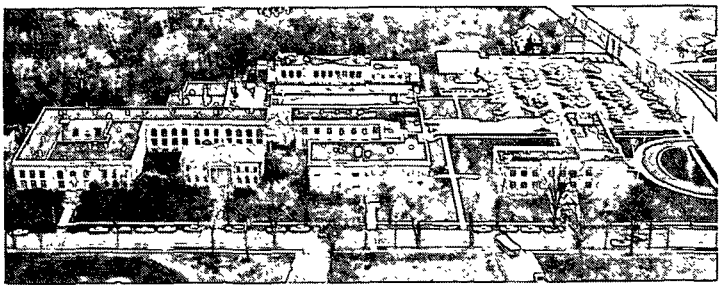

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# SOURCES OF ERROR IN THE AMALGAM METHOD FOR DETERMINING POLYSULFIDE IN KRAFT WHITE LIQUOR

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NOTE TO THE EDITOR

# Sources of error in the amalgam method for determining polysulfide in kraft white liquor

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**KEYWORDS:** analytical methods, polysulfide, kraft, white liquor

In 1982, a provisional method, TAPPI Test Method T 694, was adopted for determining polysulfide in kraft white liquor. This method is based upon the potentiometric titration of sodium sulfide before and after reduction of the polysulfide with sodium amalgam. More recently, a new method for polysulfide based on gas chromatography was developed in this laboratory (1). Part of the method development involved a comparison of results obtained by the GC and amalgam procedures. In the course of this work, a critical evaluation of the amalgam method revealed several unanticipated sources of error, described below.

## Sample dilution and quantity on amalgam

Dilution of white liquor (20 mL ——> 100 mL) and the amount of diluted liquor placed on the amalgam (10 mL) are clearly specified in T 694. Our investigation has shown that use of different dilutions and sample quantities significantly affected results of the determination (Table I). This finding has prompted two concerns: (1) The conditions specified in T 694 might not be those which yield the correct polysulfide value. No study of sample dilutions and quantities, which might resolve this question, is referenced in the Test Method. (2) Despite the warning note in T 694, analysts might use other liquor dilutions and volumes of sample on amalgam without realizing that these are critical quantities. It is not intuitive that sample dilution and volume on amalgam can

**Extent of amalgam treatment**

Prolonged contact of samples with amalgam can cause reduction of thiosulfate in the liquor to sulfide, as noted in T 694. To minimize this reaction as well as air oxidation of sulfide, samples should be swirled with amalgam no longer than is required to just reduce the polysulfide. To test the time required, a polysulfide liquor was swirled on amalgam, and aliquots were withdrawn every half minute. Polysulfide was measured in each aliquot by the triphenylphosphine GC method (1). Polysulfide did not decrease significantly after one minute of swirling. A one-minute contact time of liquor with amalgam appeared adequate for polysulfide reduction.

This investigation has shown that liquor dilution, volume placed on amalgam, and contact with air during amalgam treatment are sources of error in the polysulfide determination. The study has also raised the possibility of inherent errors in the procedure; these could occur if liquor dilution, volume on amalgam, and time of swirling have not been optimized. These errors can be averted by use of the GC procedure.

**Experimental**

Details of the sodium amalgam method are provided in TAPPI Test Method T 694 pm-82. Deoxygenated water was used for liquor dilution; all analyses on a diluted sample were completed within 1 hour. A fresh portion of regenerated amalgam was used for each sample. In order to exclude air from samples during amalgam treatment, a hose from a nitrogen cylinder was connected to a vinyl glove fitted over the modified plastic beaker. Sulfide was determined by manual potentiometric titration with mercuric chloride using a silver-sulfide ion-selective electrode and double junction reference electrode.

**Literature cited**

1. Borchardt, L. G., and Easty, D. B., J. Chromatogr. **299**: 471(1984).

2. Cardone, M. J., J. Assoc. Off. Anal. Chem. **66**: 1257(1983).

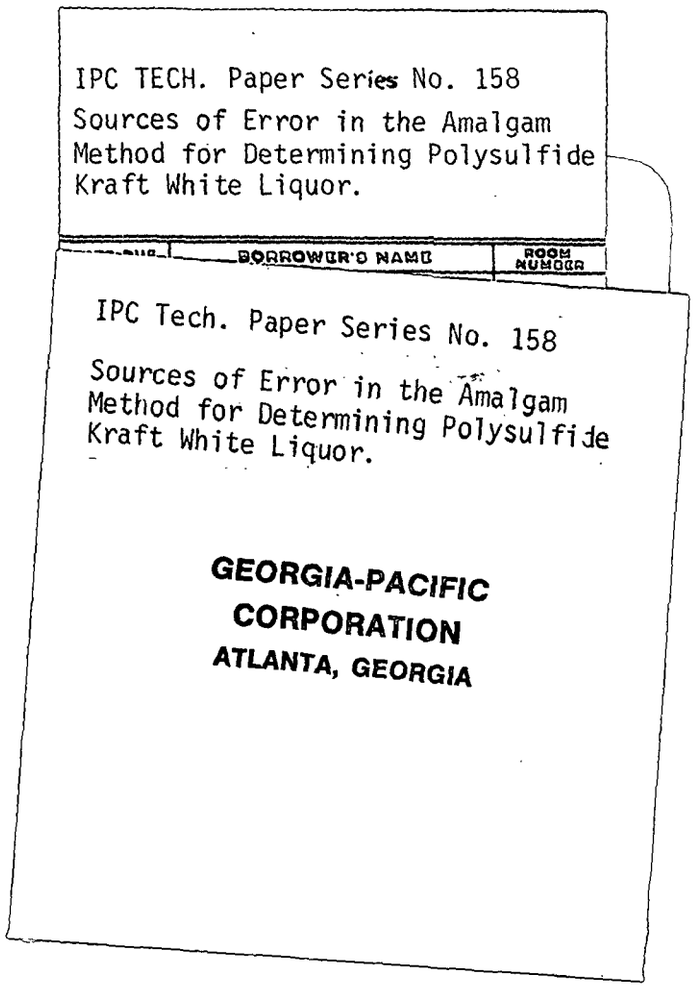
I. Effect on measured polysulfide of sample volume and concentration in contact with amalgam[a]

| Liquor Dilution | Volume of diluted liquor placed on amalgam, mL | |
|---|---|---|
| | 5 | 10 |
| 20 mL —> 100 mL | 16.7 | 16.0 |
| | 16.7 | 16.0 |
| | 16.7 | 16.1 |
| | 16.7 | 15.9 |
| 10 mL —> 100 mL | 15.6 | 15.1 |
| | 16.0 | 15.2 |
| | 15.9 | 15.1 |
| | 15.9 | 15.1 |

[a]Polysulfide values are in g/L. Fifteen mL of amalgam was used for each sample.

II. Polysulfide determinations run with and without nitrogen protection during reduction on amalgam

| Liquor | $N_2$ protected, g/L | Not protected, g/L |
|---|---|---|
| 1 | 15.9 | 14.9 |
| | 16.0 | 14.6 |
| 2 | 6.2 | 5.6 |
| | 6.1 | 5.3 |
| 3 | 7.7 | 6.8 |
| | 7.6 | 6.8 |
| 4 | 14.5 | 14.0 |
| | 14.6 | 14.1 |
| 5 | 13.7 | 12.2 |
| | 13.8 | 12.3 |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