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# GAS CHROMATOGRAPHIC DETERMINATION OF ORGANIC COMPONENTS IN EFFLUENTS FROM MILLS FOR PROCESSING WASTE PAPER

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## SUMMARY

Organic components in effluents from mills for processing waste paper, prior to and after treatment, were studied by gas chromatography. Fatty acids, esters, phenols and alcohols at concentrations from 0.01 to 0.5 mg/l were determined.

## INTRODUCTION

The process of beating waste paper in board mills is always accompanied by the contamination of recycling and waste waters with considerable amounts of various organic compounds. Studies of the composition of effluents are required in order to develop efficient treatment facilities and for qualitative and quantitative monitoring of toxic organic compounds in the effluents prior to and after treatment.

Groups of organic compounds that are formed in the beating of groundwood and pulp of different grades have been studied[1]. It was established that the mass fraction of water-soluble organic substances constitutes 0.4–2.1% based on fibres for different pulp grades and 5.3% for groundwood.

The organic composition of paper mill effluents has been studied by gas–liquid chromatography and mass spectrometry[2]. Catechol, vanillin derivatives and ethers of fatty acids such as palmitic, heptadecanoic, stearic and oleic acids were identified.

The purpose of this study was the gas chromatographic (GC) determination of organic components in effluents of mills for processing mixed raw materials, *i.e.*, pulp and waste paper, which are extracted with non-polar (*n*-hexane) and polar (diethyl ether) organic solvents.

## EXPERIMENTAL

### *Sample preparation*

Prior to the GC determination of neutral organic compounds in effluents, two methods for their separation were tried. In the first, 0.5 l of effluent (pH 7) was saturated with sodium chloride and extracted three times with *n*-hexane (75, 75 and 50 ml). The extracts were combined, dried with anhydrous sodium sulphate, filtered and concentrated under vacuum to a volume of 100 $\mu$l. In the second method, separation of a neutral group of substances was carried out according to a procedure[3]

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in which 0.5 l of effluent (pH 7) was saturated with sodium chloride and extracted four times with diethyl ether (75, 50, 30 and 20 ml). The extracts were combined and washed with 1 *M* sodium hydrogen carbonate solution. The ether layer was then separated and washed with 1 *M* sodium hydroxide solution. Neutral compounds remained in the ether layer. The sodium hydrogen carbonate and sodium hydroxide extracts were each re-extracted with diethyl ether, giving with the former an extract of acidic compounds and with the latter an extract of phenolic compounds. The ether extracts of the three groups of substances obtained dried with anhydrous sodium sulphate and concentrated under vacuum to a volume of 100 $\mu$l.

*Gas chromatographic analysis*

Extracts prepared by the above procedures were subjected to GC analysis using a Tsvet gas chromatograph with stainless-steel columns (3 m × 3 mm I.D.) were with Chromaton NAW HMDS with 15% of Reoplex 400; the column temperature was 230°C, the carrier gas was helium at a flow-rate of 12 ml/min and a flame ionization detector was used.

*Quantitative analysis*

Quantitative analysis was carried out as desorbed by Novak[4]. The mass fraction of a component in the extract was calculated from the equation[4]

$$g_i = \frac{W_s}{W_i} \cdot \frac{1}{\frac{A'_{is} w_i}{A_i w'_i}\left(1 + \frac{w_s}{w_i}\right) - 1}$$

where $g_i$ is the mass fraction of component $i$ in the extract; $W_s$ is the mass of standard added to the extract (g); $W_i$ is the mass of the extract (g); $A_i$ is the peak area of the component of interest on the extract chromatogram without standard, ($cm^2$); $A'_{is}$ is the peak area of the standard substance on the extract standard chromatogram ($cm^2$); $w'_i$ is the mass of the introduced extract sample together with the standard (g); $w_i$ is the mass of the introduced extract sample (g).

Knowing the volume of effluent sample used, it is possible to determine the content of each component in the effluent from the equation

$$B_i = \frac{g_i m}{V}$$

where $B_i$ is the mass component of interest $i$ in the effluent sample (mg/l); $g_i$ is the mass fraction of component $i$ in the extract; $m$ is the mass of extract analysed (g); $V$ is the volume of the effluent sample (l).

## RESULTS AND DISCUSSION

Absolute retention times for organic compounds found in the effluent extract are given in Table I and chromatograms of the extracts of the effluent samples are shown in Figs. 1 and 2. In the neutral-fraction extract, which was separated with

*n*-hexane, thirteen compounds were found and identified as methyl and butyl esters of aliphatic acids and hydroxy acids and aliphatic alcohols together with three aromatic compounds, isoeugenol, vanillyl alcohol and the methyl ester of *p*-hydroxybenzoic acid. Separation of the neutral-fraction extract by the second method[3] gave similar compounds.

The compounds were identified on the basis of their retention times and with the use of the method of reference spots.

Comparison between the chromatograms of the two neutral fractions indicates that the first separation method gives a more efficient extraction of low-molecular-weight non-polar compounds with the simultaneous elimination of interferences from other organic components of the effluents, *i.e.*, polar, high-molecular-weight compounds, etc. In addition, the absence of subsequent operations of involving washing the extracts with solutions of sodium hydrogen carbonate and sodium hydroxide obviates the dilution of the extract of neutral compounds. When comparing the chromatograms of the two neutral fractions, there is much less information in the chromatogram of the ether extract.

The results of the quantitative determination of the neutral-fraction components are given in Table II. The results for the mass fractions of chromatographically determined substances, based on the total amount of compounds extracted with the organic solvents, indicate a more complete extraction of non-polar compounds and a considerably lower extraction of interfering components with *n*-hexane compared with diethyl ether (Table III).

TABLE I

RETENTION TIMES FOR ORGANIC COMPOUNDS

Stationary phase, Reoplex 400; column temperature, 230°C.

| *No.* | *Component* | *Retention time (min)* |
|---|---|---|
| | *Aliphatic acids* | |
| 1 | Oleic | 16.25 |
| | *Aromatic compounds* | |
| 2 | Isoeugenol | 5.08 |
| 3 | Vanillyl alcohol | 9.83 |
| | *Methyl ethers of acids* | |
| 4 | Lauric | 4.04 |
| 5 | Stearic | 6.0 |
| 6 | Lignoceric | 7.80 |
| 7 | Unidentified | 8.95 |
| 8 | *p*-Hydroxybenzoic | 30.33 |
| | *Butyl ethers of acids* | |
| 9 | Lactic | 3.08 |
| 10 | Fumaric | 3.50 |
| 11 | Palmitic | 10.80 |
| 12 | Tartaric | 12.75 |
| 13 | Arachic | 14.30 |
| 14 | Cerotinic | 19.58 |
| 15 | Melissic | 22.60 |
| 16 | Citric | 26.20 |

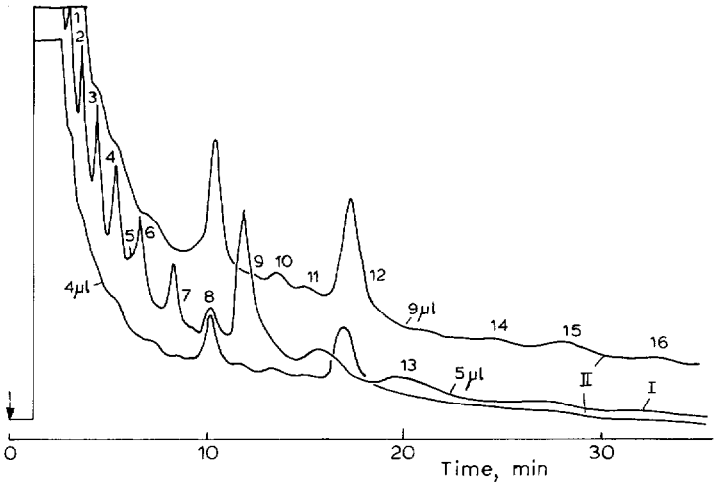


Fig. 1. Chromatograms of *n*-hexane (I) and diethyl ether (II) extracts of neutral fraction of L'vov Board Mill effluent. Methyl ethers of acids: 3 = lauric; 5 = unidentified; 6 = stearic; 7 = lignoceric; 16 = *p*-hydroxybenzoic. Butyl ethers of acids: 1 = lactic; 2 = fumaric; 9 = palmitic; 10 = tartaric; 11 = arachic; 13 = cerotinic; 14 = melissic; 15 = citric. Aliphatic acids: 12 = oleic. Aromatic compounds: 4 = isoeugenol; 8 = vanillyl alcohol. Stationary phase, Reoplex 400; column temperature, 230°C.

Comparison between the chromatograms of the neutral and acidic (re-extract of the sodium hydrogen carbonate extract) fractions, separated in accordance with ref. 3, indicates that the neutral fraction components migrate into the acidic fraction during washing of the total ether extract with sodium hydrogen carbonate solution, and the remaining components compoletely disappear, *e.g.*, ethers of arachic, lactic,

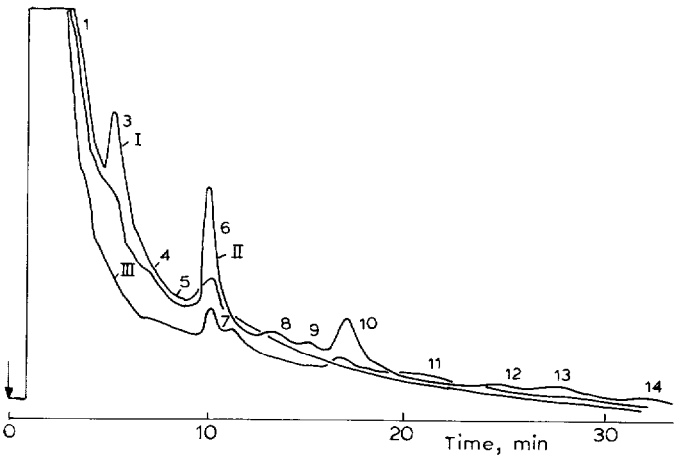


Fig. 2. Chromatograms of diethyl ether extracts of L'vov Board Mill effluent, plotted according to ref. 3: (I) phenolic; (II) neutral; (III) acidic compounds. Methyl ethers of acids: 4 = stearic; 5 = lignoceric; 14 = *p*-hydroxybenzoic. Butyl ethers of acids: 1 = lactic; 2 = fumaric; 7 = tartaric; 8 = arachic; 9 = palmitic; 11 = cerotinic; 12 = melissic; 13 = citric. Aliphatic acids: 10 = oleic. Aromatic compounds: 6 = vanillyl alcohol; 3 = isoeugenol. Stationary phase, Reoplex 400; column temperature, 230°C.

TABLE II

RESULTS OF QUANTITATIVE DETERMINATION OF NEUTRAL-FRACTION COMPONENTS OF L'VOV BOARD MILL EFFLUENT

Minimum detectable amount of components, 10 μg/l. Results are averages of four determinations. Reproducibility of results, 5%. The numbering of the compounds corresponds to that in Table I.

| *Component* | *Concentration (μg/l)* | |
|---|---|---|
| | *n-Hexane extraction* | *Diethyl ether extraction* |
| 1 | 120 | 620 |
| 2 | 380 | 70 |
| 3 | 360 | 100 |
| 4 | 420 | 90 |
| 5 | 540 | 20 |
| 6 | 10 | 60 |
| 7 | Trace | 0 |
| 8 | 60 | 20 |
| 9 | 20 | 60 |
| 10 | 250 | 10 |
| 11 | 300 | 2 |
| 12 | 450 | 80 |
| 13 | 20 | 20 |
| 14 | 31 | 5 |
| 15 | Trace | 19 |
| 16 | 114 | 50 |

fumaric, tartaric and *p*-hydroxybenzoic acids. Apparently the hydrolysing action of sodium hydrogen carbonate converts the ethers of these acids into free acids, which are not determined under the conditions used for the GC analysis. Vanillyl alcohol was also found in the acidic fraction; this alcohol cannot be related to the acidic fraction.

Comparison between neutral and phenolic (re-extract of the sodium hydroxide extract) fractions prepared according to ref. 3 indicates that the alkali treatment promotes the extraction of aromatic components, *i.e.*, isoeugenol and vanillyl alco-

TABLE III

RESULTS OF DETERMINATION OF MASS FRACTION OF CHROMATOGRAPHICALLY DETERMINABLE COMPOUNDS IN L'VOV BOARD MILL EFFLUENT FROM THE TOTAL AMOUNT OF ALL THE EXTRACTABLE COMPOUNDS

| *Total content of dry substances (mg/l)* | | *Content of organic substances determined by GC (mg/l)* | | *Mass fraction of neutral-fraction substances (%)* | |
|---|---|---|---|---|---|
| *n-Hexane extraction* | *Diethyl ether extraction* | *n-Hexane extraction* | *Diethyl ether extraction* | *n-Hexane extraction* | *Diethyl ether extraction* |
| 7.4 | 107.8 | 3.02 | 1.182 | 40.86 | 1.76 |

hol. In addition to the above components found in the phenolic fraction were some components of the neutral and acidic fractions, particularly free oleic acid and the methyl ether of stearic acid.

## CONCLUSION

It has been demonstrated that the use of diethyl ether for separating the neutral fraction of organic substances from effluents of mills for processing waste paper, according to the generally accepted method[3], is unsatisfactory because the ether extracts contain considerable amounts of compounds that interfere in the determination.

Utilization of *n*-hexane for separating the neutral fraction promotes the selective extraction of non-polar substances under mild conditions; in addition, the number of operations in the extraction prior to chromatographic analysis is reduced and losses during concentration steps are decreased, while the amount of information provided by the chromatograms obtained is increased.

It has been established that the neutral fraction of board mill effluent is mainly represented by ethers of aliphatic and hydroxy acids.

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