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Short Communication

Identification of leather preservatives by gas chromatography–mass spectrometry

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Abstract

A gas chromatographic method with mass-selective detection was developed for the identification of nine leather preservatives based on phenolic, chlorinated phenolic and heterocyclic compounds. The application of this method to the identification and confirmation of the active ingredients present in commercial formulations is described.

1. Introduction

Pentachlorophenol (PCP) was widely used as a leather preservative owing to its dual functions as a bactericide and fungicide and also its cost effectiveness. However, considering the toxicity of PCP, mostly due to contaminants present in the technical-grade product [the most toxic being the tetrachlorodibenzodioxin (TCDD)], the German Government banned the use of PCP as a leather preservative and set a maximum allowable limit of 5 mg/kg of leather [1]. Simultaneously, the US Government also banned PCP and decreed that leathers and leather products should not contain residues of PCP, its derivatives or any other pesticide that is not registered in the USA under the US Federal Insecticide Fungicide and Rodenticide Act (FIFRA) for use as biocides in raw materials, semi- or fully-finished leathers or leather goods.

The USA and Germany have suggested several substitutes for PCP, of which *o*-phenylphenol (OPP), thiocyanatomethylthiobenzothiazole (TCMTB), benzalkonium chlorides (BAC) and *n*-octylisothiazolin-3-one (OITZ) are mainly used in the leather industry [2–4]. In the international leather trade it is essential to know which preservative is used to protect leather from fungal growth and this has necessitated screening and selecting the approved preservatives from commercially available products for use during leather processing. This can be accomplished only by identifying the active ingredients by suitable analytical techniques. As the commercial formulations are complex mixtures, it is necessary to isolate the active principle prior to its identification. Even though chromatographic methods (TLC, GC, HPLC) are the techniques of choice for this purpose [5–12], additional complementary spectral data such as IR, NMR and MS data are essential for confirmation. This paper describes a GC–MS method for the identification of leather preservatives (phenolics,

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chlorinated phenolics, heterocyclic compounds, etc.).

2. Experimental

2.1. Gas chromatograph

A Hewlett-Packard Model 5890 Series II gas chromatograph fitted with an HP-5 (cross-linked 5% phenyl-methylsilicone) capillary column (25 m × 0.32 mm I.D.) with a 0.17- μ m film thickness and an HP 5971A mass-selective detector was used.

2.2. Chromatographic conditions

The injector temperature was 300°C, the interface temperature 280°C, the analyser temperature 187°C and the foreline pressure 90 mTorr. The column oven temperature was programmed from 120 to 220°C at 10°C/min. The carrier gas was helium and the inlet pressure was 80 kPa. A splitting ratio of 1:10 was used.

2.3. Chemicals and reagents

p-Chloro-*m*-cresol (PCMC) (Riedel-de Haën), *p*-chlorophenol (4CP) and 2,4,6-trichlorophenol (TCP) (BDH), *o*-phenylphenol (OPP) (Bayer), pentachlorophenol (PCP) (Fluka) and thiocyanatomethylthiobenzothiazole (TCMTB) (Buckman Labs.) were used. *n*-Octylisothiazolin-3-one (OITZ) and methylene bithiocyanate (MBT) were prepared in the laboratory. Diiodomethyl *p*-tolyl sulphone (DIMPTS) was extracted from Amical-48 (Angus Chemical). All other chemicals were of analytical-reagent grade.

2.4. Analytical procedure

The different preservatives 4CP, PCMC, TCP, OPP and PCP (25 mg each) were dissolved in 10 ml of *n*-hexane and acetylated with acetic anhydride and triethylamine at 60°C for 30 min [13], washed with water and the hexane layer was dried over anhydrous sodium sulphate and

evaporated nearly to dryness. A 25-mg amount of each of MBT, TCMTB and OITZ and 50 mg of Amical-48 were added to the acetylated mixture, dissolved in chloroform, made up to 10 ml and further diluted tenfold with chloroform. Portions of 1 μ l were injected into the GC-MS system.

Commercial leather preservative formulations based on phenols and chlorophenols were acidified to pH 2 with dilute sulphuric acid, extracted with *n*-hexane and the *n*-hexane extract was subjected to acetylation as described above and analysed by GC-MS. Other formulations were extracted with chloroform and injected directly without derivatization.

3. Results and discussion

The total ion chromatogram (TIC) of the mixture of nine leather preservatives mainly used in tanneries is shown in Fig. 1 and their mass spectral data are presented in Table 1. Phenolic compounds were acetylated prior to injection into the GC column to prevent adsorption of compounds which may lead to tailing of the peaks. For diiodomethyl *p*-tolyl sulphone obtained from the commercial formulation Amical-48, two peaks were obtained, one at 9.9 min (m/z 422) corresponding to the molecular ion and another at 6.45 min (m/z 296), which indicated the compound to be iodomethyl *p*-tolyl

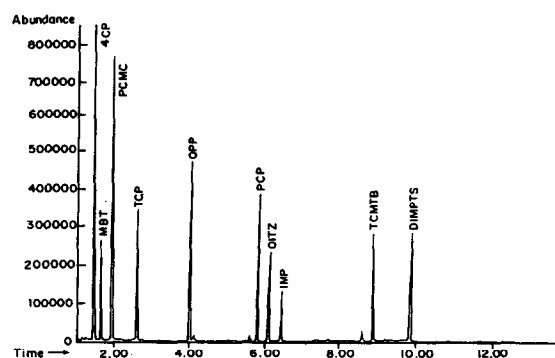


Fig. 1. Total ion chromatogram of leather preservatives. Chromatographic conditions and compound details are given in the text. Time in min.

Table 1
Retention time and mass spectral data for leather preservatives

Compound	t_R (min)	m/z^a
4CP	1.49	Ac. 170, 128, 99, 73, 65, 43
MBT	1.64	130, 72, 58, 45
PCMC	1.97	Ac. 184, 142, 107, 77, 43
TCP	2.60	Ac. 240, 238, 198, 196, 167, 132, 97, 43
OPP	4.04	Ac. 212, 170, 169, 141, 115, 89, 63, 43
PCP	5.87	Ac. 308, 268, 266, 264, 237, 167, 165, 130, 95, 60, 43
OITZ	6.14	213, 196, 180, 156, 129, 115, 114, 102, 101, 87, 58, 41
TCMTB	8.93	238, 180, 166, 136, 108, 69, 45
DIMPTS	9.93	422, 267, 231, 139, 127, 91, 65, 39

^a AC = Acetate; values in italics are base peaks.

sulphone. This may be due to an impurity in the formulation. For TCMTB, in addition to the major peak at 8.9 min (m/z 238, 180), a small peak at 8.5 min with a fragmentation pattern of m/z 238, 206 and 180 was obtained, which can be attributed to the $-N=C=S$ group. The absence of an ion at m/z 206 in the mass spectra of the major peak indicated that an $-S-C\equiv N$ group is present in TCMTB. The chromatogram and mass spectra were stored in a library for reference purposes.

Commercial preservative formulations based on phenolics and chlorinated phenolics may contain sodium salts of these compounds, which are insoluble in hexane. Hence acidification prior to extraction was essential. During the screening of various commercial leather preservative formulations, the active ingredients of two unknown samples were identified by GC-MS. Even though sample 1 was claimed to be a non-PCP-based preservative, the TIC indicated two peaks (Fig. 2) and the mass spectra confirmed the compounds to be tetrachlorophenol (t_R 4.17 min, m/z 232; acetate, m/z 274) and pentachlorophenol (t_R 5.92 min, m/z 266; acetate, m/z 308). Sample 2 on GC analysis gave several peaks (Fig. 3). The sample was identified to be a mixture of two isomers of chloroxylenol (t_R 2.46 and 2.67 min, m/z 156; acetate, m/z 198), two isomers of dichloroxylenol (t_R 3.5 and 3.8 min, m/z 190; acetate, m/z 232), trichloro-

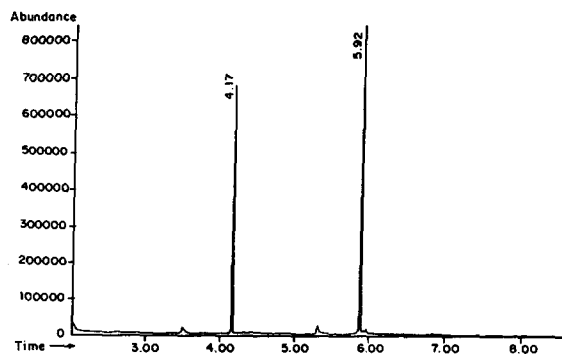


Fig. 2. Total ion chromatogram of a commercial leather preservative formulation (sample 1) obtained by GC-MS. Time in min.

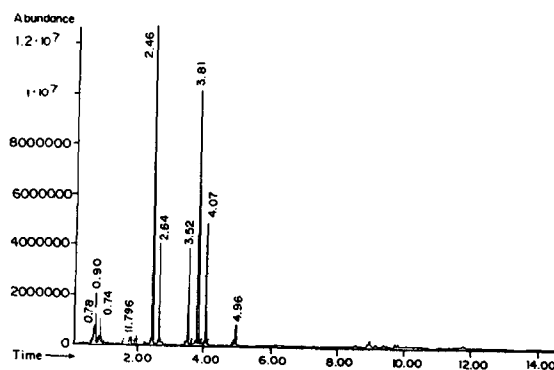


Fig. 3. GC-MS trace of a commercial leather preservative formulation (sample 2). Time in min.

xyleneol (t_R 4.96 min, m/z 224, 225; acetate, m/z 268) and *o*-phenylphenol (t_R 4.1 min, m/z 170; acetate, m/z 212) from the mass spectral data, and this sample was free from pentachlorophenol. Our identification is supported by the fact that Antimould A2, a formulation based on a mixture of chloroxylenols and the sodium salt of orthophenylphenol [14], is available from Hodgson Chemicals.

This work clearly indicates that the unambiguous identification of leather preservatives can be achieved by GC–MS. The determination of preservative residues present at trace levels in leather and leather products can be carried out by GC–MS using selective-ion monitoring mode by choosing appropriate ions of individual compounds.

4. References

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