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Note

Determination of furfural in spent sulfite liquor by gas chromatography

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Spent sulfite liquor (SSL) is a waste by-product of the manufacture of wood pulp by the acid sulfite process. Furfural is formed in the pulping process by a two-step reaction. Initially, hydrolysis converts some of the pentosan content of the pulp to pentoses which in turn are partially converted to furfural by dehydration. Evaporation of the sulfite liquor to increase its solids content results in additional conversion to furfural which collects in the condensate. A rapid and convenient method for estimation of furfural content at any stage of the process is essential for study of parameters which influence furfural formation.

Analytical methods for furfural were reviewed by Madden[1]. Most methods are based on reactions of the ring or of the aldehyde function although there is a UV method based on the characteristic absorption of furfural at 276 nm. The gas chromatographic (GC) determination of furfural in condensates from the evaporation of SSL has been reported by Rexfelt and Samuelson[2,3]. Hrutfiord and McCarthy also used GC to determine furfural in the steam volatile fraction of SSL[4].

Initially, furfural analysis was attempted by direct injection of diluted SSL samples. Poor peak area reproducibility, due to ghosting was observed. It is believed that the ghosting arises from retention of furfural by sample solids residue deposited in the injection port. The source of the retained furfural may be either free furfural initially present in the SSL sample or may be previously unconverted pentoses which convert to furfural in the hot (260 °C) injection port.

The problem of peak area reproducibility, combined with the possibility that peak area may not be representative of the initial furfural content of the sample, led to the conclusion that extraction of the furfural would be necessary to eliminate these difficulties.

An extraction procedure using chloroform to extract the furfural quantitatively from the SSL was developed. The chloroform extracts give reproducible furfural peak areas, and the extraction step ensures that no additional furfural formation takes place in the injection port since chloroform will not extract significant quantities of pentoses from the SSL.

Method development included determination of the precision of the method at two concentration levels of furfural over a period of several days. Also included were studies to determine the effect of furfural concentration level and pH on efficiency of the chloroform extraction.

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EXPERIMENTAL

Instrumentation and operating parameters

A Perkin-Elmer 900 gas chromatograph with flame ionization detector and a Hewlett-Packard 3370B integrator were used. The column was 6 ft. × 1/8 in. O.D. stainless steel packed with 60–80 mesh Porapak Q. Operating parameters were: column temperature, 240 °C; injection port temperature, 260 °C; detector temperature, 300 °C; carrier gas, nitrogen at 30 ml/min; sensitivity, $5 \cdot 10^{-10}$ A f.s.

Reagents, standards and samples

Furfural was obtained from Aldrich (Milwaukee, WI, U.S.A.; 99%). This material was used for preparation of standards and known addition experiments without purification.

Chloroform was obtained from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). Ethanol preservative in the chloroform does not interfere with the determination.

Sodium chloride (reagent grade) was obtained from Baker (Phillipsburg, NJ, U.S.A.).

A master solution of furfural in chloroform (nominal concentration, 1 μg/μl) was prepared by accurately weighing about 100 mg of furfural in a 100-ml volumetric flask and diluting to volume with chloroform. Appropriate dilutions of this solution were used for standards. Including the master solution, the concentration range (0.02–1 μg/μl) of these standards brackets the expected concentration range of furfural in the chloroform sample extracts.

To establish a working concentration range for the method, a hardwood SSL, SSL-A, was used "as received" for the high furfural concentration level sample. SSL-B, the low concentration level sample, was prepared from SSL-A by steam stripping of a major portion of the furfural. Samples with known additions of furfural for recovery experiments were prepared from SSL-A and SSL-B.

For studies of the effect of pH on extraction efficiency, a series of samples with pH ranging from 1.03 to 5.03 were prepared from SSL-A by pH adjustment with 1 *M* sodium hydroxide or 1 *M* sulfuric acid and dilution with water to give a dilution factor of 0.5. A control sample, diluted without pH adjustment, was included.

Extraction procedure

If necessary, dilute SSL samples so that furfural concentration is below 0.8 mg/ml. The pH of solutions can range from 1.0 to at least 5.0. Use volumetric pipets to transfer the SSL sample and chloroform to a screw-cap test tube. The chloroform–SSL volume ratio can be varied, depending upon the furfural concentration of the sample. For the samples reported here, the ratio was 2:3 for the dilute sample, SSL-B, and 2:2 for the more concentrated sample, SSL-A. Add approximately 0.5 g sodium chloride to the mixture, cap tube, and mix contents of the tube on a tube mixer for 2 min. The sodium chloride is necessary to make extraction of the furfural quantitative. Centrifuge for 2 min. The excess salt collects at the liquid–liquid interface. Use a disposable pipet to transfer the chloroform (lower) layer to a sample vial and cap the vial tightly.

Measurement procedure

It is preferable to use the solvent flush method for sample injection[5]. Inject nominal 5 μl sample volumes for both furfural standard solutions and chloroform sample extracts. Determine weight of furfural injected in GC sample extracts from calibration curve prepared from standard solution data. Calculate the furfural concentration in the original SSL sample from the following equation:
Furfural concentration in SSL (μg/μl or mg/ml) = (Wt. furfural inj. (μg)/Vol. GC sample (μl))·(Vol. chloroform (ml)/Vol. SSL (ml)).

RESULTS AND DISCUSSION

A typical calibration curve is shown in Fig. 1. Fig. 2 shows a chromatogram of a chloroform extract of SSL-A. The furfural elutes on the tail of the chloroform peak, but uncertainties in area integration of this type peak were reduced by operating the integrator in the tangent skimming mode.

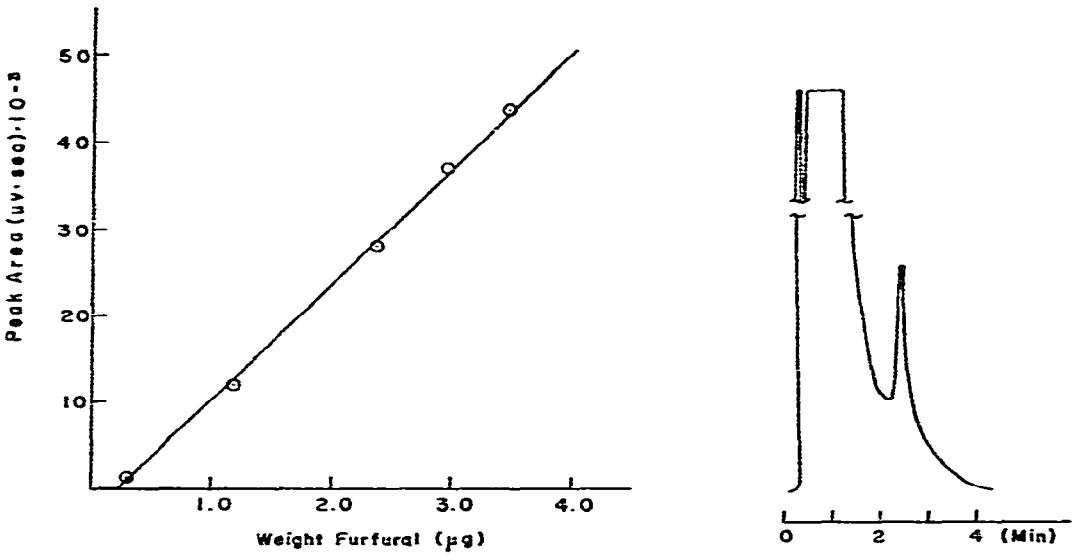

Fig. 1. Calibration curve, a plot of peak area *versus* weight of furfural, from furfural standards in chloroform.

Fig. 2. Gas chromatogram of chloroform extract of SSL. The retention time of furfural peak is 2.48 min.

A series of repeat runs were made in which SSL-A and SSL-B were analyzed on successive days to determine the precision of the method. A new calibration curve and fresh chloroform extracts were prepared at the start of each day's runs. Four replicate determinations on each sample were made each day. Results of these analyses are shown in Table I.

From Table I it is seen that the precision of the determination at the higher concentration level is about twice that of the lower concentration level (C.V., 6% *versus* 12.5%). This is expected because of the inevitable loss of precision that accompanies

TABLE I

RESULTS OF PRECISION STUDIES FOR THE DETERMINATION OF FURFURAL IN SSL

S.D. = Standard deviation; C.V. = coefficient of variation.

Furfural concentration (mg/ml)							
SSL-A				*SSL-B*			
Run	*Day 1*	*Day 2*	*Day 3*	*Run*	*Day 1*	*Day 2*	*Day 3*
1	0.47	0.51	0.56	1	0.041	0.053	0.045
2	0.49	0.51	0.49	2	0.044	0.053	0.045
3	0.45	0.52	0.49	3	0.045	0.055	0.038
4	0.48	0.50	0.47	4	0.045	0.057	0.046
Overall mean		0.50		Overall mean		0.047	
S.D.		0.030		S.D.		0.0059	
C.V.		6.0%		C.V.		12.5%	

determinations at lower concentration levels. SSL-B has a furfural concentration about tenfold lower than SSL-A. The furfural concentration of SSL-B probably represents the lower concentration limit that can be determined under the stated experimental conditions.

Furfural recovery experiments were carried out to determine the efficiency of the extraction procedure. The SSL samples with known furfural additions (described earlier) were used for this study. Four replicate runs were made for each sample. The analyses, including preparation of fresh extracts, were repeated the next day. The theoretical furfural concentration of each sample was assumed to be the sum of the average experimentally determined concentration of the original samples (Table I) plus the known addition. Results are summarized in Table II.

TABLE II

FURFURAL RECOVERY DETERMINATIONS OF SSL SAMPLES WITH KNOWN ADDITIONS

Furfural concentration (mg/ml)							
SSL-A with known addition (0.30 mg/ml added furfural)				*SSL-B with known addition (0.45 mg/ml added furfural)*			
Day 1	*Day 2*			*Day 1*	*Day 2*		
0.76	0.80			0.49	0.49		
0.73	0.76			0.46	0.53		
0.76	0.75			0.52	0.48		
0.78	0.74			0.52	0.48		
Overall mean			0.76	Overall mean			0.50
Theoretical conc.		(0.50 + 0.30)	0.80	Theoretical conc.		(0.047 + 0.45)	0.50
Recovery			95%	Recovery			100%

The recovery data in Table II show that the extraction efficiency ranged from 95 to 100% for the concentration range studied. The lower recovery at the higher concentration level indicates that this level is somewhat high for maximum quantitative

recovery by chloroform extraction under the experimental conditions. Therefore, it is recommended that SSL samples be diluted with water before extraction to give a furfural concentration less than 0.8 mg/ml to ensure that maximum extraction of fufural by chloroform is achieved.

The question was raised concerning the effect of pH on extraction efficiency because of possible interference from the furfural bisulfite addition compound (α-hydroxy-2-furanmethanesulfonic acid) which is known to exist in equilibrium with furfural in aqueous solutions containing bisulfite ions[6]. This equilibrium is pH dependent because bisulfite ion concentration varies markedly with pH[7,8]. To determine the effect of pH on extraction efficiency, furfural was determined in a series of pH adjusted solutions (described earlier) prepared from SSL-A. Results of these determinations are shown in Table III.

TABLE III

EFFECT OF pH ON EXTRACTION EFFICIENCY, SSL-A FURFURAL CONCENTRATION *versus* pH ADJUSTED SAMPLES

Values are the average of two determinations.

Sample pH	*SSL-A Furfural conc. (mg/ml)*
1.03	0.54
1.89 (Control)	0.53
2.93	0.55
5.03	0.51
	Mean 0.53

The mean value is within the range of the standard deviation of the previous determinations for this sample (Table I). It is concluded that pH does not affect extraction efficiency significantly in the pH range (1.03–5.03) investigated in this study. This is not unexpected because reduction of furfural concentration in the SSL by chloroform extraction will cause the equilibrium to shift towards furfural and reduce the concentration of the addition compound to insignificant levels.

A GC method for furfural in SSL which ensures that the furfural content of the sample is not altered by high temperatures of the instrument, has been described. The simple extraction procedure for sample preparation and rapidity of analysis make it particularly useful for monitoring the effect of process variables on furfural content of the SSL.

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REFERENCES

1 J. W. Madden, in F. D. Snell and L. S. Ettre (Editors), *Encyclopedia of Industrial Chemical Analysis*, Vol. 13, Interscience, New York, London, Sydney, Toronto, 1971, p. 232.
2 J. Rexfelt and O. Samuelson, *Sven. Papperstidn.*, 73 (1970) 689.
3 J. Rexfelt and O. Samuelson, *Sven. Papperstidn.*, 75 (1972) 299.
4 B. F. Hrutfiord and J. L. McCarthy, *Tappi*, 47 (1964) 381.
5 R. F. Kruppa and R. S. Henly, *Amer. Lab.*, 3 ,No. 5 (1971) 41.
6 E. Adler, *Sven. Papperstidn.*, 50, No. 11B (1947) 9.
7 *Instruction Manual, Sulfur Dioxide Electrode Model 94-65*, Orion Research, Cambridge, MA, 1973, p. 12.
8 J. F. Harris and L. L. Zoch, *Anal. Chem.*, 34 (1962) 201.