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Note

Determination of 9,10-anthraquinone and a mixture of 9,10-dihydroxy-1,4-dihydroanthracene and 1,4,5,8-tetrahydroanthraquinone in pulping materials by high-performance liquid chromatography

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Anthraquinones and related compounds are at present of great interest as additives in the pulping industry because they increase cellulose yields and lower energy consumption[1–3]. Recently a number of analytical methods directed at analysing 9,10-anthraquinone have been reported as satisfying environmental and processing control requirements. The methods include polarography[4,5], gas chromatography[6] and gas chromatography combined with mass spectrometry[7,8]. We report here a method based on high-performance liquid chromatography (HPLC) for determining 9,10-anthraquinone (AQ) as well as for determining the total amount of 1,4,5,8-tetrahydroanthraquinone (THAQ) and 9,10-dihydroxy-1,4-dihydroanthracene (DDA) The method is rapid, reliable and relatively economical. The detection limit is in the lower ppm range. The method is therefore a satisfactory alternative to previously reported ones.

A mixture of THAQ and DDA with a known ratio of the two compounds is used in the pulping industry. For this reason, separation of the different anthraquinones is only of minor interest, and this aspect has not been dealt with in the method reported here.

EXPERIMENTAL

Apparatus and reagents

The instrumental system consisted of an Altex 330 isocratic liquid chromatograph, with a metering pump Model 110 A, a syringe-loading sample injector with a 20-μl loop 904-42, and analytical UV detector 153. All the equipment was from Altex, Berkeley, CA, U.S.A. The column used was Spherisorb 10 ODS, PP/1096 (Chrompack, Middelburg, The Netherlands). The experiments were carried out at room temperature. An OmniScribe recorder (Houston Instruments) was used.

All reagents were of analytical grade. Methanol and methylene chloride were from E. Merck, Darmstadt, G.F.R. Standard solutions were prepared from synthetic grade AQ (Merck), and from a mixture of THAQ and DDA (Bayer, Leverkusen, G.F.R.). The purity of the latter mixture, of potential interest in the pulping industry, is unknown. The producer reports the fraction of DDA to be small compared with THAQ.

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Experiments were performed with different eluents, the most favourable being 50–60% methanol in water solutions. Recovery studies were made on black liquor, on paper and on washed pulps dried to 93%. All the materials were obtained from ordinary Kraft pulping. The standard solutions were diluted in methylene chloride (200 μg/ml) and added to the matrices.

Analytical procedures

Analysis of black liquor. Black liquor (100 ml) is extracted twice with methylene chloride (50 ml) in a 250-ml separatory funnel by shaking for 3 min by hand, and leaving for 5 min. The total extracts are washed, first with 100 ml of a mixture which is 4 *M* and 0.1 *M* with respect to sodium hydroxide and potassium dichromate, respectively, and finally with 100 ml of 4 *M* sodium hydroxide. The methylene chloride phase is then evaporated using a rotary evaporator and the resulting residue dissolved in 50 ml of methanol. The chromatography is carried out using as eluent methanol–water (60:40) and a flow-rate of 2 ml/min.

Analysis of paper-type samples (paper and washed pulps). The sample (10 g) is shaken with 150 ml of methylene chloride on a shaking machine for 20 min and filtered under suction. This procedure is repeated and the two methylene chloride extracts collected in a 500-ml separatory funnel. Subsequently, the procedure is as for the analysis of black liquor.

RESULTS AND DISCUSSION

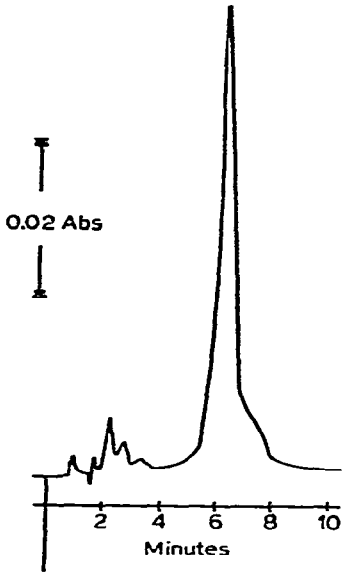
Pulping decomposes lignin (a very complex molecule consisting of more or less oxidized methoxy-rich phenylpropanoic units connected by ether and C–C linkages) to a number of phenols and other aromatic compounds which strongly absorb in the UV region. By washing the cloudy methylene chloride phase after the black liquor extraction with strong alkaline solution, most of the acidic compounds are removed. As shown in Fig. 1, no serious interferences in black liquor and paper-type samples appear in this HPLC technique.

The use of acids is not recommended for washing the methylene chloride phase because emulsions appear. Washing with 0.1 *M* potassium dichromate in alkaline solution has the effect of oxidizing the reduced forms of anthraquinones, as does air.

The effect of oxidation on the mixture of THAQ and DDA is shown in Figs. 2 and 3. The very high increase in UV absorption caused by oxidation is not fully understood, but the first peak in Fig. 2 probably includes both DDA and reduced THAQ, which are oxidized (and therefore more conjugated) anthraquinones. Since anthraquinones are less acidic than the corresponding dihydroxyanthracenes, they are preferentially retained on the column. The longer retention times have the advantage of resulting in earlier elution of the interferences.

Fig. 4 presents calibration data for black liquor with THAQ–DDA added and then treated according to the procedure given above.

Experiments were also carried out on 9,10-anthraquinone systems. The AQ and oxidized THAQ–DDA mixtures were found to have similar retention times and were detected with almost the same sensitivity.



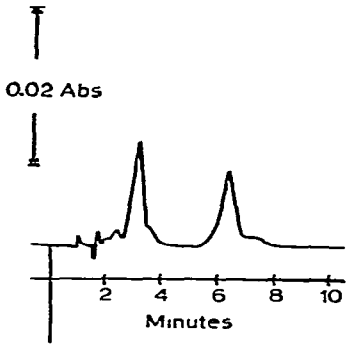


Fig. 1. Chromatogram of black liquor extract added THAQ–DDA to 10 μg/ml.

Fig. 2. Chromatogram of 20 μg/ml standard THAQ–DDA in methanol.

It is convenient to report the residues from matrices as total amounts of anthraquinones irrespective of oxidation state, because anthraquinones take part in an alternative oxidation/reduction sequence in the pulping process[3]. It should be noted that in Figs. 1 and 4 the eluent was methanol–water (60:40), whereas a 50:50 eluent was used in the experiments relevant to Figs. 2 and 3 in order to obtain the desired sum of the components as one peak only.

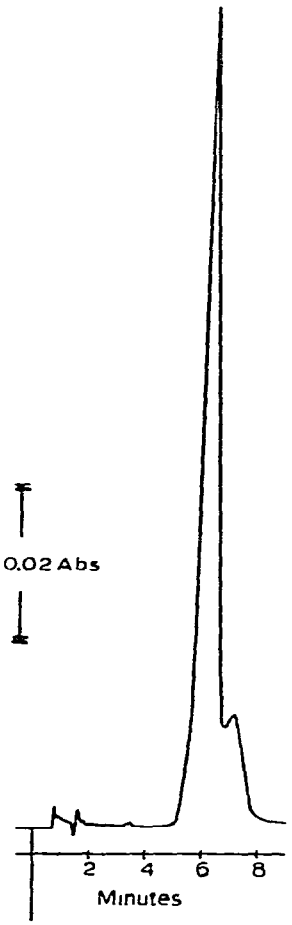
Separation of THAQ and DDA has not been performed in the present work as this is of minor interest. However, from preliminary experiments, separation is possible with acceptable resolution.

The recovery from black liquor was 90%, and 55% (for an average of 5) from paper-type samples. The recovery may to some extent be improved by longer extraction times. An exhaustive extraction by Soxhlet may be neccesary in order to extract less defibrated materials such as wood[8].

From additional experiments it seems possible to use the methylene chloride phase directly without transferring the sample via a solution of methanol. This could be performed with a gradient system, using a normal phase column with isooctane–methylene chloride as eluent. Such equipment, however, was not avaiable at our laboratory.

Anthraquinones in alcoholic solutions are photochemically reduced[5,9]. This may effect reproducibilities only if the solutions are stored in daylight and injected over a period of several weeks.

The method presented above is found to be sufficiently rapid, reliable and economical to be useful for actual purposes. With a detection limit in the lower ppm region and a precision below 5%, the sensitivity is also sufficient for applications in the pulping industry and in environmental analysis.



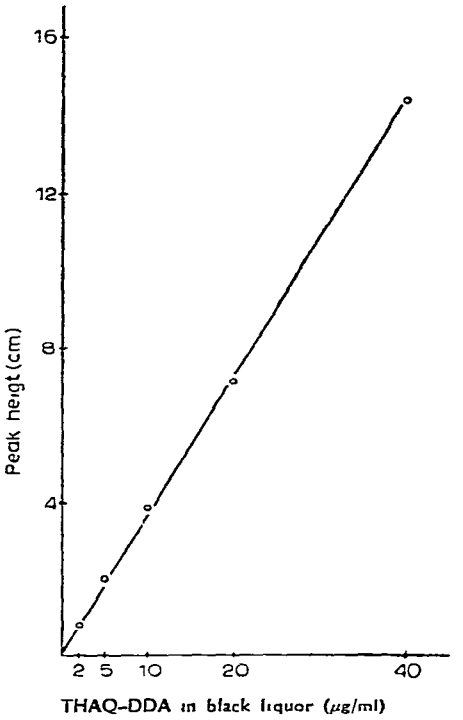


Fig. 3. Chromatogram of 20 μg/ml standard THAQ–DDA in methylene chloride after oxidation.
Fig. 4. Calibration curve of THAQ–DDA in black liquor. Sensitivity of the detector is 0.32 absorbance units, corresponding to 25 cm recorder deflection.

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