Soluble Iron in Filter Aids

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CONCLUSIONS

Collaborative study has shown that potassium acid phthalate buffer solution can serve as a standard extractant for determining soluble iron in filter aids. It consistently gives higher values than any beer tested and shows more reproducibility and less between-laboratory variation than does beer.

RECOMMENDATION

It is recommended that the method for determination of soluble iron in filter aids as given in the Appendix be accepted for publication in the ASBC *Methods of Analysis* as a reference method.

Intolerable variations between laboratories using current Filter Aids-4 (1) as a measure of soluble iron in filter aids were not resolved by collaborative study of the method compared with an alternate suggested in 1975 (2). Beers were found to vary widely in their ability to extract iron from filter aids and it was decided to await the development of an extractant which could be standardized. Subsequently, Tenney and Duensing (4) reported that potassium acid phthalate solutions extracted iron from filter aids somewhat more thoroughly than did several beers and that the relation between this extractant and any particular beer was linear. The slope of the curve is, however, not the same for all beers.

The Subcommittee undertook the task of testing a standard buffer of 1% aqueous potassium acid phthalate as an extractant for iron from filter aids to verify the linearity with beer and to further evaluate the method.

PROCEDURE

In a preliminary approach testing instructions given collaborators, seven samples of diatomaceous earth-type filter aid were submitted to four of the laboratories to be involved. Each was asked to determine soluble iron by method Filter Aids-4 using their beer and using also 1% aqueous potassium acid phthalate as an alternate extractant. This work verified the linearity observed by Tenney and Duensing (4) and demonstrated that it is necessary to include ascorbic acid at the time color is developed within the phthalate extract.

Subsequently, two pairs of filter aids were examined by sixteen different laboratories comparing the amount of iron extracted by their beer with that extracted by the phthalate buffer and following the procedure of Filter Aids-4. The samples were selected from commercial lots of calcined diatomite so as to obtain two pairs of similar material. One of the pairs had been calcined with a fluxing agent, resulting in a somewhat higher soluble iron content. Thus the experimental design of the study is the familiar block design employing two sample pairs with two different extractants.

RESULTS AND DISCUSSION

Table I records the results of the preliminary tests. The necessity for using ascorbic acid is quite apparent from the data reported by Collaborators A and D. Collaborator A shows that ascorbic acid is less important when beer is the extractant. This may be due to the presence of ascorbic acid or other reducing substances in the beer. None of the four laboratories used the same beer.

Tables II and III summarize the results reported by 16 laboratories examining four samples of filter aids which were paired. Samples A and B represented straight calcined diatomite. Samples C and D represented flux calcined diatomite. Ascorbic acid was employed in all tests. One laboratory obtained abnormally low figures for phthalate extraction and subsequently found their ascorbic acid to be oxidized. The erroneous figures, having an explainable cause, were not included in either summaries or graphs. This emphasizes the necessity for including ascorbic acid, as shown in Table I.

Consideration of the mean values in Table II shows that a definite difference did exist between the two members of each pair of samples and also between the four samples. Comparison of the standard deviation (δ) values points to less variation for the determinations made, using phthalate buffer as extractant. The values of range, R, show less spread for the phthalate data.

Four of the collaborators also analyzed the extracts for iron by atomic absorption as well as by the colorimetric method. The means of the values obtained by atomic absorption are slightly higher than the mean values for colorimetric data and the between-laboratory agreement is better than for the colorimetric. These values have been included in the derivation of both Tables II and III as though they were separate collaborators.

Table III summarizes the collaborative data after elimination of outliers determined by Dixon's method (3) at 95% confidence level.

TABLE I
Effect of Ascorbic Acid on Determination of Soluble Iron in Beers and in Phthalate Buffer
(μg/g soluble iron)

	Collaborator A				Collaborator B		Collaborator C		Collaborator D	
Extractant	Beer A		Phthalate		Beer B	Phthalate	Beer C	Phthalate	Beer D	Phthalate
Ascorbic Acid	no	yes	no	yes	yes	yes	yes	yes	no	no
Sample										
1	15.4	17.0	2.7	31.1	10.8	29.2	15.6	35.6	13.4	3.2
2	30.8	30.6	4.6	43.3	27.2	40.0	31.2	39.0	29.4	8.6
3	41.9	42.2	3.2	50.3	36.4	50.8	45.2	47.8	43.8	0.4
4	46.0	49.9	4.0	56.2	48.0	58.8	50.0	53.6	45.6	4.0
5	9.2	9.7	2.7	22.2	8.0	22.8	9.6	22.4	7.8	4.6
6	25.4	24.9	3.5	43.5	18.8	37.2	26.0	39.2	30.2	4.0
7	41.9	40.6	1.6	48.1	40.0	48.0	41.6	45.0	38.8	4.0

Calculations at the 99% level would have thrown out two points which should be included upon inspecting the graphic presentation. The difference in samples is further confirmed by the large increase in calculated F ratio compared to critical values shown in columns 8 and 9. Note that all sources of error are less from phthalate extractions except that of the within-laboratory error for the A-B pair. This may be traced to operator technique.

Figures 1, 2, 3, and 4 are Youden plots of the two sample pairs for each of the two extractants. Note the greater dispersion of points along the diagonal for those tests conducted with beer as extractant. This is associated with between-laboratory variation. Clustering is noticeably closer for the phthalate data points. Dispersion away from the diagonals is related to within-laboratory variation and is a standoff between the two pairs. The A-B pair appears better than C-D for beer extraction but C-D appears better than A-B for phthalate extraction. At this point, one could not correlate this with either magnitude of iron content or with manner in which diatomite was fluxed, and both may have an influence.

In examining the data for linearity, we may refer to Fig. 5, in which data for the four samples obtained by extraction with beer is plotted against the values obtained by phthalate extraction. The trend line is that of the first approximation of the method of least

Figs. 1–4. Youden plots of collaborative data showing μg/g iron extracted from filter aids.

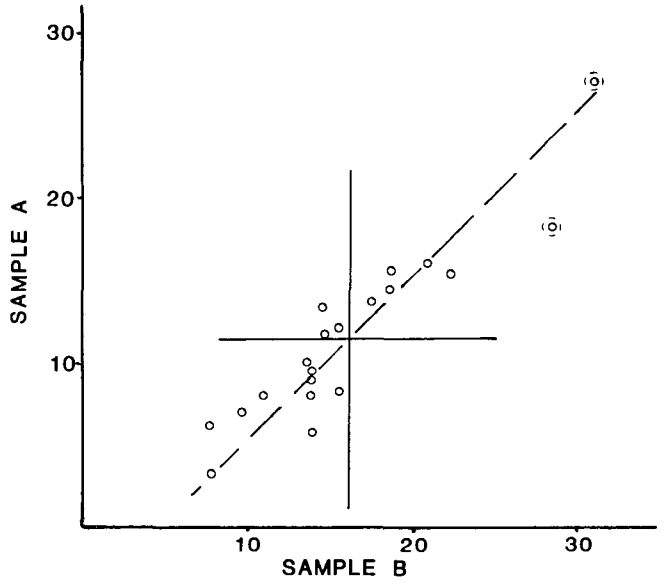

Fig. 1. Samples A and B. Extractant: beer.

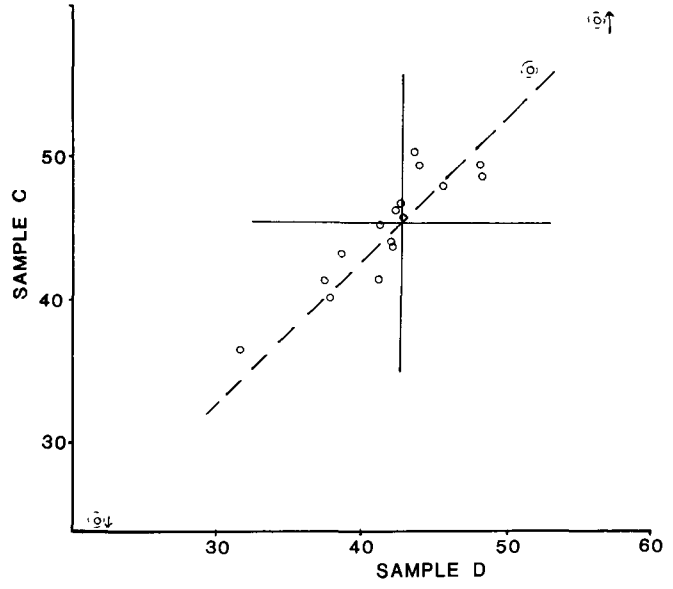

Fig. 2. Samples C and D. Extractant: beer.

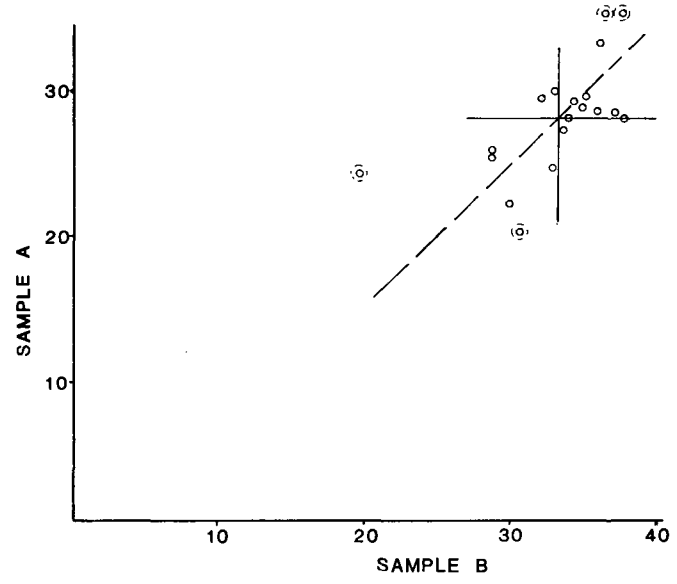

Fig. 3. Samples A and B. Extractant: phthalate.

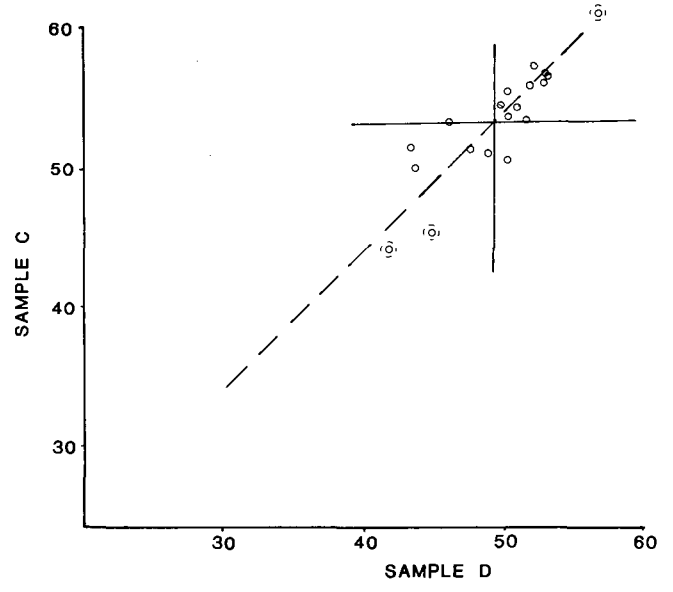

Fig. 4. Samples C and D. Extractant: phthalate.

squares. Note how well distributed the individual values are about this line. Its equation is: BSI = 1.31 PSI − 24.07, in which BSI = Beer Soluble Iron and PSI = Phthalate Soluble Iron. The calculated coefficient of correlation is 0.82. While this does establish that the general relationship is linear, it should be pointed out that this graph involves an averaging of 16 beers. Tenney and Duensing (4) have already shown that the lines for different beers do not have the same slope. Hence, the above formula should not be used except as an approximation for any particular beer.

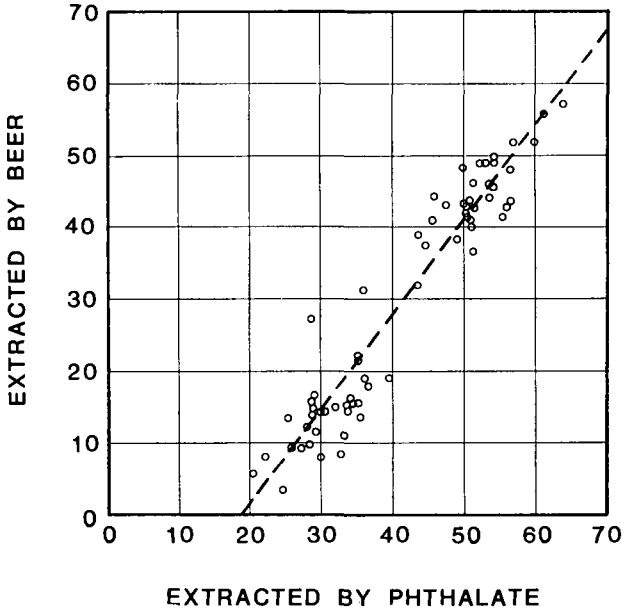

Fig. 5. Samples A, B, C, and D. Data obtained by extraction with beer plotted against data obtained by extraction with phthalate.

The relation between the ability of any specific beer and that of the standard phthalate buffer to extract iron from filter aids should be calculated from data comparing that beer with the standard extractant. At least four samples of filter aid should be examined using the two extractants. If these samples vary in iron content over the expected range to be met, and if the values obtained from the beer are plotted against those obtained from phthalate, a straight line can be fitted visually between these points. This will adequately allow BSI values to be predicted from PSI results. Because any given brand of beer may vary with compositional changes in ability to extract iron, the predictive curve should be reestablished whenever changes are suspected.

TABLE II
Collaborative Results—Iron in Filter Aids Solubilized by Beer and by Phthalate Buffer (μg/g soluble iron found)

Extractant	Beer				Phthalate			
Sample	A	B	C	D	A	B	C	D
Summation of values	232.1	325.7	900.9	852.2	532.2	630.8	1008.9	939.5
Mean	11.6	16.3	45.0	42.6	28.0	33.2	53.1	49.4
Std. dev.	5.4	6.1	7.9	7.6	3.9	4.4	4.1	4.2
R (range)	23.8	20.8	28.0	37.8	13.1	19.8	17.3	15.1
n	20	20	20	20	19	19	19	19
Outliers	2	2	3	3	3	2	3	1

TABLE III
Statistical Summary—Soluble Iron in Two Pairs of Samples by Two Extractants

Sample	Extractant	n^a $\overline{\overline{X}}$	Grand Mean[b] S_r	Within-Lab Error[c] S_b	Between-Lab Error[d] S_t	Total Error[e]	Calc. F Ratio[f]	Critical F Ratio[g] 99%	Coef. of Variation CV[h]	Radius of Confidence RCC[i]
Pair I	Beer	17	12.91	1.20	3.55	5.16	18.39	3.405	40.0	2.95
A and B	Phthalate	15	30.73	1.64	2.16	3.47	4.46	3.73	11.3	4.03
Pair II	Beer	16	44.03	1.90	3.80	4.25	5.01	3.522	9.65	4.65
C and D	Phthalate	16	51.71	1.40	2.41	3.68	6.89	3.522	7.1	3.43

[a]n = Number of collaborative values.

[b]Grand Mean $\overline{\overline{X}} = \frac{(x+y)}{2n}$; (x = individual values for sample A or C and y = individual values for B or D).

[c]$S_r = \sqrt{\frac{D^2/2 - (D)^2/2n}{n-1}}$ where D = x − y.

[d]$S_b = \sqrt{S_t^2 - S_r^2}$

[e]$S_t = \sqrt{\frac{S_T 2/2 - (T)^2/2n}{n-1}}$

[f]F ratio = S_t^2/S_r^2.

[g]Critical F ratio is from tables.

[h]CV = 100 $S_t/\overline{\overline{X}}$.

[i]RCC = the radius of circle of confidence at 95% = 2.448 × S_r.

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1. AMERICAN SOCIETY OF BREWING CHEMISTS. Methods of analysis (7th ed.). Filter Aids-4. The Society: St. Paul, Minn. (1976).
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3. DIXON, W. J. Processing data for outliers. *Biometrics 9*: 74 (1953).
4. TENNEY, R. I., and DUENSING, W. J. Determination of soluble iron in filter aids. *J. Amer. Soc. Brew. Chem. 34*: 120 (1976).

APPENDIX

SOLUBLE IRON IN FILTER AIDS

This method is designed as a reference method (2). Beers vary in ability to extract iron (1), but they may be specifically correlated to the standard buffer (3) used here. Iron concentration in the extracted solution may be determined by either the *Methods of Analysis* procedure Beer–18A or procedure Beer–18B.

Reagents

a) For determination of iron, see *Methods of Analysis* procedure Beer–18A or procedure Beer–18B.
b) *Extractant.* Potassium hydrogen phthalate. Reagent grade, a primary standard. Prepare as a 1% w/v solution in iron-free distilled or deionized water. pH of this solution should be 4.0 at 20°C.
c) *Ascorbic acid.* It is essential to use ascorbic acid, USP quality, iron-free, ground to a fine powder, as described in Beer–18A. It must not have become oxidized through age or contact with oxidant vapors.

Apparatus

As described under Filter Aids–4.

Method

Adjust the temperature of 200 ml of extractant (1% w/v potassium hydrogen phthalate) in a 1000-ml flask to 24° C. Add 5.0 g filter aid to the solution and start stopwatch at moment of addition. Swirl flask to put all filter aid into suspension. Swirl flask again for 10 sec at 1, 2, 3, 4, and 5 min of elapsed time, allowing filter aid to settle after each swirling. Swirl flask again at 5 min 50 sec and immediately transfer entire suspension to a funnel fitted with iron-free filter paper.

Discard filtrate collected during first 30 sec. Collect filtrate for next 150 sec and determine iron concentration of filtrate by *Methods of Analysis* procedure Beer–18A or procedure Beer–18B. Also determine iron concentration of a portion of the extractant solution which has not contacted the filter aid.

Calculation

Subtract the iron concentration of the untreated extractant from that of the filtrate from the portion exposed to filter aid. Under the conditions described above the difference obtained is that contributed by 5 g of filter aid in 200 ml of solution. This is expressed as mg/l., so actual weight of iron extracted from the 5 g is D/5 and from 1 g D/5 × 5. Therefore:

$$\frac{D \times 100}{5 \times 5} = D \times 40 = \text{mg iron/kg filter aid}$$

Example

Iron concentration of phthalate extract = 0.9 mg/l.
minus iron concentration of blank −0.1
Difference D 0.8

Soluble iron = D × 40 = 0.8 × 40 = 32 mg/kg filter aid

References

1. AMERICAN SOCIETY OF BREWING CHEMISTS. Report of subcommittee on beer soluble iron in filter aids. *Proc. 33*(3): 96 (1975).
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3. TENNEY, R. I., and DUENSING, W. J. Determination of soluble iron in filter aids. *J. Amer. Soc. Brew. Chem. 34*: 120 (1976).