# Quantitative analysis of lignosulphonate using benzethonium chloride – preliminary investigations

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## Abstract

The standard method for the analysis of lignosulphonates in sulphite pulp mill effluents uses 2-naphthylamine as the precipitant. This chemical has been declared a carcinogen and a safer precipitant needed to be found.

Hyamine-1622 or benzethonium chloride, is a high molecular mass quaternary ammonium compound normally used as a germicide. It was found that the chemical could be used to give consistent results for the determination of lignosulphonate in the effluents from a sulphite pulp mill and in the concentrates and permeates resulting from the ultrafiltration of such effluents. Details of an analytical procedure are presented. Although the initial findings appear promising they should be considered to be preliminary.

## Introduction

At a sulphite wood pulping mill, wood chips are delignified by batch cooking in autoclaves with calcium bisulphite liquors. At the end of the digestion process, a concentrated lignosulphonate/sugar effluent known as spent liquor and containing over 16% total dissolved solids (TDS) is discharged from each autoclave via flash tanks. After discharge from the autoclaves the pulp is washed out giving a dilute effluent known as wash pit liquor.

During tests carried out on the recovery of lignosulphonate from these liquors by ultrafiltration, it was necessary to be able to determine the lignosulphonate content of feeds, permeates and concentrates (Neytzell-de Wilde, 1985).

The standard pulp mill method specified by the Technical Association of Pulp and Paper Industry, (TAPPI), method T 629 m – 53 of 1953, uses 2-naphthylamine as the precipitant for the lignosulphonate and is identical to that developed by Partansky and Benson (1936). The Food and Drug Administration (FDA), USA and the UK Carcinogenic Substances Regulations (Searle, 1986) have declared this substance a carcinogen and safer precipitants should therefore be sought.

The range of concentrations of lignosulphonate in the investigation on ultrafiltration was wide, varying from a few milligrams per litre in the permeate to over 300 g/ℓ in the concentrate solutions. The spectrophotometric method described by Schöning and Johansson (1965) and also by Kleinert and Joyce (1957), is suitable as a monitoring procedure for low concentrations of lignosulphonates in permeate solutions from ultrafiltration processes. This method, however, requires high dilutions for analysis of the concentrate liquors.

It was decided therefore, to examine alternative gravimetric procedures to accommodate the high concentration liquors and to avoid the use of a carcinogenic precipitant.

An examination of the literature did not reveal any satisfactory gravimetric procedures for lignosulphonates other than those already referred to by Partansky and Benson (1936). However, Croon and Swan (1963) and also Sato (1943), made early reference to the use of long-chain quaternary ammonium compounds such as cetyltrimethylammonium bromide to precipitate sodium lignosulphonate from spent liquor. Quimby and Goldschmid (1966), in their work on molecular mass fractionation of the quaternary ammonium salts of lignin sulphonates, used as precipitant di-isobutylcresoxyethoxyethyldimethylbenzylammonium chloride monohydrate (Hyamine 10-X). This product is however no longer readily available.

Hyamine-1622, also known as benzethonium chloride, is di-isobutylphenoxyethoxyethyldimethylbenzylammonium chloride monohydrate with structure as shown in Figure 1 (United States Pharmacopeia, 1980; Merck Index, 1976 and Lonza Inc. Product Information Bulletin 5-84). This product is readily available today.

It is a crystalline ammonium germicide manufactured to meet quality standards set forth in the United States Pharmacopeia (1980). This material was selected for use in the investigations described in this paper. Only calcium bisulphite liquors were considered.

The calcium bisulphite pulping mill where the investigations were carried out, uses hardwoods and the sulphite spent liquor will differ from that produced from softwoods in a number of respects. The analytical method developed by Partansky and Benson (1936) and recommended by TAPPI, is designed for the determination of lignosulphonate derived from softwoods.

Softwood lignins consist of guaiacylpropane residues with small amounts of syringyl and parahydroxyphenyl residues. Hardwood lignins, on the other hand, consist of guaiacylpropane and syringylpropane units. Further, the hardwoods show pronounced species variation, the ratio of syringylpropane to guaiacylpropane units being an important variable as found by Sarkanen *et al.* This aspect needs to be considered in accurate analytical determinations of lignosulphonates in spent liquor, but is not covered in this preliminary examination.

## Experimental

### Preparation of spent liquor samples from a calcium bisulphite pulp mill

Calcium bisulphite is present in significant quantities in spent liquors containing free sulphur dioxide. The solubility of calcium sulphite decreases with decreasing partial pressure of sulphur dioxide and in cold water (18°C), the solubility is only 0,004 g per 100 mℓ (Weast, 1983-1984). It is important therefore, to remove sulphur dioxide before the analytical precipitation of Hyamine lignosulphonate to avoid co-precipitation of calcium sulphite.

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*Received 5 December 1986.*

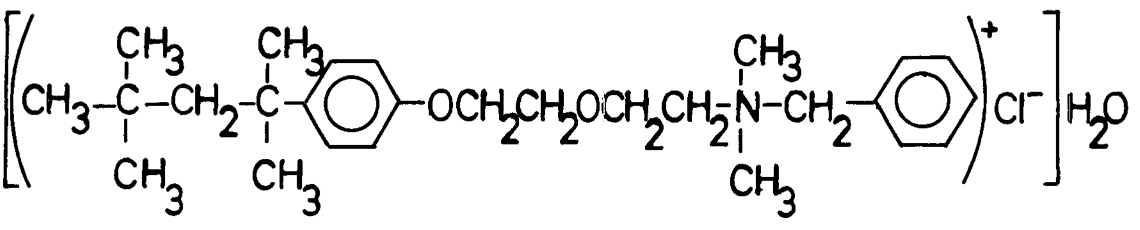

*Figure 1*
*Structure of Hyamine-1622 or benzethonium chloride*

**Preparation of precipitant**

A sample of Hyamine-1622 was obtained from Lonza Inc., USA. Hyamine-1622 is soluble in water and a suitable concentration can thus be prepared with ease, but at pH values below 2,0 solutions will become turbid. In the precipitation of lignosulphonate with 2-naphthylamine, the composition of the precipitate according to Partanksy and Benson (1936) is considered to be:

$$(C_{10}H_{10}O_3)_3(HSO_3^-)(C_{10}H_{10}N^+)(H_2O)$$

The molecular composition of the Hyamine precipitate is taken, in the first instance, as $[(L)(HSO_3^-)((CH_3)_2N^+ . R_1 . R_2)] H_2O$, where L is the lignin shard and $(CH_3)_2 N^+ . R_1 . R_2 . H_2O$ represents the Hyamine-1622 ion.

It should be noted that quaternary ammonium compounds such as Hyamine-1622 will react with and precipitate compounds such as anionic detergents and will tend to come out of solution in the presence of high salt concentrations. In applying the method using the quaternary ammonium compound to effluents other than bisulphite pulp mill effluents, consideration must be given to the effects mentioned.

**Source of lignosulphonate**

In this preliminary investigation two grades of lignosulphonate from Borregaard Industries Ltd. were used. Borresperse NA, a commercial sodium lignosulphonate made from Norwegian spruce, a softwood, was used to determine the precision of the method. This material contains about 70% lignosulphonate. Ultrazine NA, also made from Norwegian spruce is a purified sodium lignosulphonate. This material was used to obtain conversion factors. Samples of the calcium bisulphite pulp mill effluent were also used where stated.

The mill concerned uses mainly eucalyptus wood, which is a hardwood. In subsequent investigations it will be desirable to dialyse a sample of the actual spent liquor to obtain a representative 'pure' lignosulphonate, typical for that mill.

## Results

Using the 2-naphthylamine method (TAPPI-T629 m – 53) as a base, the Hyamine-1622 method was developed. A 77,84 g/ℓ Hyamine-1622 solution was used throughout the following tests. This solution has the same molarity as the 2-naphthylamine reagent employed in method TAPPI-T629 m – 53. Various aspects were examined to select the best conditions for analysis. These included the effect of final volume, mass of precipitant, pH, coagulation and drying time.

The results of these tests are given in Tables 1 to 7.

It was found that by digesting the mixture of sample and reagent for one hour on a boiling water bath helps the agglomeration of the precipitate and leads to more rapid settling of the precipitate. A drying time of 24 h at 105°C was sufficient to achieve constant mass.

TABLE 1
EFFECT OF TOTAL VOLUME ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| Sulphite liquor mℓ | Hyamine-1622 reagent mℓ | Equivalent mass of Hyamine-1622 g | Water mℓ | Total volume mℓ | Lignin g/ℓ |
|---|---|---|---|---|---|
| 10 | 25 | 1,95 | 0 | 35 | 26,3 |
| 10 | 25 | 1,95 | 5 | 40 | 26,0 |
| 10 | 25 | 1,95 | 10 | 45 | 26,1 |
| 10 | 25 | 1,95 | 20 | 55 | 23,7 |
| 10 | 25 | 1,95 | 50 | 85 | 18,6 |

The source of lignosulphonate was a sample of sulphite spent liquor diluted to approximately 30 g/ℓ as lignin.

TABLE 2
EFFECT OF VARYING THE MASS OF HYAMINE-1622 (FINAL VOLUME CONSTANT) ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| Sulphite liquor mℓ | Hyamine-1622 reagent mℓ | Equivalent mass of Hyamine-1622 g | Lignin g/ℓ |
|---|---|---|---|
| 10 | 25 | 0,45 | 31,2 |
| 10 | 25 | 1,95 | 27,2 |
| 10 | 25 | 2,50 | 24,2 |
| 10 | 25 | 3,20 | 21,4 |
| 10 | 25 | 3,89 | 16,6 |

The source of lignosulphonate was a sample of sulphite spent liquor diluted to approximately 30 g/ℓ as lignin.

TABLE 3
EFFECT OF MASS OF HYAMINE-1622 REAGENT (FINAL VOLUMES NOT CONSTANT) ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| Hyamine-1622 reagent mℓ | Equivalent mass of Hyamine-1622 g | Lignin g/ℓ |
|---|---|---|
| 25 | 1,95 | 24,14 |
| 15 | 1,17 | 25,08 |
| 10 | 0,78 | 25,91 |
| 7 | 0,54 | 26,83 |
| 5 | 0,39 | 27,35 |
| 3 | 0,23 | 11,41 |
| 1 | 0,08 | 1,04 |
| 0,3 | 0,02 | 0,15 |

The source of lignosulphonate was Borresperse NA solution containing approximately 30 g/ℓ as lignin (10 mℓ solution used in tests).

### TABLE 4
### EFFECT OF MASS OF HYAMINE-1622 REAGENT (FINAL VOLUME CONSTANT) ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| Hyamine-1622 reagent mℓ | Equivalent mass of Hyamine-1622 g | Water mℓ | Lignin g/ℓ |
|---|---|---|---|
| 25 | 1,95 | 0 | 24,11 |
| 15 | 1,17 | 10 | 24,50 |
| 10 | 0,78 | 15 | 25,28 |
| 7 | 0,54 | 18 | 25,81 |
| 5 | 0,39 | 20 | 26,03 |
| 3 | 0,23 | 22 | 10,86 |
| 1 | 0,08 | 24 | 1,88 |
| 0,3 | 0,02 | 24,7 | 0,20 |

The source of lignosulphonate was Borresperse NA solution containing approximately 30 g/ℓ as lignin (10 mℓ solution was used in tests).

### TABLE 6
### RATIO OF LIGNIN TO HYAMINE-1622 BY MASS WHICH GIVES MAXIMUM PRECIPITATE YIELD

| Derived from | Ratio of lignin (recovered after analysis) to Hyamine-1622 by mass | Ratio of estimated lignin to Hyamine-1622 by mass |
|---|---|---|
| Table 2 | 1 : 1,44 | 1 : 1,30 |
| Table 3 | 1 : 1,42 | 1 : 1,30 |
| Table 4 | 1 : 1,50 | 1 : 1,30 |
| Table 5 | 1 : 1,52 | – |
| Table 5 | 1 : 1,52 | – |
| Table 5 | 1 : 1,52 | – |
| Average | 1 : 1,49 | 1 : 1,30 |

### TABLE 5
### EFFECT OF MASS OF HYAMINE-1622 (FINAL VOLUMES NOT CONSTANT) ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| Sulphite liquor (dilutions as specified in last 3 columns) mℓ | Hyamine-1622 reagent mℓ | Equivalent mass of Hyamine-1622 g | Lignin in liquor, g/ℓ | | |
|---|---|---|---|---|---|
| | | | as is | 2 x dilution | 3 x dilution |
| 10 | 2 | 0,16 | – | 15,7 | 16,0 |
| 10 | 5 | 0,39 | 34,6 | 31,1 | 25,7 |
| 10 | 10 | 0,78 | 57,5 | 51,3 | – |
| 10 | 15 | 1,17 | 84,9 | 40,8 | 20,7 |
| 10 | 20 | 1,56 | 102,6 | 33,4 | – |
| 10 | 30 | 2,34 | 83,7 | 27,6 | 16,4 |
| 10 | 50 | 3,90 | 66,0 | 26,4 | 14,8 |

The lignosulphonate source was a sample of spent liquor concentrated by ultrafiltration.

### TABLE 7
### EFFECT OF pH OF HYAMINE-1622 REAGENT ON MASS OF HYAMINE LIGNOSULPHONATE PRECIPITATE

| pH of Hyamine-1622 reagent | g/ℓ lignin |
|---|---|
| 2,0 | 27,08 |
| 3,0 | 26,56 |
| 4,0 | 25,49 |
| 8,3 | 23,39 |

The source of lignosulphonate was Borresperse NA solution containing approximately 30 g/ℓ as lignin (10 mℓ solution and 5 mℓ reagent used in tests).

Calculate gram per litre of lignin, correcting for dilution and the factor given below:

Lignin = Hyamine lignosulphonate x 0,4198
Sodium lignosulphonate = lignin x 1,2265

## Evaluation of Hyamine-1622 as a precipitant

Using the most suitable conditions as set out in the analytical method, the Hyamine-1622 precipitant was compared with the 2-naphthylamine precipitant on a 30 g/ℓ solution of Ultrazine NA containing approximately 30 g/ℓ as lignin. The results are shown in Table 8.

### TABLE 8
### COMPARISON OF RESULTS OBTAINED USING 2-NAPHTHYLAMINE AND HYAMINE-1622

| Precipitant | Lignin g/ℓ * |
|---|---|
| 2-naphthylamine | 29,87; 29,83; 30,17; 29,83; 30,10; 30,56; 29,63; 29,49; 29,72; 30,09 |
| Hyamine-1622 | 27,03; 27,28; 27,30; 27,16; 27,12; 27,10; 27,17; 26,94; 27,17; 27,01 |

* The results by the 2-naphthylamine method include a correction factor of 1,22 to account for lignin not precipitated by the TAPPI method T629 m – 53. No correction factor was used in the Hyamine-1622 method.

The source of lignosulphonate was Ultrazine NA solution

TABLE 9
RESULTS OBTAINED ON SULPHITE LIQUOR USING HYAMINE- 1622

| Sulphite liquor | Lignin g/ℓ |
|---|---|
| (i) Dilute liquor from pulp washing. | 10,7; 10,5; 10,7; 11,0 |
| (ii) Spent liquor; the first discharge from autoclaves. | 73,9; 75,0; 73,1; 74,3 |
| (iii) Concentrate liquor from ultrafiltration unit. | 134,9; 135,6; 136,8; 134,5<br>133,3; 132,6; 133,4; 133,7 |

(10 mℓ of sulphite liquor (solution 3) and 5 mℓ of Hyamine-1622 reagent used throughout.)

containing approximately 30 g/ℓ as lignin (10 mℓ solution and 5 mℓ reagent were used throughout).

The results of tests conducted on sulphite liquors of various concentrations are listed in Table 9.

## The analytical method

Details of an analytical method for the determination of lignosulphonate using Hyamine-1622 are given below based on the tests already described.

### Preparation of reagent

Dissolve 77,84 g of Hyamine-1622 (benzethonium chloride) in 1 litre distilled water. Adjust pH of reagent to 2,0 while stirring, using concentrated hydrochloric acid.

### Preparation of sample for analysis

Pipette 50 mℓ of sample into a 250 mℓ beaker. Add 5 drops of concentrated sulphuric acid while stirring. Place on a boiling water bath for 1 h to expel free sulphur dioxide.

Transfer quantitatively into a 50 mℓ volumetric flask. Make up to the mark with distilled water and mix well. Filter through glass microfibre filter (solution 1).

### Procedure of analysis

Pipette 1 mℓ of clear filtrate (solution 1) into a 1 litre volumetric flask and make up to the mark. This will be equal to a 1 000 x dilution (solution 2).

Estimate the apparent lignin concentration in gram per litre using a calibration curve prepared from Ultrazine NA standards by reading the ultra-violet absorbance of solution 2 at 208 nm. Dilute or concentrate solution 1 to give an approximate lignin concentration of 30 g/ℓ (solution 3).

Transfer 10 mℓ of solution 3 into a pre-weighed 100 mℓ beaker. Add with stirring, 5 mℓ of Hyamine-1622 reagent. Cover with a watch glass and digest on a boiling water bath for 1 h. Then stand at room temperature overnight.

The Hyamine lignosulphonate precipitate should be dark brown in appearance and of a soft gummy consistency. Carefully decant the clear supernatant. The precipitate adheres to the beaker. Wash the precipitate free of Hyamine-1622 reagent with a minimum quantity of distilled water (not exceeding 10 mℓ of total washings), carefully decanting the clear washings each time.

Dry the clean precipitate in an oven at 105 °C until constant mass is achieved (approximately 24 h). Cool in a desiccator and weigh as Hyamine lignosulphonate monohydrate.

### Construction of curve for estimation of lignin content

Construct a graph of absorbance at 208 nm versus gram per litre of lignin diluted down to different concentrations and finally diluted 1 000x.

The absorbance readings should be in the range 0,300 to 0,550 units (using a 1 cm cell) if accurate results are to be obtained.

### Calculation

A solution of Ultrazine NA containing 30 g/ℓ was analysed according to the method described above. Assuming that the dried Ultrazine was equivalent to 100% sodium lignosulphonate, the conversion factor for Hyamine-lignosulphonate to sodium lignosulphonate was found to be 0,5377 and to lignin 0,4178.

## Discussion and conclusion

The optimum ratio of lignin to Hyamine-1622 was found to average 1:1,5. If an excess of Hyamine-1622 is added, it tends to suppress the precipitation of Hyamine lignosulphonate.

The final volume in the analytical procedure must be constant in order to achieve consistent results and the pH of the solution under which optimum precipitation occurs is near 2 ( but not below 2).

Standard deviations for the 2-naphthylamine and Hyamine-1622 methods using spruce lignin (Table 8) were 0,31 and 0,11 respectively for approximately 30 g/ℓ lignin. The results of analysis of the sulphite pulp mill concentration liquor (Table 9) had a standard deviation of 1,4 (for a concentration of approximately 134 g/ℓ lignin). In general, the consistent results obtained on different strengths of sulphite liquor imply that the Hyamine-1622 method can be applied to many of the calcium bisulphite process effluents containing lignosulphonate.

Results obtained using Hyamine-1622 are approximately 10% lower than those using 2-naphthylamine. If necessary, a small correction factor could be applied to the Hyamine method as is done in the 2-naphthylamine method. It is considered, however, that a satisfactory preliminary method using a non-carcinogenic reagent has thus been developed.

Work is in progress on a volumetric determination of lignin using Hyamine-1622. This is likely to speed up the analytical procedure for routine control purposes.

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