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Note

Analysis of N-alkylphthalimides and N,N′-polymethylene-bis-phthalimides in industrial dye carrier formulations by gas chromatography-mass spectrometry

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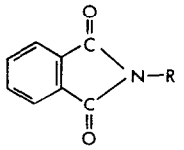
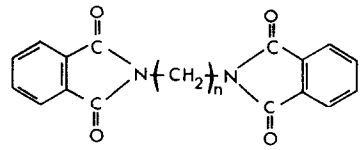
N-Alkylphthalimides (NAPs) (I) and N,N′-polymethylene-bis-phthalimides (NNPMBPs) (II) are valuable chemicals in many areas of industry. For example, NAPs are widely used as dye carriers for dyeing polyester/wool and polyester/cellulose triacetate fiber blends with disperse dyes[1]. In contrast to other dye carriers, these compounds are largely free from odour, non-toxic and biodegradable[2]. Similarly, N,N′-hexamethylene-bis-phthalimide was reported to improve the dyeability of polyester fibers[3].



I

R = ethyl, isopropyl, *n*-butyl, *n*-pentyl, isopentyl



II

n = 2, 4, 6

The identification and determination of chemical components, including NAPs and NNPMBPs, in imported products is of importance for tariff classification purposes and is one of the major activities[4] of this laboratory. To this end, the usefulness of gas chromatography–mass spectrometry (GC–MS) for separating and identifying some of the NAPs and NNPMBPs used in dye-carrier formulations was investigated.

EXPERIMENTAL

Reagents and materials

Amines were obtained from Eastman (Rochester, NY, U.S.A.), Anachemia (Montreal, Canada) and Matheson Coleman and Bell (Norwood, OH, U.S.A.).

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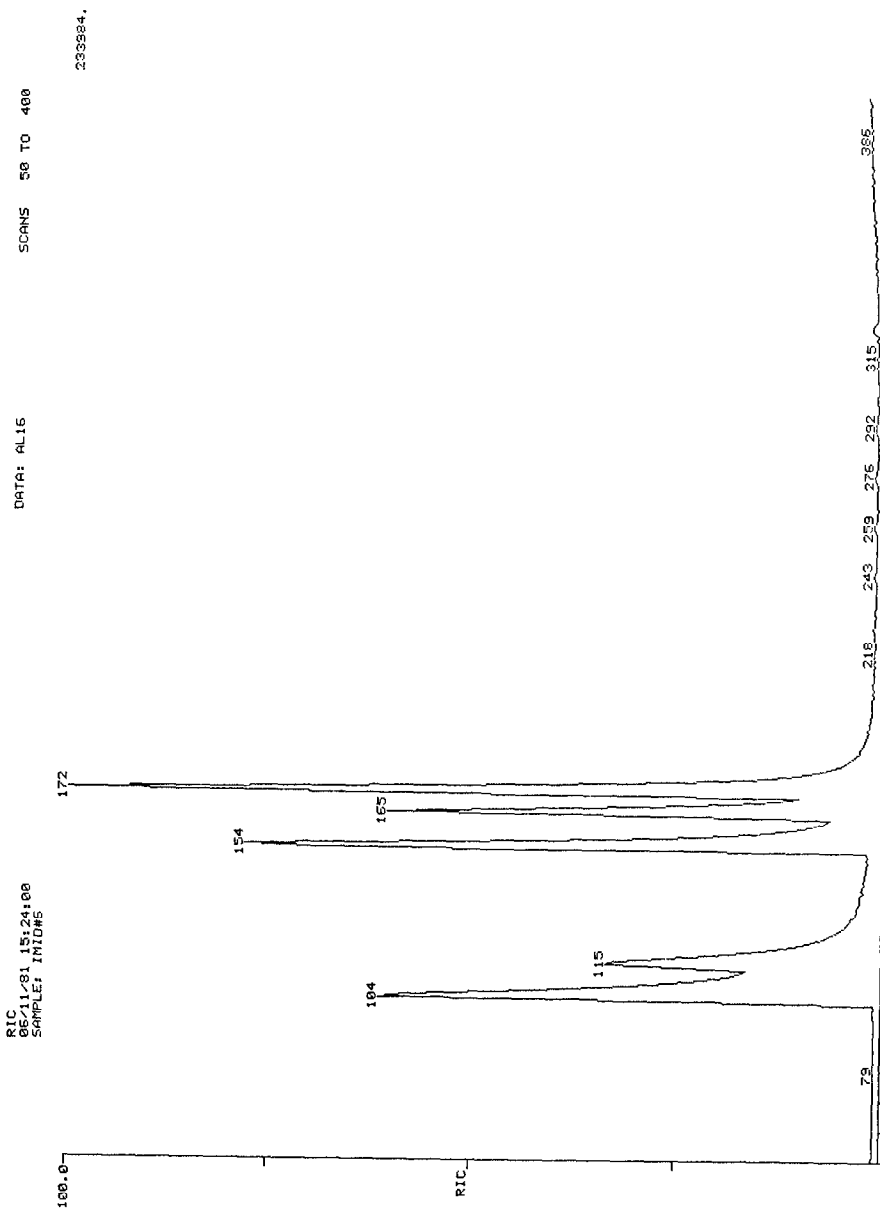


Fig. 1. Gas chromatographic separation of N-ethyl- (104), isopropyl- (115), *n*-butyl (154), isopentyl (165) and *n*-pentylphthalimide (172).

Phthalic anhydride and glacial acetic acid were obtained from Anachemia. All solvents used were analytical reagent grade.

Instrumentation and procedure

The gas chromatograph–mass spectrometer (Finnigan model 1020) was equipped with a jet separator, an electron impact source and a Nova 4 data system. The mass spectrometer was set up and tuned according to the manufacturer's instructions. The scanning rate was 4 sec/scan in the range 40–440 a.m.u. The GC instrument (Perkin-Elmer Sigma-3B) was fitted with a 3 ft. × 0.125 in. O.D. (WA–DMCS) stainless-steel column packed with 1.5% Dexsil 300®* on 60–80 mesh Chromosorb W. The oven temperature was kept at 100°C for 5 min then programmed to 350°C at 10°C/min. The injector temperature was maintained at 300°C and the carrier gas was helium, at 25 ml/min.

NAPs and NNPMBPs were prepared from phthalic anhydride and the corresponding amine according to the procedure described by Vanags[5,6]. NAPs and NNPMBBs were extracted from commercial dye carrier formulations with *n*-heptane. The completeness of the extraction was ascertained by the absence of the 1710–1780 cm^{-1} split carbonyl phthalimide band in the infrared (IR) spectrum of the extraction residue. IR spectra were recorded using a Digilab Model FTS-1C Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

Preliminary GC–MS analysis was performed using a synthetic mixture consisting of approximately equal amounts of N-ethyl-, isopropyl-, butyl-, pentyl- and isopentyl phthalimides (1.4% in toluene). The chromatogram resulting from the injection of 0.1 μl of the solution is shown in Fig. 1. A good separation was achieved with the Dexsil 300 column, selected for its stability at high temperatures. Fig. 2 shows the GC separation of three N,N′-polymethylene-bis-phthalimides with N-ethylphthalimide as reference (0.2-μl injection of a 0.7% toluene solution). The above results indicate that Dexsil 300 provides a versatile and suitable phase for the separation of the NAPs and NNPMBPs investigated.

The electron impact fragmentation pattern of NAPs and NNPMBPs has been previously reported[7,8]. Our mass spectra agree well with these published data and exhibit fragment ions typical of NAPs and NNPMBPs. The peak due to the cleavage of the C–C bond β with respect to the nitrogen was generally the most intense, *viz.* *m/e* 160 in N-ethyl-, butyl-, pentyl- and isopentylphthalimides, and in the polymethylene-bis-phthalimides; however, N-isopropylphthalimide exhibited a base peak at *m/e* 174. The expected fragment ions at *m/e* 146, 133, 130, 105 and 76 were also observed. In the case of N,N′-polytetramethylene-bis-phthalimide, a low-abundance ion at $m/e = 215$ (*i.e.* $M - 133$) was observed. The formation of the $[M - C_6H_4(CO)_2 + H]$ ion in the fragmentation pattern of NNPMBPs has been previously described[8].

Fig. 3 shows the trace obtained during the GC–MS analysis of a sample produced by solvent extraction of a commercial dye carrier formulation. Peak No. 134 consists of a major and a minor component. The selected ion monitoring technique

* Carborane–methylsilicone copolymer.

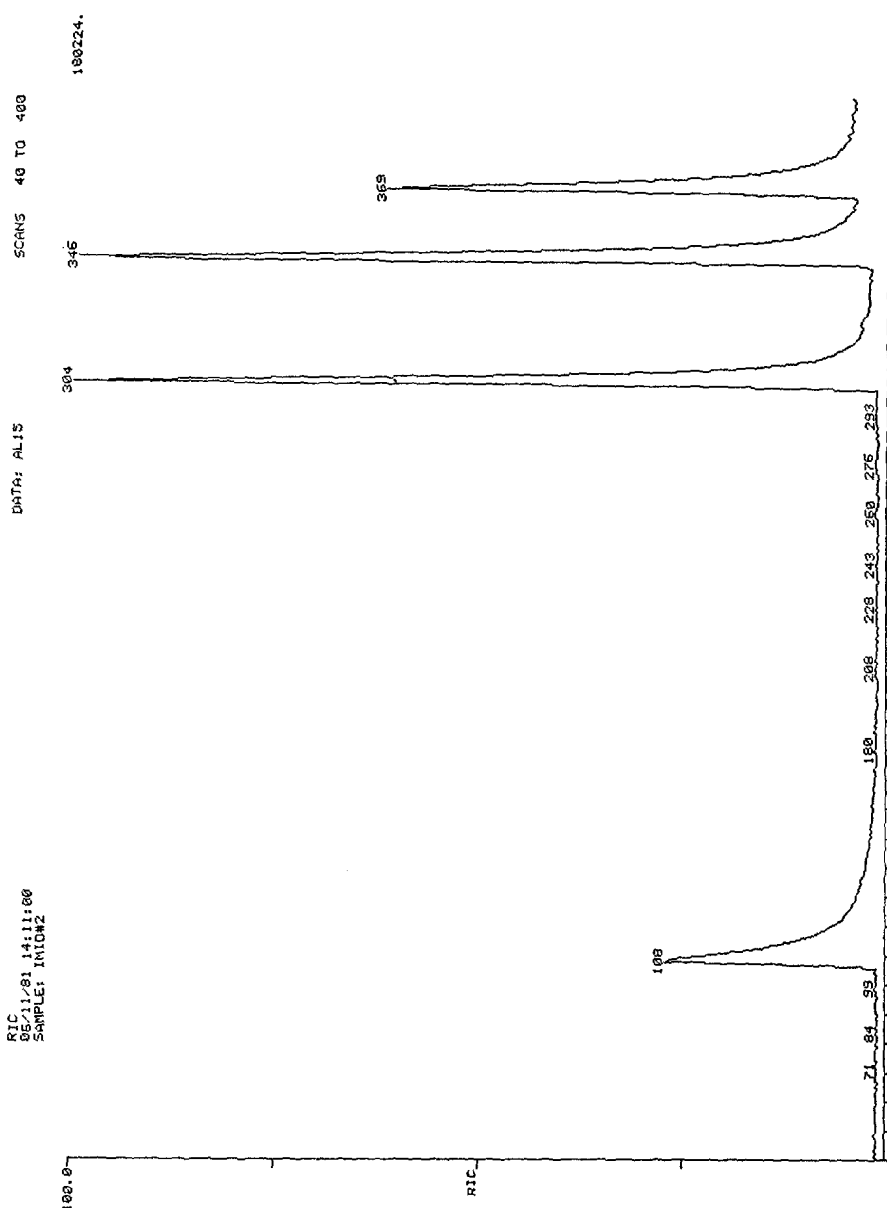


Fig. 2. Gas chromatographic separation of N-ethylphthalimide (100), N,N′-dimethylene (304), tetramethylene (346) and *hexamethylene-bis-phthalimide* (369).

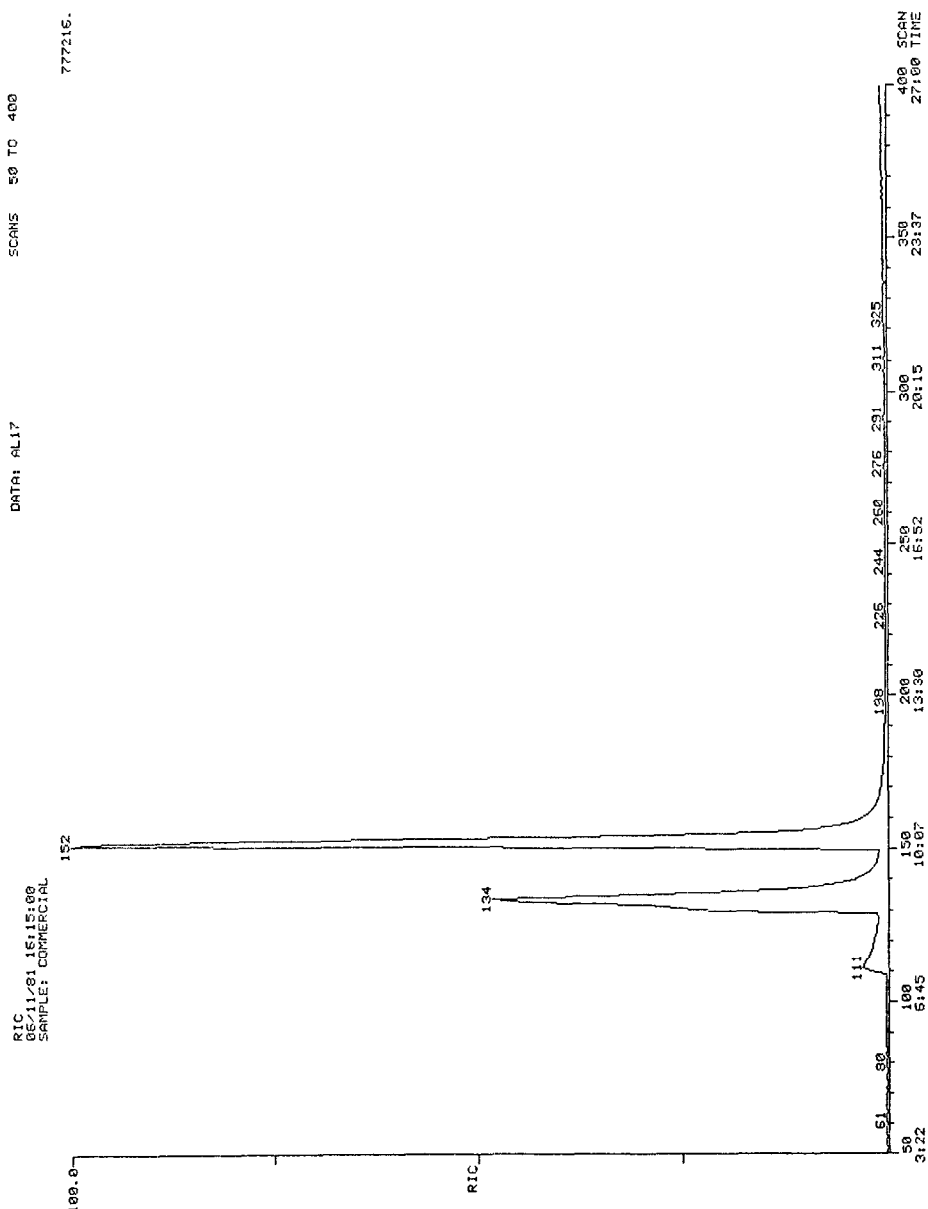


Fig. 3. Chromatogram of a NAP mixture obtained by solvent extraction of a commercial dye carrier formulation.

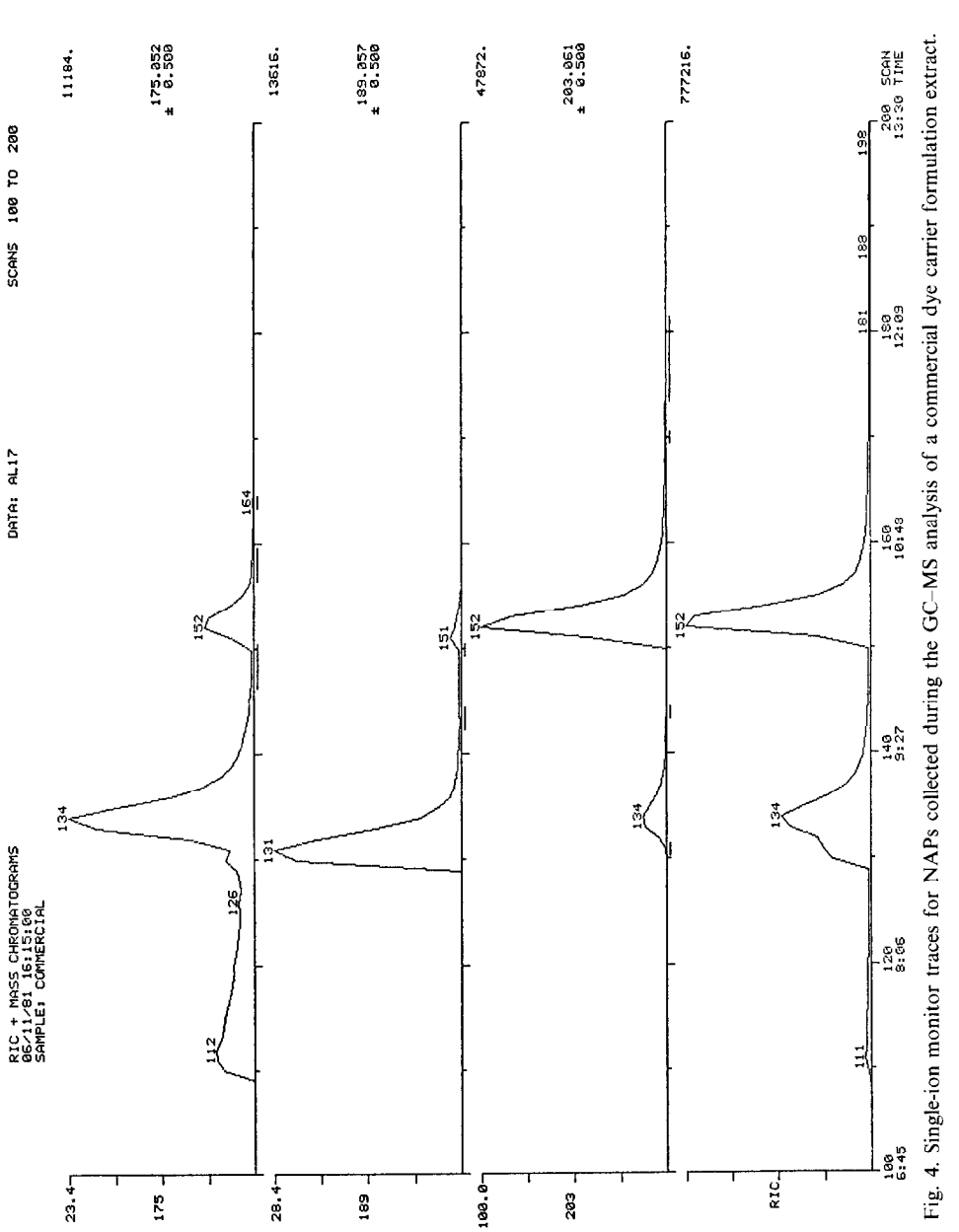
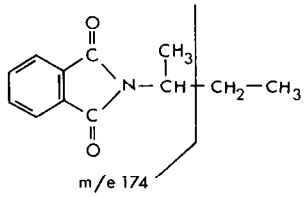


Fig. 4. Single-ion monitor traces for NAPs collected during the GC–MS analysis of a commercial dye carrier formulation extract.

provided the selectivity required for the specific identification of all the components in the mixture. The single ion monitor traces in Fig. 4 clearly indicate the presence of four components in the extract. The MS corresponding to peak no. 134 exhibited a molecular ion peak at *m/e* 203 (aliphatic side-chain with four carbon atoms) and a base peak at *m/e* 174 (*i.e.* $M - 29$) formed by β-cleavage of the C–C bond next to the nitrogen and loss of an ethyl group. Peak No. 134 was therefore identified as corresponding to N-*sec.*-butyl-phthalimide (III). The minor component at no. 131 gave a



III

distinct mass spectrum consistent with the structure of N-*n*-propyl-phthalimide. Peaks 111 and 152 were identified as N-ethyl- and *n*-butylphthalimide, respectively, on the basis of comparison of their mass spectra with the spectra of authentic samples. No NNPMBPs were detected in the above commercial sample.

It is concluded that GC–MS is suitable as a rapid and specific technique (when the instrument is available) for the separation and identification of NAPs and NNPMBPs.

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