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Note

Determination of resin and fatty acids in pulp and paper mill effluents and white waters by gas–liquid chromatography

O. I. KAL'CHENKO* and W. P. SVITEL'SKY
Ukrainian Pulp and Paper Research Institute, 252133 Kiev (U.S.S.R.)

The problems associated with effluent treatment to remove organic compounds are of paramount importance for the pulp and paper industry. Studies on the composition of organic components accumulating in white waters can contribute to their efficient removal and lower discharge loads.

Gas–liquid chromatography (GLC) has been successfully used for monitoring organic components. Usually the GLC analysis itself is preceded by the isolation of organic components from water samples[1–3]. Therefore, choosing correctly the isolation procedure and the separation of compounds into groups is a complex problem. When using multi-component effluents, the similar physico-chemical properties of the components to be determined can lead to the similarities in their chromatographic characteristics. On the other hand, when classical isolation procedures are used[4], different chemical conversions can occur, with further distortion of the results obtained.

In this work, the compositions of the organic components extracted with a mixed solvent (chloroform–diethyl ether) from white waters from thermomechanical pulping of spruce, the filtrate of a bleached kraft pulp suspension (pine) and effluents from a board mill and waste paper recycling plant (1:1) were investigated.

EXPERIMENTAL

The extracts of the water samples, prepared as described previously[5], were analysed a Tsvet series gas chromatograph equiped with a flame ionization detector using a 3 m × 3 mm I.D. stainless-steel column with a 5% DC 550 on Chromaton N AW HMDS. Helium was used as the carrier gas and the column temperature was 180°C.

RESULTS AND DISCUSSION

Fig. 1 shows that from white waters from thermomechanical pulping of spruce, C_{12}-C_{21} fatty acids (linoleic acid predominates), resin acids (abietic acid predominates) and aromatic compounds (of phenols vanillin predominates and of phenolic acids cinnamic acid predominates) are extracted. Fatty acids, aromatic acids, phenols

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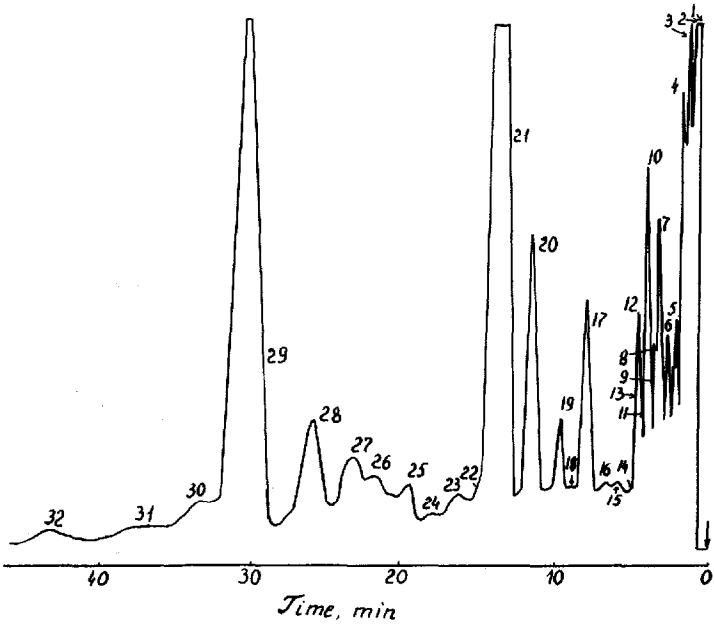

Fig. 1. Chromatogram of the extract of white waters from thermomechanical pulping. For conditions, see Experimental. 1 = *p*-Cresol; 2 = guaiacol; 3 = pyrocatechol; 4 = hydroquinone; 9 = isoeugenol; 10 = vanillin; 15 = pyrogallol. Acids: 5 = isolauric; 7 = lauric; 8 = cinnamic; 11 = vanillic; 12 = sebacic; 13 = cumaric; 14 = gallic; 16 = myristic; 18 = isopalmitic; 19 = palmitic; 20 = stearic; 21 = linoleic; 22 = arachic; 23 = isoheneicosanoic; 24 = pimaric; 25 = isopimaric + sandaracopimaric; 26 = levopimaric + palustric; 28 = dehydroabietic; 29 = abietic; 31 = neoabietic; 6,17,27,30,32 = unidentified.

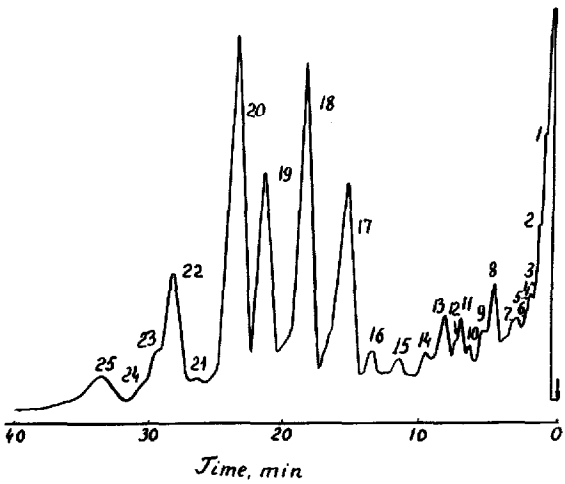

Fig. 2. Chromatogram of extract of board mill effluent. For conditions, see Experimental. 1 = *p*-Cresol; 2 = guaiacol; 4 = eugenol; 5 = isoeugenol. Acids: 3 = lauric; 6 = vanillic; 7 = isomyristic; 8 = myristic; 11 = palmitic; 12 = heptadecanoic; 13 = stearic; 14 = linoleic; 15 = arachic; 16 = pimaric; 17 = isopimaric + sandaracopimaric; 18 = palustric + levopimaric; 19 = dehydroabietic; 20 = abietic; 21 = neoabietic; 9,10,22–25 = unidentified.

and resin acids account for 29, 3, 20 and 30%, respectively, of the total amount of bound substances (fats, waxes or acid-soluble lignin). Farry acids, phenols, aromatic acids and resin acids account for 7, 15, 6 and 75%, respectively, of the total amount of free substances.

In the filtrate of a kraft pulp suspension (pine), C_{14}–C_{20} fatty acids (myristic acid predominates), aromatic compounds (pyrocatechol predominates) and resin acids (levopimaric and palustric acids predominate) were detected. Resin and fatty acids account for 41 and 39%, respectively, of the total amount of extracted substances.

TABLE I

GLC DETERMINATION OF ORGANIC COMPONENTS (%) IN WHITE WATERS OF THERMO-MECHANICAL PULPING AND BOARD MILL EFFLUENTS

The measurement error of organic substances at a confidence limit of 0.95 is about 15%.

Type	*Component*	*Filtrate of kraft pulp suspension*	*Board mill effluent*	*White waters of thermomechanical pulping*
Phenols	*p*-Cresol	Traces	2.50	1.13
	Guaiacol	Traces	1.23	5.71
	Vanillin	1.20	n.d.[a]	8.35
	Isoeugenol	0.45	1.11	Traces
	Pyrogallol	n.d.	n.d.	0.24
	Eugenol	1.92	Traces	n.d.
	Pyrocatechol	3.60	n.d.	3.50
	Hydroquinone	n.d.	n.d.	5.90
Aromatic acids	Vanillic	2.80	Traces	Traces
	Cinnamic	n.d.	n.d.	1.18
	Cumaric	n.d.	n.d.	Traces
	Gallic	n.d.	n.d.	Traces
Aliphatic acids	Sebacic	8.05	n.d.	4.80
	Isolauric	n.d.	n.d.	2.82
	Lauric	n.d.	0.50	4.70
	Isomyristic	n.d.	0.99	n.d.
	Myristic	22.42	3.26	0.24
	Isopalmitic	n.d.	n.d.	Traces
	Palmitic	Traces	2.32	1.53
	Heptadecanoic	n.d.	Traces	n.d.
	Stearic	5.64	2.72	8.00
	Linoleic	Traces	0.79	27.10
	Arachic	2.80	1.09	Traces
	Isoheneicosanoic	n.d.	n.d.	0.41
Resin acids	Pimaric	0.87	1.53	0.12
	Isopimaric + sandaracopimaric	6.30	12.60	0.82
	Levopimaric + palustric	11.80	20.00	0.33
	Dehydroabietic	8.93	12.10	2.82
	Abietic	10.75	22.40	17.10
	Neoabietic	1.96	0.25	0.18
	Unidentified	10.51	14.61	3.02

[a] Not detected.

Board mill effluents (pine kraft pulp + secondary fibres) contained C_{12}–C_{20} fatty acids (lauric acid predominates), resin acids (abietic acid predominates) and aromatic compounds (*p*-cresol predominates). Resin acids and fatty acids account for 69 and 12%, respectively. The chromatogram of components isolated from board mill effluents shown in Fig. 2.

Tannins can be a source of aromatic compounds with free hydroxyl groups (pyrogallol and gallic acid series), and water-soluble lignin can be a source of substances with methoxy groups (vanillin and related compounds). The sources of fatty acids are fats, waxes, salts of acids and free acids.

Organic substances were determined by an internal standard procedure (with methyl stearate as the standard) and the results are summarized in Table I. Qualitative analysis was performed by comparing the elution times of substances on the chromatograms with those of standard substances.

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