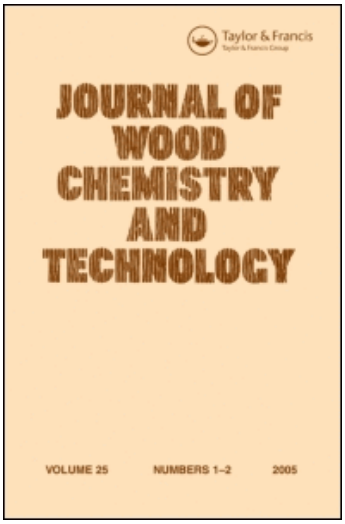

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DETERMINATION OF 9,10-ANTHRAQUINONE AND SOME DERIVATIVES IN PULPING LIQUORS

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ABSTRACT

9,10-Anthraquinone (AQ), anthraquinone-2-sulfonic acid (AMS), and anthraquinone-1-acetic acid (AMA) were determined in alkaline pulping liquors by adsorption on Amberlite XAD-2 from liquors diluted with ethanol (AQ) or water (AMS and AMA). After washing, AQ was eluted with 99% ethanol, AMS with acidified 25% ethanol and AMA with alkaline 25% ethanol.

The final determinations were made by chromatography in aqueous methanol on silica gel containing octadecyl groups. In the experiments with the derivatives the eluent contained tetrabutylammonium ions to increase the retention.

INTRODUCTION

Anthraquinone (AQ) and anthraquinone derivatives promote the delignification[1] and stabilize the carbohydrates[2] during alkaline pulping of wood. This has led to world-wide research on cooking with quinone additives, and to industrial applications in some pulp mills. Extraction with dichloromethane followed by gas chromatography[3] or liquid chromatography[4] has been used for the determination of AQ in pulping liquors. Difficulties are encountered due to foaming and precipitation of AQ in the aqueous phase[3]. A method based on reoxidation of the hydroquinone form by air and filtration of the cooled liquor through a layer of diatomaceous earth (Celite Hyflo Super-Cel), followed by

washing with water and displacement of AQ with acetone, has been used in our laboratory for several years[5]. The final determination is made by gas chromatography.

In attempts to improve the stabilization of the carbohydrates by reoxidation of the cooking liquor with oxygen during a pretreatment stage, it was found that anthraquinone-2-monosulfonic acid (AMS) and anthraquinone-1-acetic acid (AMA) were more effective than AQ for this specific purpose[6,7]. Methods for the determination of AQ and these derivatives in liquors preoxidized by air to convert the hydroquinone form to the quinone are described in this report. The analyses were based on prefractionation, to remove interfering compounds, by adsorption on a nonionic styrene-divinylbenzene resin (Amberlite XAD-2) and elution with aqueous ethanol, or ethanol, followed by liquid chromatography on silica gel with covalently linked octadecyl groups (ODS-Hypersil). A similar chromatographic technique on silica gel has previously been applied for the separation of AMS from other sulfonic acids in aqueous solution[8].

EXPERIMENTAL

The spent liquor analyzed after an addition of known amounts of quinones, was from a soda cook of spruce with an addition of 28% NaOH calculated on dry chips, at a ratio of liquor to wood equal to 4.5:1. The cooking was made for 3 hr at 170^{o} and resulted in a pulp of kappa number 49 in a yield of 45.5%. The calculated amount of dissolved wood substance in the liquor corresponded to 121 grams per liter.

AQ and AMS were commercial products of puriss grade. AMA was prepared in connection with a previously reported investigation[6].

A glass column (350 x 4 mm) was packed with Amberlite XAD-2 (Rohm and Haas, Philadelphia, USA), which had been crushed and sieved to obtain a particle size of 120-190 μm. The resin was extracted with ethanol and chloroform, and transferred to the column as a slurry in ethanol. The column was conditioned with

water. The samples to be analyzed were introduced through a sample loop (0.6 ml in the experiments with AMS and AMA; 1.0 ml with AQ) and displaced into the column with water of room temperature. The flow rate during displacement and subsequent washing was 1.3 ml min^{-1}. The UV-absorption of the effluent was recorded continuously at 280 nm (Buchler Instruments, Chicago, USA).

The column was washed with different solvents dependent on the quinone compound to be analyzed. Elution was made with aqueous ethanol, or ethanol, and the eluates evaporated to dryness. The residues containing AMS or AMA were dissolved in 1.0 ml of water, while 2.0 ml of 92.4% ethanol was used to dissolve AQ, which is sparingly soluble in water. These solutions were applied to the ODS-Hypersil column. All ethanol concentrations are given as per cent by weight.

Colored solutes adsorbed onto XAD-2 remained after the elution of AQ and of the quinone derivatives. These solutes were removed and the column restored by treatment with sodium hydroxide (pH 12) in 80% ethanol after every fifth sample.

The chromatographic separations on ODS-Hypersil with a particle size of 5 µm (Shandon Southern Products, Runcorn, Great Britain) were made in a steel column (100 x 5 mm) with a 20 µl sample loop. Elution of AMS and AMA was made at room temperature with 5 mM tetrabutylammonium hydroxide in aqueous methanol of increasing concentration. Gradient elution with a methanol concentration increasing linearly from 30 to 100% (v/v) was achieved with a Constametric Gradient HPLC System from Laboratory Data Control (Riviera Beach, Fl., USA). Isocratic elution from ODS-Hypersil with 55% (v/v) methanol without addition of quaternary ammonium ions was used for the determination of AQ. The absorbance was measured at 254 nm (Altex Scientific, Berkeley, USA).

The amounts of quinone derivatives were calculated from the peak areas integrated automatically (Hewlett-Packard, Avondale, Pa, USA), by comparison with those obtained in calibration ex-

periments in which known weights dissolved in distilled water were injected directly on the ODS-Hypersil column. For AQ, standard solutions in 92.4% ethanol were used.

RESULTS AND DISCUSSION

Prefractionation of AMS and AMA

In the determinations of AMS or AMA the liquors were applied directly to the XAD-2 column, which was then washed with water until the absorbance was negligible. The volume of water corresponded to approximately five column volumes. Continued washing with five bed volumes gave no detectable loss of the quinone compounds.

For liquors containing AMS, which is a strong acid, elution was made with aqueous ethanol acidified with formic acid to pH 3. At this pH a large proportion of the aromatic compounds remained in the column. A complete elution of AMS was obtained with 60 ml (corresponding to 14 bed volumes) of 25% ethanol, while a larger volume was required at a lower concentration. Blanks carried out with liquors free from added quinone compounds showed that solutes which gave rise to a slight absorbance in UV were eluted from the ODS-Hypersil column at the same position as AMS. As shown in Fig. 1, the interference of these solutes was small when the elution from XAD-2 was made with 25% ethanol. With 30% ethanol the interference was much larger.

AMA, which is nondissociated in acid medium, was held much more strongly than AMS by the XAD-2 resin in acidified aqueous ethanol. After the washing with water the column was therefore treated at room temperature with 40% ethanol, acidified with formic acid to pH 2.5. The washing was continued until the base line was approached. Approximately 4 bed volumes were required. No detectable losses of AMA were obtained when 10 bed volumes were passed through the column. An alkaline solution of ethanol (60 ml) was then introduced to displace AMA in its anionic form. Dilute sodium hydroxide (pH 12) in 25% ethanol was used in the experiments reported below.

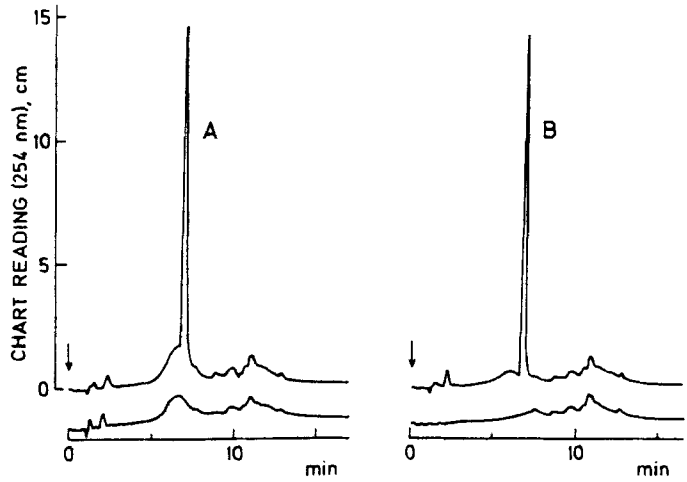

FIGURE 1. Chromatographic determination of AMS on ODS-Hypersil after prefractionation on XAD-2 by elution at pH 2.8 with (A) 30% ethanol and (B) 25% ethanol. The upper chromatograms refer to experiments with an addition of 43 µg of AMS and 0.15 ml spent liquor and the lower chromatograms to blanks with the same volume of spent liquor without an addition of AMS.

Prefractionation of AQ

With AQ precipitation can occur when the liquor is brought in contact with air so that the hydroquinone form is converted to AQ. This must be taken into consideration when samples of liquors are withdrawn. The solubility of AQ is much higher in ethanol than in water, and since it was found that AQ was held strongly by XAD-2 even in 50% ethanol, the prefractionation was made in this medium. In principle, ethanol can be added to the liquor and a sample taken after removal of insoluble matter. In the experiments described below, the liquor was instead acidified to pH 3 with formic acid to avoid uncontrolled boiling, and evaporated to dryness in a film evaporator at 35°C. The sample was then treated with 50% ethanol, at pH 3, to dissolve anthraquinone together with most other compounds present. Insoluble material was removed by sedimentation and a 1 ml sample of the clear solution corresponding to 0.2 ml of the liquor

was applied to the XAD-2 column. A large proportion of the organic solutes were displaced by washing with 5 bed volumes of water and 50% ethanol at pH 3 until the absorbance at 280 nm was negligible (15 bed volumes). No losses occurred when the volume of 50% ethanol was increased to 30 bed volumes. The elution of AQ was made conveniently in 99% ethanol, with 20 ml of formic acid added per liter of ethanol. The eluent volume was 15 bed volumes.

A chromatogram from the ODS-Hypersil column recorded for a spent liquor with 12 µg of added AQ, following prefractionation on XAD-2 is in Fig. 2 compared with that recorded for the same amount of AQ dissolved in 2 ml 92.4% ethanol. Since the volume of the sample loop was 20 µl the recorded chromatograms corresponded to additions of 0.12 µg. It can be seen that in the experiment with spent liquor added before the prefractionation an elevated base line was obtained. As confirmed in experiments without addition of AQ, no solutes which interfered

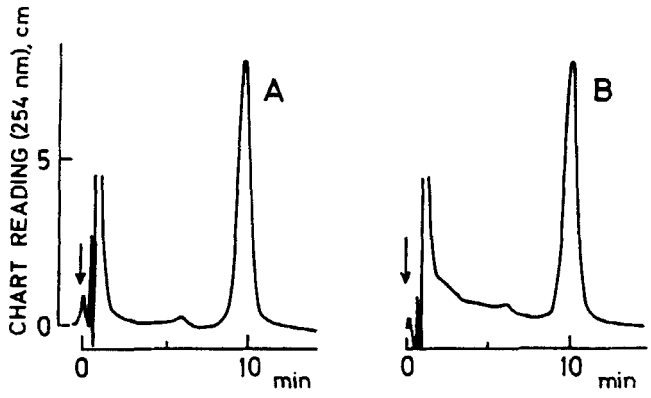

FIGURE 2. Chromatograms on ODS-Hypersil

A. Direct injection of an aliquot of a solution of 12 µg AQ in 2 ml ethanol.
B. Injection of the same aliquot of 2 ml ethanol solution containing AQ recovered after evaporation and prefractionation of a sample containing 12 µg AQ and 0.2 ml spent liquor.

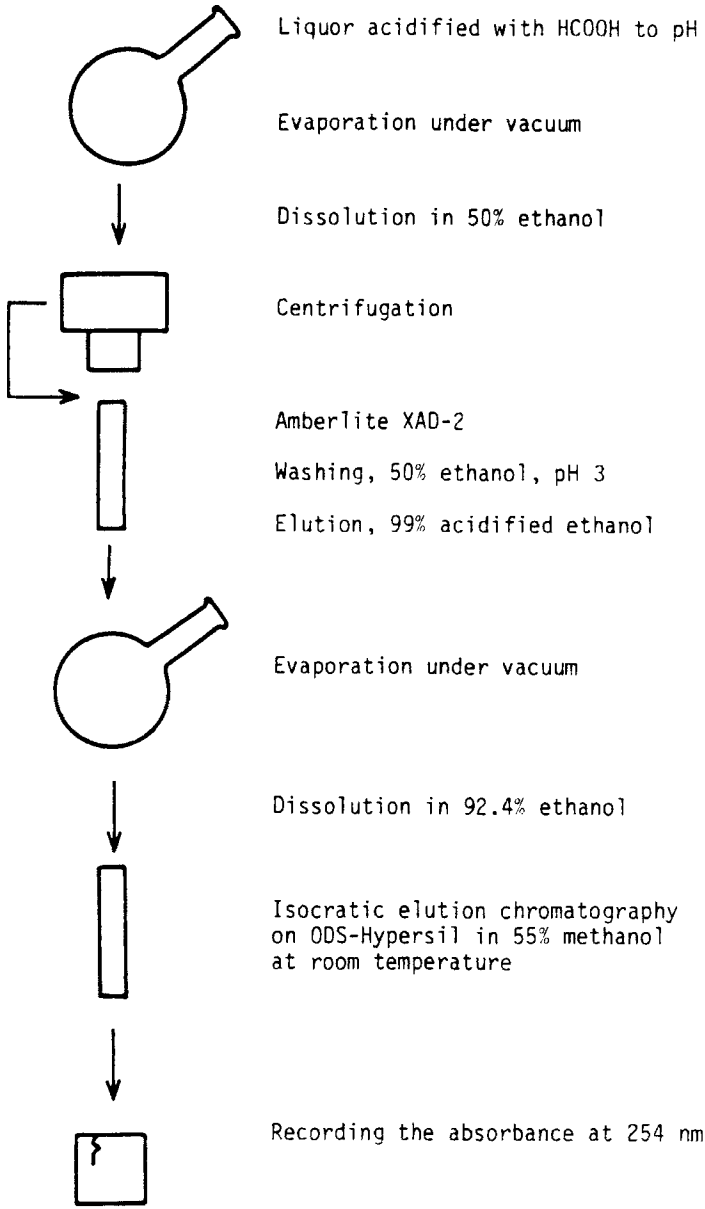

FIGURE 3. Determination of AQ in Black Liquor

TABLE 1

Recovery of AMS, AMA, and AQ after Prefractionation on Amberlite XAD-2 and Chromatography on ODS-Hypersil.

Addition in the prefractionation stage	Quinone compound, µg Added	Recovered
AMS in water	60.0	59.1
	30.0	29.9
	15.0	15.1
AMS in sodium hydroxide	30.0	29.9
	15.0	15.4
AMS in spent liquor	60.0	59.5
	30.0	29.6
	15.0	14.6
AMA in sodium hydroxide	12.0	11.5
	6.0	5.9
AMA in spent liquor	18.0	17.2
	12.0	12.0
	6.0	5.8
AQ in aqueous ethanol	12.0	11.9
	8.0	7.8
	4.0	4.1
AQ in spent liquor	12.0	11.8
	8.0	7.8
	4.0	3.9

The reported amounts refer to the prefractionation stage. AMS and AMA were added in 0.6 ml of either water, sodium hydroxide or an aqueous solution containing 0.15 ml spent liquor. AQ was added in 1.0 ml of either acidified aqueous ethanol (50%) or acidified aqueous ethanol containing 0.2 ml spent liquor.

with the AQ determination were present. A scheme illustrating the procedure is given in Fig. 3.

Reproducibility and recovery

The reproducibility of the final stage used for the determination of the quinone compounds by chromatography on ODS-Hypersil was checked by repeating the injection of the same sample solutions and comparing the areas printed by the integrator. In experiments with AMS the maximum relative deviation from the mean was 0.4% while in those with AMA and AQ the maximum deviations were 0.9% and 1.2%, respectively. A dilution of a solution containing 30 mg of AMS per liter with an equal volume of water led to a decrease in the recorded area by 49.0% instead of the calculated 50%. When a solution of AMA containing 12 mg per liter was diluted in the same proportion, the recorded area decreased by 50.6%. For AQ a dilution from 4.0 mg per liter to 2.0 mg per liter led to a decrease by 50.2%. Hence, the calibration curves can for practical purposes be taken as straight lines.

The recovery of the quinone compounds after addition of a known amount to either water, sodium hydroxide solution (25 g/liter), or diluted spent cooking liquors from soda cooking (NaOH cooking) of spruce without prior addition of quinone compounds is shown in Table 1. The last column refers to the amounts found after prefractionation on XAD-2 according to the procedures given above and chromatography on ODS-Hypersil. The areas of the elution peaks printed by the integrator were compared with those printed in calibration experiments with known amounts of the quinone compounds added directly to the ODS-Hypersil column. The small losses observed in these experiments are without practical significance.

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