and Lubert, D. J. *J. Am. Soc. Brew. Chem.* 39:112.
5. Youden, W. J., and Steiner, E. H. Statistical Manual. Assoc. Off. Anal. Chem.: Washington, DC, 1975.