Journal of Chromatography, 520 (1990) 175–183
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 1935

Packed column gas chromatography–capillary column gas chromatography–mass spectrometry coupling for the qualitative characterization of technical products

DIETRICH ESTEL*, JÜRGEN OHL and CLAUS EBERHARDT DÖRING
VEB Leuna-Werke, DDR-4220 Leuna (G.D.R.)

ABSTRACT

Packed column–capillary column–mass spectrometry coupling was found to be a valuable technique for the enrichment and identification of trace components in products of the chemical industry. Results are presented that were obtained by applying a SiChromat 2 gas chromatograph in the total transfer mode coupled with a Hewlett-Packard MSD 5970 B mass-selective detector for the investigation of some technical products (methanol, caprolactam, dimethylformamide).

INTRODUCTION

Two-dimensional gas chromatography (GC), as a mode of high-resolution capillary GC, is widely applied in the chemical industry, particularly in the form of capillary column–capillary column coupling. This is illustrated, among others, by the analysis of components of technical hydrocarbons [1], oxygen-containing additives in gasoline [2] and oxo-synthesis reaction mixtures [3].

On the other hand, packed column–capillary column coupling has not attained a similar widespread application. Its main field of application, the enrichment and separation of trace components from different matrices, however, is increasing in importance, especially in connection with quality problems with feedstocks, intermediates and final products. In many instances, this implies the identification of newly appearing peaks, which, is best realized by coupling with a mass spectrometer. A suitable system was therefore considered to be packed column–capillary column–mass spectrometry (PC–CC–MS) coupling.

This paper reports our investigations of technical samples with such a coupled system.

EXPERIMENTAL

A prototype of a PC–CC–MS coupled system was described by Ligon and May [4–6]. The present investigations were carried out using a Siemens SiChromat 2 gas chromatograph combined with a Hewlett-Packard HP 5990 B mass-selective detector. The column coupling was used in the total transfer mode and the laboratory

0021-9673/90/$03.50

made gas chromatograph–mass spectrometer interface was of the open split type. Electrolytic hydrogen was used as the carrier gas for the whole system.

The total transfer mode was realized by following steps: freezing of the selected part of the sample to be transferred onto the capillary column on a trapping device; backflushing of the packed precolumn during the transfer phase; adjustment of the gas flow-rate in the trapping device to that of the capillary column; and transfer of the trapped parts of the sample into the capillary column by rapid heating.

RESULTS AND DISCUSSION

Enrichment, location of the cuts

PC–CC coupling is advantageous when the substances of interest separated on the packed precolumn are to be transferred quantitatively onto the capillary column. The quality of the resulting capillary chromatogram will depend on the gas flow-rate in the trapping device during the transfer of the trapped substance into the capillary column. Too low a gas flow will give impaired resolution, particularly at the start of the chromatogram, and too high a gas flow will lead to a loss of substance, as in that event the sample will be split before entering the capillary column.

As the optimum sample volumes for packed columns and capillary columns differ by a factor of 100–1000 [7,8], the enrichment factors are assumed to be of the same magnitude. Therefore, this mode of operation is helpful in avoiding expensive off-line enrichment techniques. An illustration of this is the identification of trace impurities in recycled trichloroethene from the caprolactam process. Fig. 1a shows the analysis of such a sample by ordinary GC–MS coupling. In this instance only a few minor components are detectable. Fig. 1b shows the chromatogram of the same sample after enrichment by total transfer. To achieve a similar enrichment effect in a one-dimensional mode of operation the sample to be analysed would need to be enriched by distillation by a factor of 100–1000.

Schomburg [9] considered the two-dimensional operating mode from the point of view of a selective sampling technique. Appropriate selection of the cut taken from the precolumn eluate is a prerequisite for a succesful enrichment. The most favourable situation is when the components of interest elute prior to the main peak. In that event the cut can practically be taken from the injection point up to the beginning of the main peak. The length of the cut is not critical.

If the trace components of interest elute after the main peak, cuts that are only as broad as is required should be taken, as in that event the tailing of the main component is trapped together with the trace components and the degree of enrichment of the trace components is thereby decreased. Fig. 2 shows the results for the identification of homologous alcohols in a methanol sample. Even if a narrow cut (*e.g.*, 10 s) is taken, far away from the main peak (3–5 min), the main component methanol will still be detectable.

Combination of separation columns

The stationary phase of the packed precolumn must be characterized by extremely low bleeding. All bleeding constituents of the packed column are transferred with the same effectiveness as the sample components together into the capillary column and are rechromatographed. In unfavourable cases the background noise

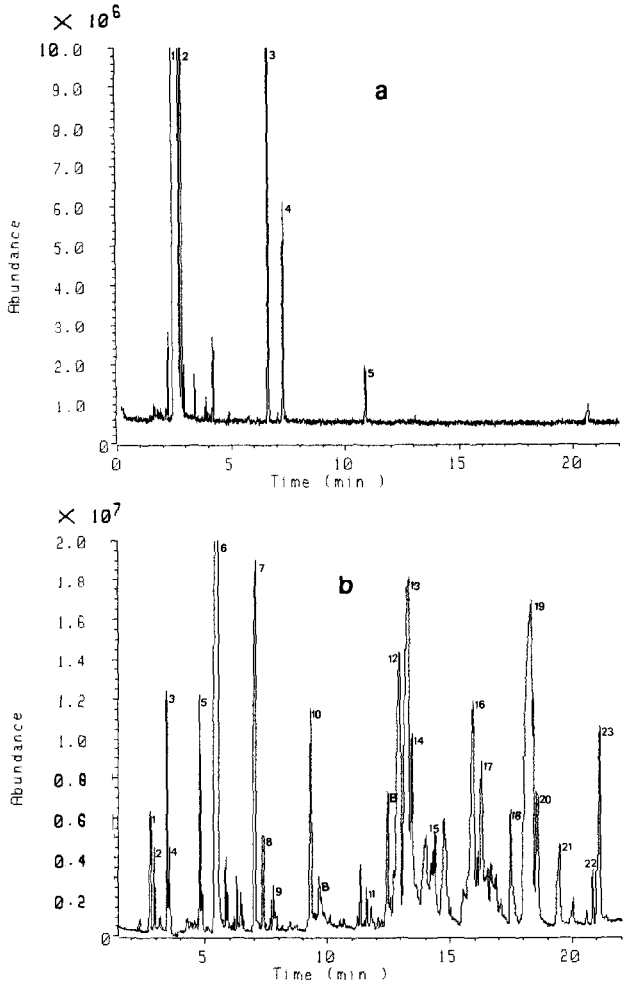

Fig. 1. Trace components in trichloroethene extractant from caprolactam synthesis. (a) Detection by means of CC–MS coupling. Compounds: 1 = trichloroethene; 2 = tetrachloroethene; 3 = trichloroethane; 4 = cyclohexanone; 5 = cyclohexenone. Column: fused silica (50 m × 0.25 mm I.D.), CP-Wax 52 CB, d_f = 0.20 μm. Temperature programme: 5 min isothermal at 80°C, heated at 10°C/min to 220°C. (b) Detection by means of PC–CC–MS coupling. Compounds: 1 = acetone; 2 = 1,1-dichloroethene; 3 = trichloroethene; 4 = tetrachloroethene; 5 = trichloroethane; 6 = cyclohexanone; 7 = cyclohex-2-en-1-one; 8 = cyclohex-3-en-1-one; 9 = *n*-pentadecane; 10 = nitrocyclohexane; 11 = nitrobenzene; 12 = tetrahydrobenzofurazan; 13 = cyclohexanone oxime; 14 = cyclohexylcyclohexanone oxime; 15 = amide; 16 = cyclohexenylidenecyclohexanone; 17 = cyclohexenone oxime; 18 = cyclohexenylidenecyclohexenone; 19 = cyclohexenylcyclohexanone + cyclohexylidene cyclohexanone; 20 = cyclohexylideneaniline; 21 = C-methylcaprolactam; 22 = 4-cyclohexylaniline; 23 = caprolactam; B = background peak. Precolumn: packed column (2 m × 2 mm I.D.), 10% Carbowax 20M–Porolith (0.1–0.2 mm). Temperature programme: 5 min isothermal at 50°C, heated at 5°C/min to 150°C, Sample volume, 20 μl. Main column: fused silica (60 m × 0.25 mm I.D.), CP-Wax 52 CB, d_f = 0.25 μm. Temperature programme: 2 min isothermal at 40°C, heated at 10°C/min to 200°C.

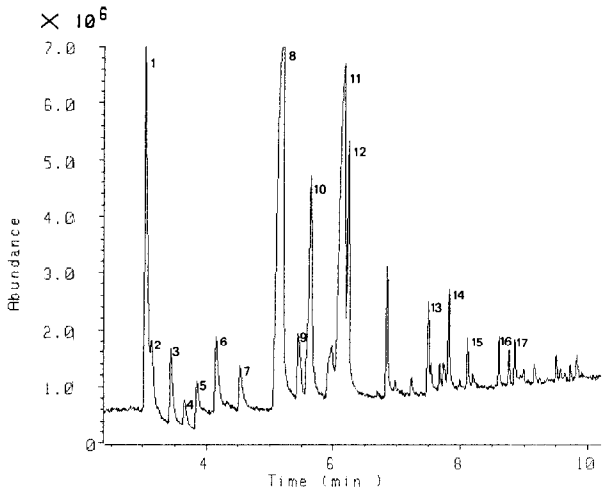

Fig. 2. A drawback of a cut localization behind a main peak on a packed precolumn. The tailing of the main peak extends over a large range of the chromatogram (see text). Compounds: 1 = methanol; 2 = ethanol; 3 = *n*-propanol; 4 = *sec.*-butanol; 5 = isobutanol; 6 = *n*-butanol; 7 = 1,1-diethoxyethane; 8 = 3-methylbutan-1-ol; 9 = 4-methylpentan-2-ol; 10 = pentan-1-ol; 11 = hexan-3-ol; 12 = hexan-2-ol; 13 = heptane-4-one; 14 = heptan-2-one; 15 = heptan-3-ol; 16 = methyl hexanoate; 17 = octan-3-one. Conditions as in Fig. 1b.

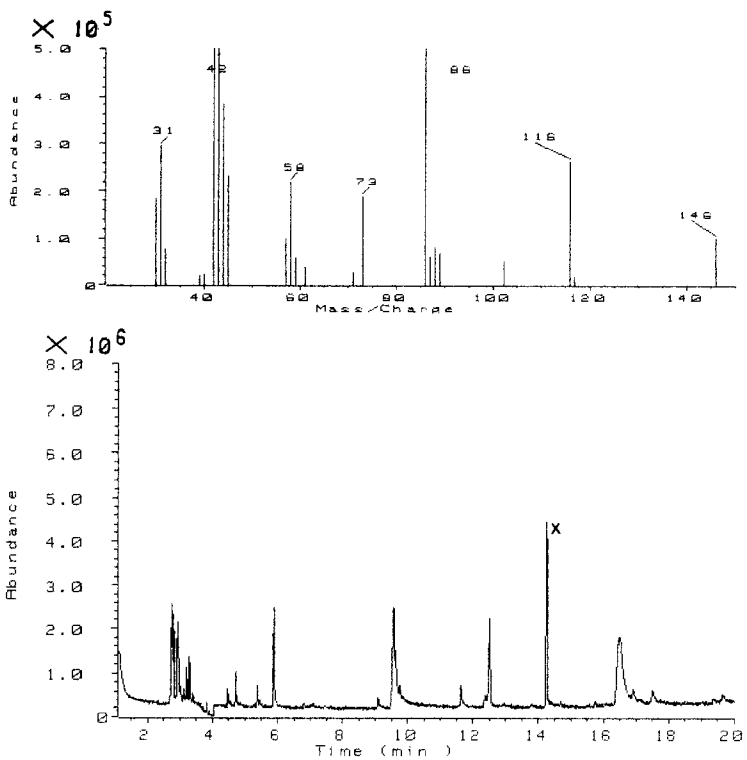

Fig. 3. Background peaks from the bleeding of a Carbowax 20M precolumn (peak X correspondens to scan 1401). Conditions as in Fig. 1b.

may exceed the component signals. This can occur, *e.g.*, with Carbowax 20M at temperatures above 200°C.

Fig. 3 shows the identification of an ethylene glycol oligomer from the bleeding of a Carbowax phase. Well suited are all OV phases, especially OV-1 in the non-polar range and OV-275 in the strongly polar range. It proved to be of particular advantage if the polarities of the precolumn and the main column differed markedly. The polarity difference to be applied depends on the problem to be investigated. In the examples discussed here a combination of a polar precolumn and a non-polar main column was preferred. Fig. 4 shows the chromatogram of a methanol sample with a polar packed precolumn (Carbowax 20M) and a non-polar capillary column (DB-1). It is possible to separate non-polar minor components (*e.g.*, *n*-octane, b.p. 125.7°C) having much higher boiling temperatures than the main component methanol without any difficulty.

Type of samples

Not all types of samples can be successfully treated using this technique. Samples with a high water content present great difficulties. Water can completely clog the trapping column; it prevents an undisturbed transfer of the cut into the capillary

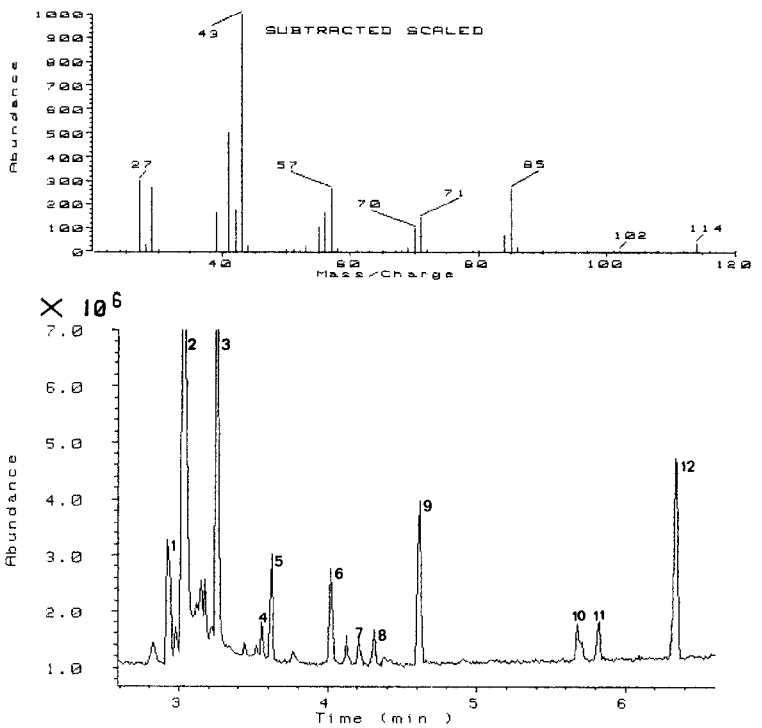

Fig. 4. Identification of traces of hydrocarbons with a higher boiling point than methanol in a technical methanol fraction by PC–CC–MS coupling. Compounds: 1 = ethanol; 2 = methyl formate; 3 = methyl acetate; 4 = 1,1-dimethoxymethane; 5 = *n*-hexane, 6 = 2,2-dimethoxypropane; 7 = 2-methylhexane; 8 = 3-methylhexane; 9 = *n*-heptane; 10 = 2-methylheptane; 11 = 3-methylheptane; 12 = *n*-octane (scan 507). Conditions as in Fig. 1b, except main column contained DB-1, d_f = 0.25 μm.

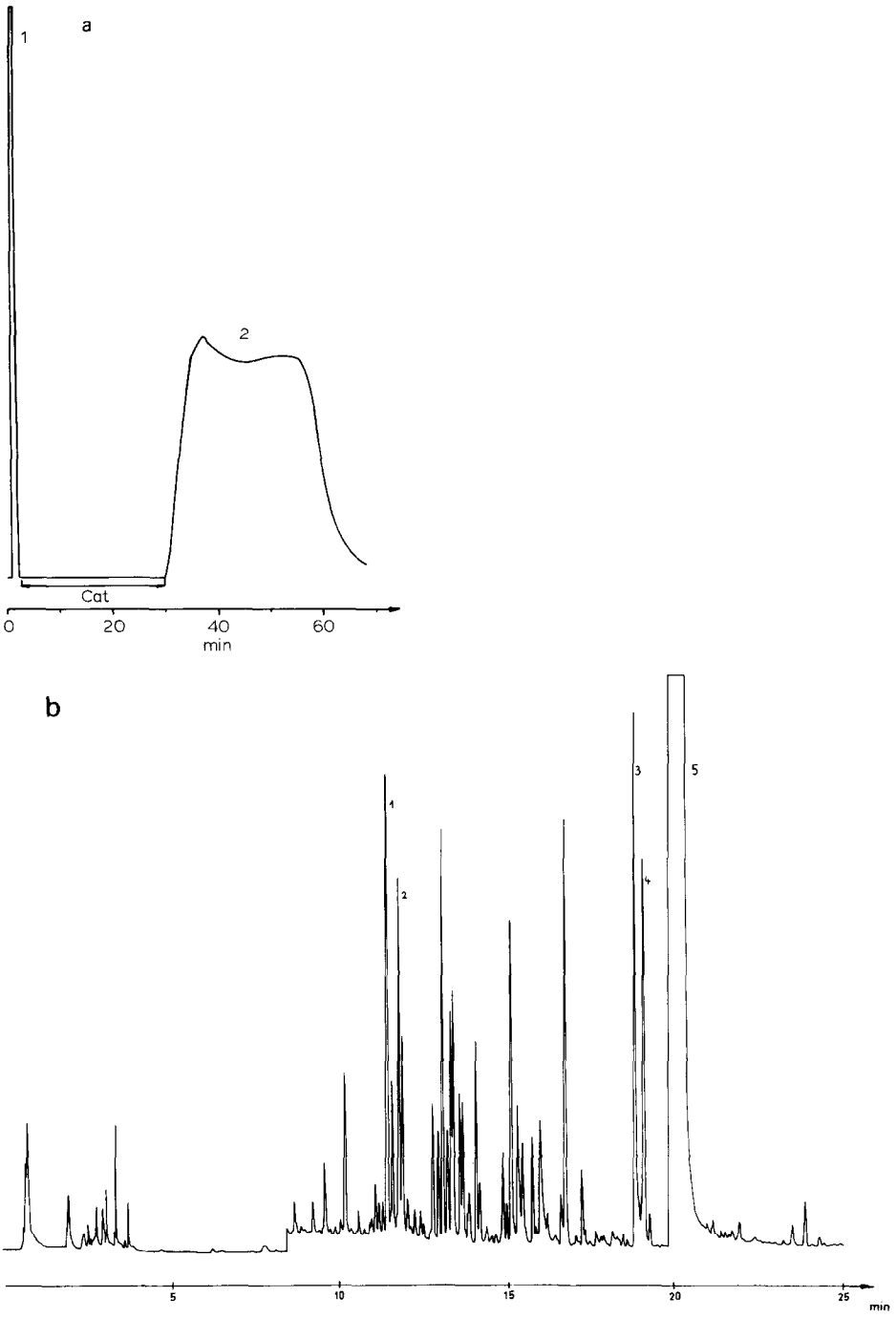

Fig. 5. Analysis of a sample of crude caprolactam by the total transfer technique. (a) Precolumn, as in Fig. 1b. Compounds: 1 = trichloroethene; 2 = caprolactam. (b) Main column, as in Fig. 1b. Compounds: 1 = aniline; 2 = tetrahydrobenzofurazan; 3,4 = C-methylcaprolactam; 5 = caprolactam.

column. The handling of easily crystallizing solids (*e.g.*, carprolactam, F. 69.2°C) also presents many problems. Large amounts of such solids should not be allowed to enter the trapping column. If the main peak is backflushed from the precolumn, this substance will crystallize on any cold part of the set-up after the injector (needle valve, solenoid valve) and block the gas flow. To avoid this, the main component must be flushed efficiently to the detector.

Fig. 5 shows the investigation of a sample of crude caprolactam according to this technique. The main peak transferred to the flame ionization detector is plotted at the beginning of the time axis.

CC–MS coupling

If CC–MS coupling is used, the gas balance will depend on the performance of the MS pump system. In the present instance the maximum take-in flow was *ca.* 1 ml/min of hydrogen. To transfer the components to be identified into the mass spectrometer without any loss the gas flow should not exceed this amount. On the other hand, the gas flow in the packed precolumn is not critical. Further, the enrichment effect achieved by using PC–CC–MS coupling has the advantage of giving back-

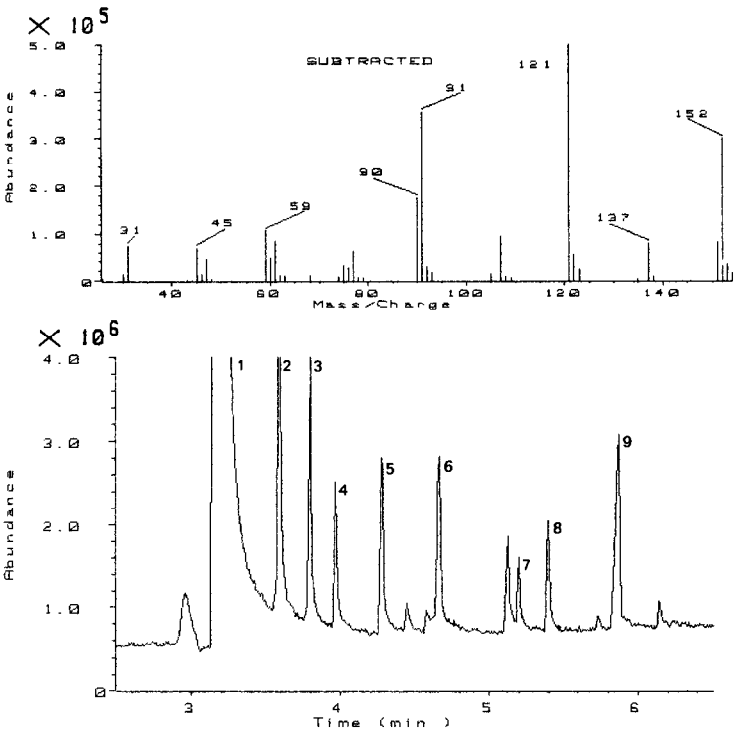

Fig. 6. Detection of a 0.1-ppm peak of tetramethoxsilane in a methanolic matrix using PC–CC–MS coupling. Compounds: 1 = methanol; 2 = *n*-propanol; 3 = *sec.*-butanol; 4 = isobutanol 5 = *n*-butanol; 6 = pentan-2-ol + pentan-3-ol; 7 = 3-methylbutan-1-ol; 8 = 3-methylbutan-2-ol; 9 = tetramethoxysilane (scan 604). Conditions as in Fig. 1b.

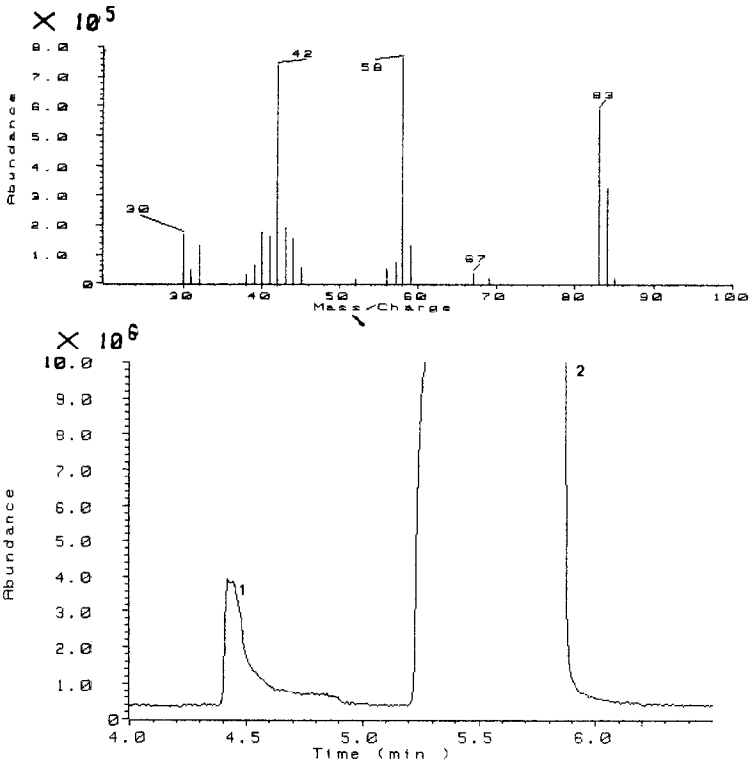

Fig. 7. Identification of an unknown trace component as dimethylamino acetonitrile in a dimethylformamide sample using PC–CC–MS coupling. Compounds: 1 = dimethylaminoacetonitrile (scan 354); 2 = dimethylformamide. Conditions as in Fig. 1b.

ground-free mass spectra also from peaks present in the original sample in only low concentrations (<0.1 ppm).

Fig. 2 and Figs. 6 and 7 illustrate this. Fig. 6 shows the identification of an unknown trace component (*ca.* 0.1 ppm) in a methanolic matrix as tetramethoxysilane. The recorded mass spectrum (Fig. 6) is in agreement with the spectrum from the NBS library [10] and the mass spectrum of a reference sample. Fig. 7 shows the identification of a trace component in a dimethylformamide sample as dimethylaminoacetonitrile. In this instance also comparison with the spectrum of a reference sample was helpful in the assignment of the structure.

REFERENCES

1 F. P. Di Sanzo, J. L. Lane and P. E. Yoder, *J. Chromatogr. Sci.*, 26 (1988) 206.
2 G. Schomburg, F. Weeke, F. Müller and M. Oreans, *Chromatographia*, 16 (1983) 87.
3 D. E. Willis, *J. Chromatogr. Sci.*, 24 (1986) 417.
4 W. F. Ligon and R. J. May, *Anal. Chem.*, 52 (1980) 901.
5 W. F. Ligon and R. J. May, *J. Chromatogr.*, 294 (1984) 77.
6 W. F. Ligon and R. J. May, *J. Chromatogr. Sci.*, 24 (1986) 2.

7 L. S. Ettre, in P. Sandra (Editor), *Sample Introduction in Capillary Gas Chromatography*, Vol. 1, Hüthig, Heidelberg, Basle, New York, 1985, Ch. 1, p. 3.
8 G. Schomburg, *Gaschromatographie: Grundlagen, Praxis, Kapillartechnik*, Verlag Chemie, Weinheim, 1987, p. 53.
9 G. Schomburg, in P. Sandra (Editor), *Sample Introduction in Capillary Gas Chromatography*, Vol. 1, Hüthig, Heidelberg, Basle, New York, 1985, Ch. 12, p. 235.
10 *NBS Mass Spectral Date Base*, U.S. National Bureau of Standards, Office of Standard Reference Data, Washington, DC.