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DETERMINATION OF ANTHRAQUINONE IN PULPING LIQUORS BY USING C_{18} CARTRIDGES AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A rapid procedure was developed for determining anthraquinone in liquors from pulping investigations employing anthraquinone as a catalyst. C_{18} Sep-Pak cartridges were used to extract the organic compounds from the liquors; then the anthraquinone and other organic compounds were eluted from the cartridge with methanol which was analyzed for anthraquinone by high-performance liquid chromatography. More than 200 black liquors, bleach solutions, filtrates, and other pulping liquors have been analyzed. From 0.5 to 170 ppm anthraquinone in black liquors was determined with a standard deviation of 0.54. Pulp filtrates having 0.04–0.75 ppm anthraquinone were analyzed by concentrating the anthraquinone either fourfold or tenfold through adjustment of the ratio of sample volume to eluent volume.

INTRODUCTION

Pulping investigations conducted with anthraquinone as a catalyst have shown catalytic amounts of anthraquinone improve delignification of wood and increase pulp yield. In addition, these studies have created a need for analytical methods capable of measuring anthraquinone in pulping process liquors such as black liquors, bleaching liquors, wash waters, and filtrates.

Several analytical procedures have been reported for trace amounts of anthraquinone in pulping liquors. Currah[1] applied a gas chromatography–mass spectrometry procedure to the analysis of black liquors for anthraquinone. The black liquor was diluted with water and then extracted four times with chloroform in a separatory funnel. After filtering, the combined chloroform layers were evaporated to about 2 ml in a beaker, and then transferred to a test tube for final evaporation to less than 0.5 ml before analysis. According to Currah, the ease of analysis of pulping liquors varied considerably depending on their composition, with acidified black liquors being particularly difficult. In all analyses, the chief problem was achieving a clean phase separation of the aqueous and chloroform layers in the extraction step.

Using differential pulse polarography, Brønstad *et al.*[2] determined anthraqui-

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none in water samples and black liquors. A water sample was shaken with chloroform and allowed to stand 30 min for separation of the layers. After the chloroform layer was evaporated in a rotary evaporator, the residue was dissolved in methanol for measurement of anthraquinone with the polarograph. For black liquors, a different preparation procedure was used. The black liquor, diluted with water, was placed in a modified Bleidner device to continuously steam distill and extract the anthraquinone into isooctane during a 4-h period. The isooctane phase was subsequently evaporated in a rotary evaporator and methanol was added to dissolve the residue for polarographic measurement of the anthraquinone.

The relative immiscibility of acetonitrile in soda and kraft liquors allowed Mortimer and Fleming[3] to extract anthraquinone. Dioctylphthalate was added to the liquor as an internal standard to compensate for the decrease in acetonitrile volume due to mutual solubilities. The acetonitrile phase was analyzed in a high-performance liquid chromatograph equipped with a UV absorbance detector set at 254 nm. This wavelength, however, is on the vertical rise of the dioctylphthalate spectrum. Therefore any slight shift in detector setting can result in considerable analytical error.

Black liquors, condensates and pulp washings have been analyzed for anthraquinone by spectrophotometry and by thin-layer chromatography (TLC)[4]. In the spectrophotometric method, the sample was extracted three times with toluene which was subsequently evaporated to dryness. After the residue was dissolved in toluene, the anthraquinone was reduced to anthrahydroquinone by sodium dithionite under nitrogen gas. The resulting color was measured at 416 nm. This method is very sensitive to lessening of color by traces of oxygen and has a detection limit of 10 μg anthraquinone. In the second procedure, the sample was extracted three times with ether. After evaporation of the ether, the residue was dissolved in methylene chloride and separated by TLC. Elution of the anthraquinone from the plate and measurement by spectrophotometry completed the analysis. The detection limit was 25 μg anthraquinone.

In a high-performance liquid chromatography (HPLC) determination of anthraquinone[5], the black liquor was twice extracted with methylene chloride. After repeated washings with sodium hydroxide and potassium dichromate solutions, the methylene chloride was evaporated in a rotary evaporator. The residue was dissolved in methanol for the chromatographic analysis.

All these sample preparation techniques suffer from shortcomings of phase separation difficulties, transfers, evaporations, or considerable preparation time. The availability of cartridges, which have a filling similar to ODS analytical columns, prompted the development of a rapid and simple preparation procedure. With these cartridges, a pulping liquor is passed through a cartridge which is subsequently washed with water to remove salts. Then anthraquinone, and other organic compounds, are eluted with methanol for determination by reversed-phase liquid chromatography.

EXPERIMENTAL

Instrumentation

An SP8000 high-performance liquid chromatograph with a data system and

printer was connected to a Model VUV-10 Varichrom variable-wavelength detector. A 25 cm × 4.6 mm I.D. 10-μm particle size Zorbax ODS column and a Micro-Guard holder with an ODS-10 cartridge were installed in the chromatograph. The sample valve was replaced with a Rheodyne Model 7125 syringe-loading injector with a 100-μl sample loop, which was filled using a 1-ml gas-tight syringe. HPLC grade methanol and distilled water were passed through a 47-mm diameter 5-μm pore size Mitex filter and degassed with helium before use. C_{18} Sep-Pak cartridges (Waters Assoc., Milford, MA, U.S.A.), 10- and 20-ml gas-tight syringes, and two 10-ml hypodermic syringes fitted with three-way valves were used for sample preparation.

A stock anthraquinone solution was prepared weekly by dissolving 150 mg of reagent grade anthraquinone in absolute ethanol in a 1000-ml volumetric flask. By appropriate serial dilution of the stock solution, a calibration solution containing 0.300 μg anthraquinone/0.1 ml was prepared daily.

Procedure

Dilute the black liquors 1:10 with distilled water. Dilute 1:20 if the anthraquinone concentration is greater than 100 ppm. Pulp filtrates, bleaching liquors, and wash waters are not diluted. Then adjust the pH of all samples to about 7 by titrating with 1 *N* nitric acid or sodium hydroxide. Note the volumes of sample taken and titrant required.

Attach a C_{18} Sep-Pak cartridge to a syringe and prewet before use by flushing with 2 ml of methanol followed by 2 ml of distilled water. Transfer the prewetted cartridge to a 20-ml gas-tight syringe barrel and pipet 5.0 or 20.0 ml of pH-adjusted dilute black liquor or undiluted filtrate, respectively, into the syringe. Insert the syringe plunger and slowly push the liquid, followed by air, through the cartridge. Then transfer the cartridge to a 10-ml syringe containing distilled water and slowly push the water through the cartridge. Fill a second 10-ml syringe with air, attach the cartridge, and expel the air through the cartridge. Repeat with a second volume of air. Then transfer the cartridge to a 10-ml gas-tight syringe barrel and pipet 5.0 ml of methanol into the barrel. Insert the plunger and slowly push the methanol, followed by approximately 5 ml of air, through the cartridge to elute the anthraquinone and organics. Collect the methanol in an amber vial equipped with a PTFE-lined screw cap.

The chromatographic conditions for analyzing the methanolic eluate are a Zorbax ODS column maintained at 35°C, a mobile phase of water–methanol (20:80) at a flow-rate of 1.0 ml/min, a printer chart speed of 0.5 cm/min, and an UV absorbance detector set at a wavelength of 250 nm, a normal time constant and a band width of 8. Use a 1-ml gas-tight syringe to fill the injector sample loop. Inject the anthraquinone calibration solution several times to obtain peak areas for determining an average calibration factor. Enter the factor in the data system. Inject the eluate in the same manner; the chromatogram will be complete in about 20 min. Using the anthraquinone peak area and the calibration factor, the data system will calculate and print the micrograms of anthraquinone/0.1 ml of eluate. Then calculate the concentration of anthraquinone in the original sample by:

Anthraquinone, ppm (wt./vol.) = $A/0.1 \cdot B/C \cdot (D+E)/D \cdot F/G$ where: A = anthraquinone (μg/g); B = final volume of diluted liquor (ml); C = volume of liquor taken for dilution (ml); D = volume of diluted liquor taken for titration (ml);

E = volume of titrant (ml); F = volume of methanol eluate (ml); G = volume of titrated, diluted liquor passed through the cartridge (ml).

RESULTS AND DISCUSSION

The composition of the mobile phase was optimized for best separation of anthraquinone from other aromatic compounds present in a methanolic eluate. For this, an eluate was prepared from an anthraquinone-free black liquor and a portion of this eluate was spiked with anthraquinone. Injections of the anthraquinone-free and spiked eluates were made in the chromatograph with the mobile phase having various compositions between 70 and 95% methanol. A comparison of the chromatograms obtained with each mobile phase composition showed the best separation was obtained with water–methanol (20:80). This composition gave a well separated anthraquinone peak with a retention time of 9 min. Higher percentages of methanol resulted in overlapping peaks, and although excellent separations were obtained with lower concentrations of methanol, the analysis times were too long.

A series of ethanol solutions containing only anthraquinone was used to investigate detector response. These solutions were prepared from a stock solution and contained 0.153, 0.305, 0.458, 0.610 and 0.915 μg anthraquinone/0.1 ml. Injections of these solutions showed the detector response was linear over this concentration range. For the particular detector used, the maximum response was at 250 nm; a variation of ± 5 nm in the wavelength setting did not appreciably change the detector response. Therefore an absorbance detector with a fixed wavelength of 254 nm could be used.

The method has been applied with good replication to more than 200 black liquors, filtrates, and other pulping liquors. In Table I, analytical results are given for some black liquors which contained various concentrations of anthraquinone. The standard deviation is 0.54. Black liquors with more than 100 ppm anthraquinone

TABLE I

DETERMINATION OF ANTHRAQUINONE IN BLACK LIQUORS

Sample	*Anthraquinone (ppm)*		
	Detn. 1	*Detn. 2*	*Average*
A	169	171	170
B	158	160	159
C	115	113	114
D	74.0	74.3	74.2
E	65.4	65.2	65.3
F	39.8	39.5	39.7
G	34.7	36.5	35.6
H	30.3	30.6	30.5
I	24.4	25.1	24.8
J	17.3	17.0	17.2
K	16.8	16.2	16.5
L	10.9	11.9	11.4
M	3.6	3.6	3.6
N	3.0	3.0	3.0

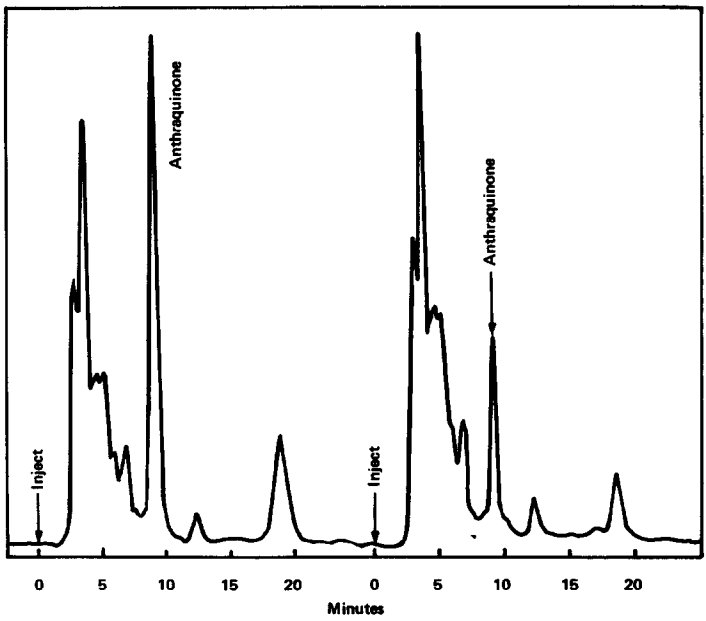

Fig. 1. Chromatograms of eluates from black liquors.

were diluted twentyfold with distilled water; those with lower concentrations were diluted tenfold. After the pH was adjusted to about 7, the diluted black liquor was passed through a cartridge. Then the cartridge was washed with water and the anthraquinone was eluted with methanol for measurement by HPLC. Recovery was ascertained by analyses of liquors spiked with known amounts of anthraquinone. Typical chromatograms of eluates from black liquors are shown in Fig. 1. As can be seen, the anthraquinone had a retention time of 9 min and was sufficiently separated from adjacent peaks for measurement. The chromatograms were back to the baseline in about 20 min.

A set of alkaline pulping liquors was also analyzed in duplicate for anthraquinone. After a ten-fold dilution and pH adjustment, 5-ml portions of the liquors were extracted with cartridges to collect the anthraquinone and organics. After flush-

TABLE II

ANALYSIS OF ALKALINE PULPING LIQUORS FOR ANTHRAQUINONE

Sample	*Anthraquinone (ppm)*		
	Detn. 1	*Detn. 2*	*Average*
A	11.5	11.4	11.5
B	10.1	9.9	10.0
C	5.9	6.0	6.0
D	3.7	4.1	3.9
E	1.4	1.1	1.3
F	0.5	0.5	0.5

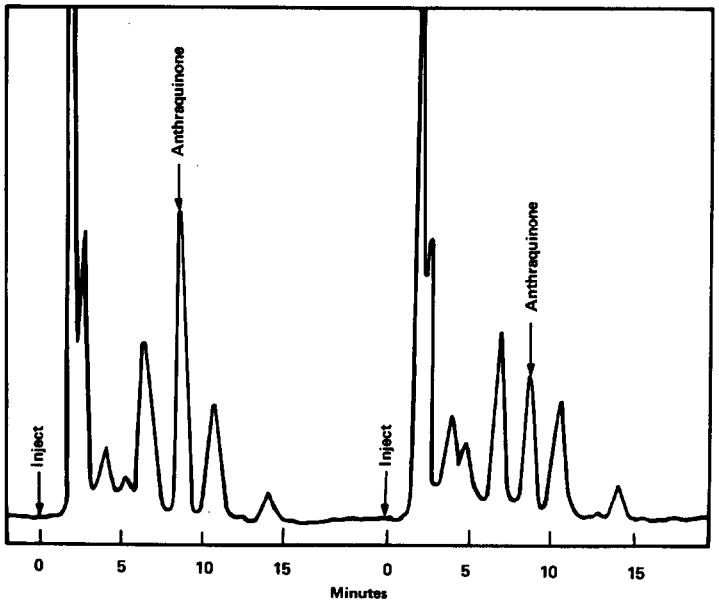

Fig. 2. Chromatograms of eluates from alkaline pulping liquors.

ing the cartridge with water, 5 ml of methanol were used to elute the anthraquinone. Table II presents the data from analyses of the eluates; the standard deviation is 0.12. Fig. 2, typical chromatograms of the eluates, shows the anthraquinone peak was well separated from the other peaks. The retention time of the peak was verified by spiking an eluate.

Pulp filtrates such as bleach solutions and wash liquors from pulps have been analyzed for anthraquinone. These filtrates had low levels of anthraquinone and other organic compounds, and did not require dilution to reduce viscosity for passage through a cartridge. The analytical results in Table III are for wash liquors which had anthraquinone concentrations ranging from 0.13 to 0.75 ppm. The standard deviation is 0.008. These filtrates, with pH values from 9.0 to 11.7, were neutralized by titrating 50-ml portions with 1 *N* nitric acid. Then 20 ml of neutralized filtrate were passed through a cartridge which was subsequently washed with water. The

TABLE III

ANALYSIS OF WASH LIQUORS FOR ANTHRAQUINONE

Sample	*Anthraquinone (ppm)*		
	Detn. 1	*Detn. 2*	*Average*
A	0.75	0.74	0.75
B	0.50	0.47	0.49
C	0.42	0.43	0.43
D	0.28	0.28	0.28
E	0.12	0.13	0.13

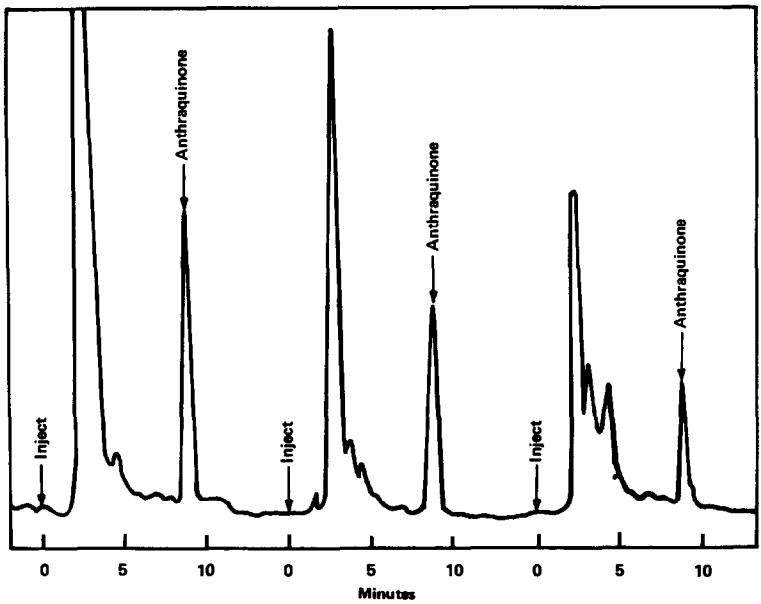

Fig. 3. Chromatograms of eluates from wash liquors.

anthraquinone and other organics were eluted with 5 ml of methanol which was analyzed. An eluate was spiked to ascertain recovery and verify the location of the anthraquinone peak. These filtrates were nearly free of other aromatic compounds as can be seen in the chromatograms of the eluates (Fig. 3). In Table IV, data are tabulated for another set of filtrates secured during a bleaching study on a pulp. The standard deviation is 0.012. These filtrates had 0.14 to 0.66 ppm anthraquinone, and the pH ranged from 2.0 to 11.7 which required titration with either 1 *N* nitric acid or 1 *N* sodium hydroxide. In the analysis, the anthraquinone was transferred from a 20-ml portion of neutralized filtrate into 2 ml of methanol in the usual manner with a cartridge. This resulted in a tenfold concentration of the anthraquinone. Fig. 4 shows chromatograms of three eluates. As can be seen, there were few aromatic compounds in the filtrates.

After this method was developed, other C_8 and C_{18} cartridges and two vacuum

TABLE IV

DETERMINATION OF ANTHRAQUINONE IN FILTRATES FROM A BLEACHING STUDY

Sample	*Anthraquinone (ppm)*		
	Detn. 1	*Detn. 2*	*Average*
A	0.65	0.67	0.66
B	0.20	0.23	0.22
C	0.10	0.08	0.09
D	0.08	0.05	0.07
E	0.03	0.05	0.04

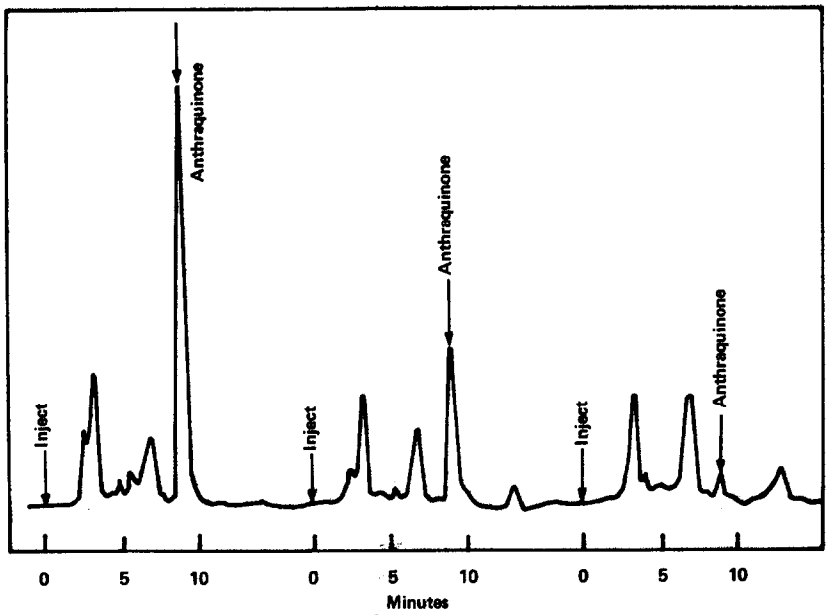

Fig. 4. Chromatograms of three eluates from bleaching study liquors.

devices for drawing liquids through cartridges have become commercially available. These have not been tried with this method, but they appear to be applicable and may offer some convenience over syringes in transferring anthraquinone from the pulping liquors into the methanol.

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