

CHROM. 16,968

Note

Gas chromatographic determination of elemental and polysulfide sulfur in kraft pulping liquors

LEROY G. BORCHARDT and DWIGHT B. EASTY*

Chemical Sciences Division, The Institute of Paper Chemistry, P.O. Box 1039, Appleton, WI 54912 (U.S.A.)

(Received June 14th, 1984)

Addition of polysulfide to pulping liquor has long been known to increase the yield of wood pulp from the kraft process. Methods heretofore available for determining polysulfide in pulping liquors require either spectrophotometric measurements or indirect, multistep, titrimetric procedures.

Absorbance measurements at 285 nm¹ or 297 nm² have been employed for polysulfide determinations, but they cannot be used on colored spent liquors.

Indirect methods for polysulfide in which thiosulfate is measured before and after the polysulfide is decomposed with sulfite are used for analysis of white and black (spent) liquors^{3,4}. An acidimetric titration may also be used to determine polysulfide from consumption of sulfite in the same decomposition reaction⁵. Polysulfide may be reacted with copper gauze to form copper sulfide; the sulfide is decomposed in acid and the hydrogen sulfide (H₂S) evolved is determined iodometrically⁶. In a newer method, polysulfide is represented by the increase in the liquor's sulfide content following reduction of the polysulfide with sodium amalgam⁷. Reaction of dissolved organics with the amalgam prevents use of this technique on black liquors. Results from this method are influenced by a high thiosulfate content in the liquor and also by the extent to which the sample is diluted for contact with the amalgam⁸.

Many of the indirect methods lose precision at low polysulfide levels because the analytical result is a small difference between large numbers. Furthermore, results of all of these procedures are strongly influenced by the analyst's ability to avoid oxidative losses of polysulfide from the sample before and during the determination. Oxygen must be rigorously excluded during preparation of standards for the spectrophotometric methods.

This report describes the development of a gas chromatographic (GC) method for determining polysulfide in all types of kraft pulping liquors. Polysulfide is decomposed to elemental sulfur in buffer (pH 5.5), and the elemental sulfur is derivatized with triphenylphosphine. The resulting triphenylphosphine sulfide is determined by flame ionization-GC.

In contrast with spectrophotometric methods, the new procedure is calibrated with a pure, commercially available compound, triphenylphosphine sulfide. All operations prior to GC are performed in sealed septum vials; this effectively eliminates loss of polysulfide due to air oxidation. This direct method of measuring po-

lysulfide employs straightforward sample preparation techniques which are adaptable for the concurrent analysis of large numbers of liquors.

EXPERIMENTAL

Reagents and liquors

Buffer solution (pH 5.5) was prepared by mixing 50 ml 0.1 *M* potassium acid phthalate with 36.6 ml 0.1 *M* sodium hydroxide. Triphenylphosphine, triphenylphosphine sulfide, and anthracene were purchased from Aldrich (Milwaukee, WI, U.S.A.).

Synthetic polysulfide liquors were prepared by dissolving 15 g $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ in deoxygenated, nitrogen-sparged water and adding 0.2–0.8 g elemental sulfur (99.999% pure, Aldrich) previously dispersed in water. The elemental sulfur was dissolved in the sodium sulfide solution by stirring with a magnetic stirrer and heating to 60–70°C while bubbling nitrogen into the solution. The solution was then diluted to 100 ml volume with deoxygenated water. Aliquots were transferred to 10-ml serum bottles which were completely filled to exclude air and capped with PTFE-lined septa and crimped aluminum seals.

Commercial polysulfide liquors were prepared by oxidizing kraft white liquor in a pilot-scale MOXY® reactor⁹. Samples were stored in the dark with a layer of paraffin oil covering the liquor. To minimize the frequency of opening the main supplies of polysulfide liquors, a number of 10-ml serum bottles of each liquor were filled, capped, and wrapped with aluminum foil.

Procedures for polysulfide determination

Triphenylphosphine method. A volume of 40 ml buffer (pH 5.5) and 10.0 ml toluene containing anthracene (about 0.1 mg/ml weighed accurately) were placed in a 60-ml serum bottle. The mixture was purged with nitrogen for a few seconds before capping with a PTFE-lined septum and crimped aluminum seal. Triphenylphosphine reagent (200 μl of a 2% solution in toluene) was injected into the sealed bottle. This was followed by injection of 25–50 μl of kraft liquor into the aqueous phase. The bottle was placed on its side with its length in the direction of travel and shaken on the horizontal shaker for 10 min. About 1 ml of the toluene layer was removed and stored in a stoppered bottle until injection (5 μl) on the gas chromatograph. Sulfur was computed by the internal standard method with anthracene as the internal standard. For commercial liquors, the procedure was repeated using buffer (1% sodium carbonate pH 11.5) to correct for elemental sulfur originally present in the sample.

GC analysis was performed on a Hewlett-Packard 5840A chromatograph with a flame ionization detector. The 0.25-in. glass column (6 ft. \times 2 mm I.D.) was packed with 3% OV-17 on Gas-Chrom Q 100/120. Column temperature was programmed from 120 to 280°C at 8°C/min. Carrier gas was helium at a flow-rate of 30 ml/min. A Hewlett-Packard 5985B was used for GC–mass spectrometry (MS) analysis.

Sodium amalgam method. Details are provided in TAPPI Test Method T 694 pm-82⁷. Portions (5 ml) of liquor were diluted to 50 ml with deoxygenated water, and 10-ml aliquots were taken for analysis. Polysulfide was reduced to sulfide by contact with sodium amalgam. In this investigation the amalgam reduction was found to be quite sensitive to variations in technique, leaving the optimum procedure

in doubt. Consequently, reductions were conducted for 1 and 2 min, with and without nitrogen padding to protect the sample from exposure to air. Sulfide was then determined by manual potentiometric titration with mercuric chloride using a silver-sulfide ion-selective electrode and double junction reference electrode (both from Orion Research, Cambridge, MA, U.S.A.). A fresh portion of regenerated amalgam was used for each sample. Amalgam reduction and polysulfide sulfur determination were always performed before determining the original sodium sulfide in the sample. In this way the effect of the slow decomposition of polysulfide in diluted liquor was minimized.

RESULTS AND DISCUSSION

Demonstration of concept

Triphenylphosphine (TPP) has been reported to react rapidly with elemental sulfur to yield triphenylphosphine sulfide (TPPS)¹⁰. Initial studies involved an examination of this reaction and the GC-MS analysis of its products. TPP and sulfur in toluene were found to yield TPPS, as demonstrated by comparison of the mass spectra of authentic TPPS and the reaction product. The reaction is virtually instantaneous at room temperature, and the product is stable for at least 24 h.

When a known amount of sulfur was reacted with an excess of TPP, the sulfur was totally converted to TPPS. Dissolved oxygen in the sample was converted to triphenylphosphine oxide (TPPO). Formation of TPPO is minimized by use of fresh TPP and protection of samples from oxygen. A typical chromatogram is shown in Fig. 1.

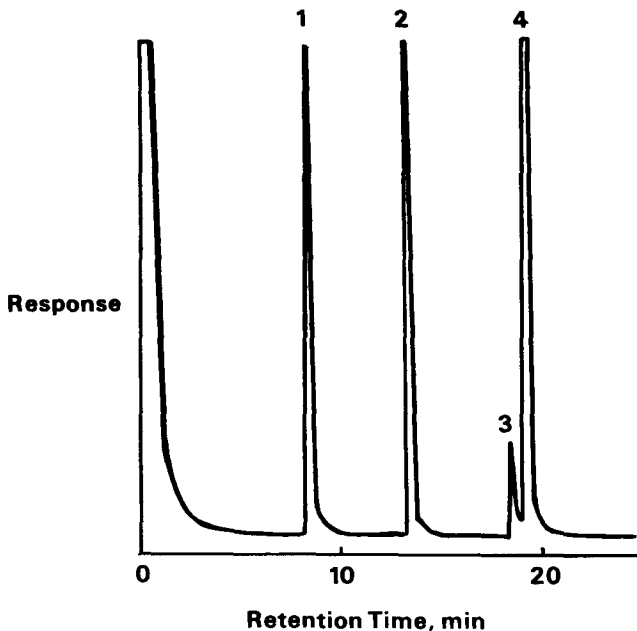


Fig. 1. Gas chromatogram obtained in the determination of sulfur by the TPP method. Peaks: 1 = internal standard; 2 = TPP; 3 = TPPO; 4 = TPPS.

Orienting studies demonstrated that polysulfide sulfur could be converted to elemental sulfur by acidification to pH 5.5. This permitted determination of polysulfide in the presence of potentially interfering thiosulfate, which would yield elemental sulfur at lower pH. Conversion of the unstable polysulfide into elemental sulfur as the first step of the determination constitutes a distinct advantage of this method. In older procedures the initial operation is dilution of the sample, which without great care can lead to polysulfide loss.

Analysis of synthetic liquors

Three polysulfide solutions and one sodium sulfide solution without added elemental sulfur were prepared and analyzed by the TPP method. The first analysis was performed immediately after preparation of the sample, and the duplicate was done a week later using the same sample stored in a sealed serum bottle. Results in Table I indicate good recovery of the sulfur used in preparing the liquors.

Analyses indicated that trace quantities of sulfur originated from the TPP reagent, water, buffer solution, sodium sulfide, and sodium thiosulfate. The amounts were found to be insignificant compared with the sulfur content of a polysulfide cooking liquor. Background levels of elemental sulfur which are not polysulfide were determined by replacing the buffer (pH 5.5) with a buffer at pH 11.5. This measurement performed on a synthetic polysulfide liquor revealed only a trace (<0.1 g/l) of elemental sulfur, and it confirmed that polysulfide is not decomposed at pH 11.5.

Analysis of commercial liquors

The TPP method and the TAPPI sodium amalgam method were used to determine polysulfide in six commercial polysulfide liquors and in the feed liquor used for polysulfide liquor preparation. Results from the TPP method are corrected for background levels of elemental sulfur in the polysulfide liquors; amounts ranged from 0.3 g/l in samples 2 and 5 to 0.9 g/l in sample 1. All determinations by the TPP procedure were performed in duplicate. Polysulfide values obtained by the TPP method on the commercial polysulfide liquors with concentrations ranging from 6 to 17 g/l have a standard deviation of 0.24 g/l. As indicated in Table II, results from the TPP method are similar to those from the amalgam procedure.

TABLE I
ANALYSIS OF SYNTHETIC POLYSULFIDE LIQUORS

Sample	Sulfur added (mg)*	Sulfur found (mg)**	Recovery (%)
1	0.2415	0.2245	93.0
1	0.2415	0.2381	98.6
2	0.1172	0.1190	102
2	0.1172	0.1238	106
3	0.3843	0.3711	96.6
3	0.3843	0.3813	99.2
4	0	0.014	—
4	0	0.0053	—

* In 50- μ l sample.

** Corrected for elemental sulfur in sodium sulfide.

TABLE II
POLYSULFIDE SULFUR IN COMMERCIAL LIQUORS

Sample	TPP method (g/l)	Amalgam method (g/l)*
1	17.0	15.6-18.0
2	7.4	6.1- 7.3
3	6.2	5.4- 6.1
4	7.5	6.5- 7.4
5	14.1	13.7-15.6
6	17.1	15.3-17.6
Feed liquor	0.3	0.3

* Range of values representing 1 and 2 min contact with amalgam, with and without exposure to air.

Two samples of kraft black liquor were analyzed in duplicate by the TPP method using buffers at pH 5.5 (to determine polysulfide plus elemental sulfur) and pH 11.5 (to determine elemental sulfur). Results in Table III suggest that both liquors contained elemental as well as polysulfide sulfur.

The validity of results from analysis of commercial liquors by the TPP method is further documented by the spike recovery data in Table IV. Excellent recoveries were achieved in analysis of the white and polysulfide liquors. The slightly lower value for the black liquor may have resulted from emulsion formation during extraction. Although interferences on the chromatograms from organics extracted from the black liquor had been anticipated, they were not observed.

TABLE III
POLYSULFIDE AND ELEMENTAL SULFUR IN KRAFT BLACK LIQUORS

	pH 5.5 (g/l)*	pH 11.5 (g/l)**
Black liquor A	0.40	0.14
Black liquor T	0.99	0.54

* Polysulfide plus elemental sulfur.

** Elemental sulfur.

TABLE IV
SPIKE RECOVERY FROM POLYSULFIDE, WHITE, AND BLACK LIQUORS

Sample	Sulfur present (mg)*	Sulfur added (mg)	Sulfur found (mg)	Recovery (%)
Polysulfide liquor A	0.2503	0.1922	0.4143	93.6
Polysulfide liquor B	0.1287	0.1922	0.3214	100
White liquor	0.0055	0.1922	0.1999	101
Black liquor T	0.0492	0.1922	0.2230	92.4

* In 25 μ l of white and polysulfide liquors; in 50 μ l of black liquor.

Results of this study indicate that the TPP method is a valid, versatile, and significantly improved method for determining polysulfide in pulping liquors. Elemental sulfur, not formerly determined in pulping liquors, can also be measured.

ACKNOWLEDGEMENTS

The authors acknowledge with gratitude the polysulfide liquors provided by M. J. Fine and G. C. Smith, the suggestion of triphenylphosphine by P. Mathiaparanam, and skillful analyses by J. E. Johnson.

REFERENCES

- 1 A. Teder, *Svensk Papperstidn.*, 70 (1967) 167.
- 2 W. C. Harris, E. P. Crowell and D. H. McMahon, *Tappi*, 57(1) (1974) 82.
- 3 A. J. Danielsen, K. Johnsen and P. Landmark, *Nor. Skogind.*, 23 (1969) 378.
- 4 J. Papp, *Svensk Papperstidn.*, 74 (1971) 310.
- 5 P. Ahlgren, *Svensk Papperstidn.*, 70 (1967) 730.
- 6 E. Bilberg, *Nor. Skogind.*, 13 (1959) 307.
- 7 *TAPPI Test Method T 694 pm-82*, Technical Association of the Pulp and Paper Industry, Atlanta, GA, 1982.
- 8 M. J. Fine and G. C. Smith, The Mead Corporation, Chillicothe, OH, unpublished results.
- 9 G. C. Smith, S. E. Knowles and R. P. Green, *Pap. Trade J.*, 159 (1975) 38.
- 10 P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 78 (1956) 3710.