Journal of Chromatography, 322 (1985) 200–205
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,540

Note

Thick-film capillary column gas chromatography–field ionization mass spectrometry

A complementary technique for the rapid analysis of volatiles

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(Received January 2nd, 1985)

The properties of field ionization (FI) mass spectrometry (MS) in providing molecular ion spectra and strongly reduced fragmentation have been known for many years[1]. Damico and Barron[2] first demonstrated the utility of gas chromatography (GC)–FIMS in the analysis of volatile natural products in spite of the sensitivity disadvantages over electron impact (EI)MS. Several years later, Milberg and Cook[3] reported the packed column GC–FI mass spectra of pesticides and drugs.

Recent studies have shown pyrolysis (Py) capillary column GC–FIMS[4] to be a powerful technique in complementing the direct characterization of tobacco by Py–FIMS and factor analysis[5]. The present paper demonstrates for the first time the combined capillary column GC–FIMS technique. The method is illustrated by injection of essential oils on to a thick-film capillary column connected directly to a commercially available mass spectrometer ion source.

MATERIALS AND METHODS

Essential oils

Orange oil samples (Florida and California) were obtained from Orissa Dreb-ing, Hamburg, F.R.G. A perfume sample from the desert flower purple sage was purchased from commercial sources in Albuquerque, NM, U.S.A.

Gas chromatography

A Varian 3700 gas chromatograph was employed equipped with a Gerstel (Labormechanik Gerstel, Mülheim/Ruhr, F.R.G.) split/splitless injector. The fused-silica capillary column, chemically bonded with CpSil5 phase (1.25 μm film thickness; Chrompack, Middelburg, The Netherlands) had dimensions 26 m × 0.32 mm I.D. and was programmed from 100°C to 250°C at 10°C/min. The helium carrier gas pressure was 1 bar, the split vent was set at 20 ml/min and 0.5 μl of each oil was

0021-9673/85/$03.30

injected. The column was connected directly to the mass spectrometer ion source via a deactivated fused-silica line (45 cm × 0.1 mm I.D.; Scientific Glass Engineering, Weiterstadt, F.R.G.).

Mass spectrometry

A Finnigan MAT 212 mass spectrometer equipped with a combined EI–FI–field desorption (FD) ion source was employed. In the FI mode, the accelerating voltage and emitter potential were 3 kV; the counter electrode was at −8 kV; the electron multiplier, 2.2 kV; scanning speed 1.1 sec/decade; mass range *m/z* 50–500. The high-temperature activated carbon emitter was prepared according to published methods[6,7].

In the EI mode, the ionizing energy was 70 eV and the mass range was *m/z* 33–500. Spectra were recorded by repetitive magnetic scanning via the Finnigan SS300 data system for further processing including the formation of specific mass chromatograms.

RESULTS AND DISCUSSION

A simple test involving the injection of same amounts of limonene on to the column in both modes gave a sensitivity decrease in FI of 1:20 for the molecular ion, *m/z* 136. However, no special steps were undertaken to optimize the sensitivity in the FI mode, *e.g.* ion source temperature or the distance between the fused-silica interface line and the emitter. The FI source was found to be easily tuned in both modes and

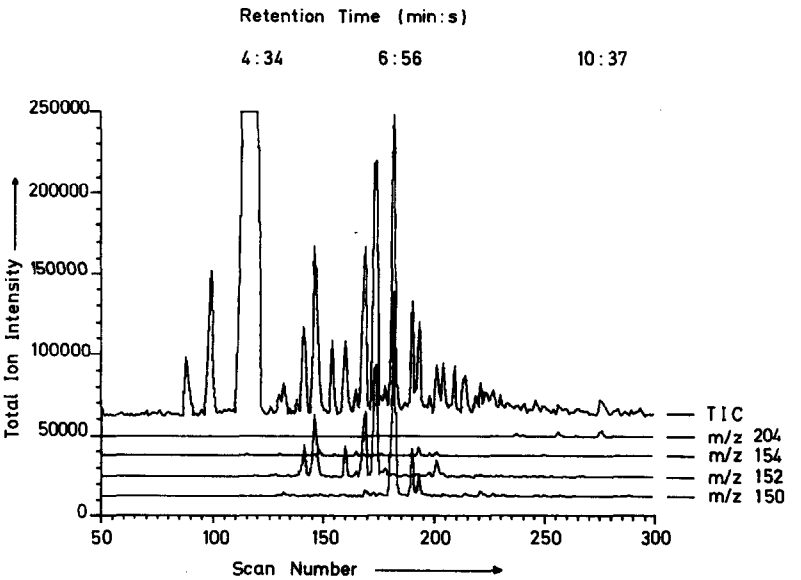

Fig. 1. Thick-film capillary column GC–FIMS mass chromatogram obtained from a sample of Californian orange oil revealing retention times of components having molecular ions *m/z* 150, 152, 154 and 204. The largest peak (retention time 4 min 34 sec) in the total ion current chromatogram corresponds to limonene, the major constituent.

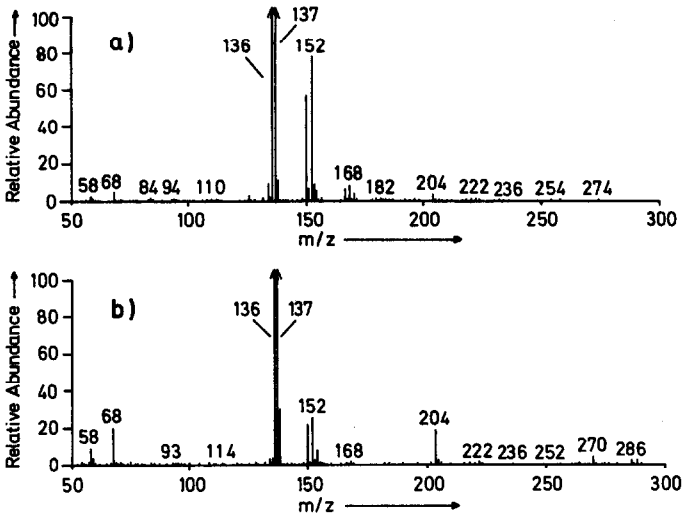

Fig. 2. Examples of time-integrated GC–FI mass spectra summarizing the contents of the GC–MS runs: (a) California orange oil, normalized to *m/z* 136 (limonene, major component) multiplied by a factor five and (b) Florida orange oil similarly normalized and multiplied by a factor twenty. The differing proportions of minor components are revealed.

to be stable for up to two days with a single emitter. Switchover to the EI mode was accomplished within 20 sec, including focussing.

In spite of the difference in sensitivity achieved, the results show that useful complementary data can be obtained from the capillary column combination.

Orange oils

A mass chromatogram (FI) of an orange oil is shown in Fig. 1. The total ion current is displayed together with specific ion chromatograms at *m/z* 150, 152, 154 and 204. The major component is limonene (*m/z* 136). The prominent signal at *m/z* 204 (retention time, 10 min 37 sec) was confirmed to be due to valencene by reference to the EI spectrum at the corresponding retention time.

Other components tentatively identified by their EI spectra and FI spectra at the corresponding relative retention times are (mol. wts. in parenthesis) *n*-nonane (128), α-pinene (136), myrcene (136), β-pinene (136), linalool (154) and geranial (152). A series of important hydrocarbons having molecular weights 150, 152 and 154 are readily revealed by the FIMS method. A comparison of the Florida and California oils is conveniently carried out by integration of all the GC–MS data as shown in Fig. 2. The spectra are shown multiplied by suitable factors since limonene (*m/z* 136) is by far the major component. The potential use of such time-integrated spectra in aiding rapid computerized sample–library comparison is high.

Purple sage perfume

Total ion current profiles obtained by GC–MS of the purple sage perfume under similar chromatographic conditions are shown in Fig. 3a (FI) and b (EI). Differences in the relative intensities are to be expected since most of the ion current in the EI case consists of fragment ions whereas in FI fragmentation is much less

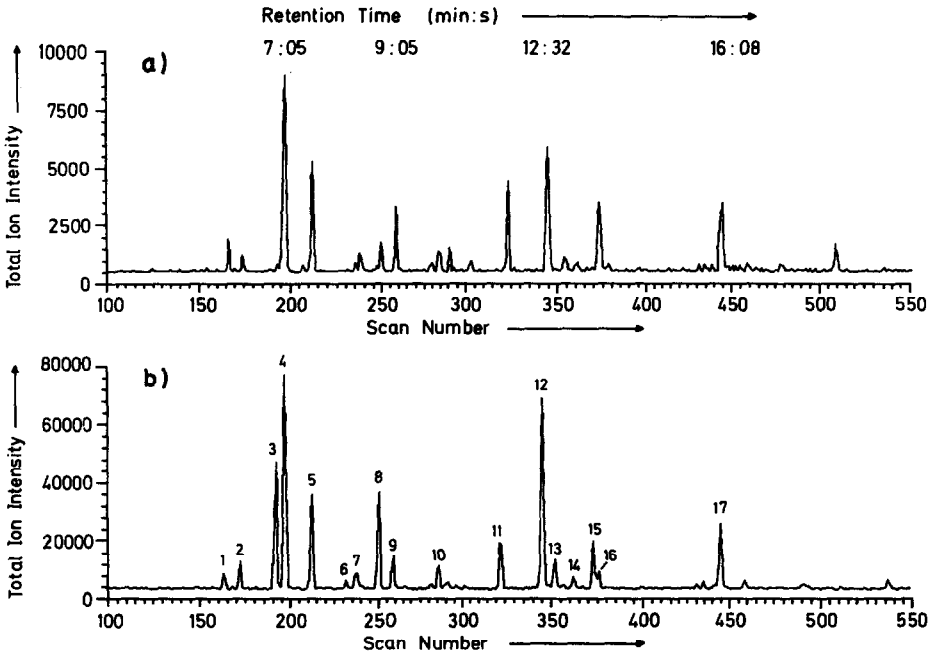

Fig. 3. Capillary column GC–MS total ion current profiles obtained from New Mexico purple sage perfume under same chromatographic conditions: (a) FIMS, (b) EIMS.

significant. However, certain sensitive compounds such as linalool and linalyl acetate which have very small or lack molecular ions in their EI spectra depending on the ion source conditions, exhibit significant fragmentation in their FI spectra. As an illustration, the FI spectra of limonene, linalool and linalyl acetate from the purple sage sample are shown in Fig. 4a, b and c, respectively.

Retention data of components of EI and FI chromatograms were compared by calculation of retention indices based upon published values[8] for three clearly identified components, limonene (1030), linalyl acetate (1246) and diethyl phthalate (1565) obtained on OV-101, a similar liquid phase. A regression equation was calculated on this basis:

$$I = 576 + 1.22t \qquad (r = 0.9999)$$

where I is the calculated index and t the retention time in seconds. Further important components tentatively identified are given in Table I, together with their calculated indices. Such calculated index values are not intended to have any absolute significance but only to act as a cross reference between the EI and FI chromatograms. However, published index values[8] for the tentatively identified components are also given in Table I for comparison. Fairly good agreement was generally obtained with some notable exceptions, *e.g.* benzyl alcohol. The regression procedure can easily be extended and improved to include further clearly identified components.

The described retention index procedure has potential for the computer-assisted comparison of EI and FI or EI and chemical ionization (CI) spectra obtained from separate GC–MS runs under similar conditions.

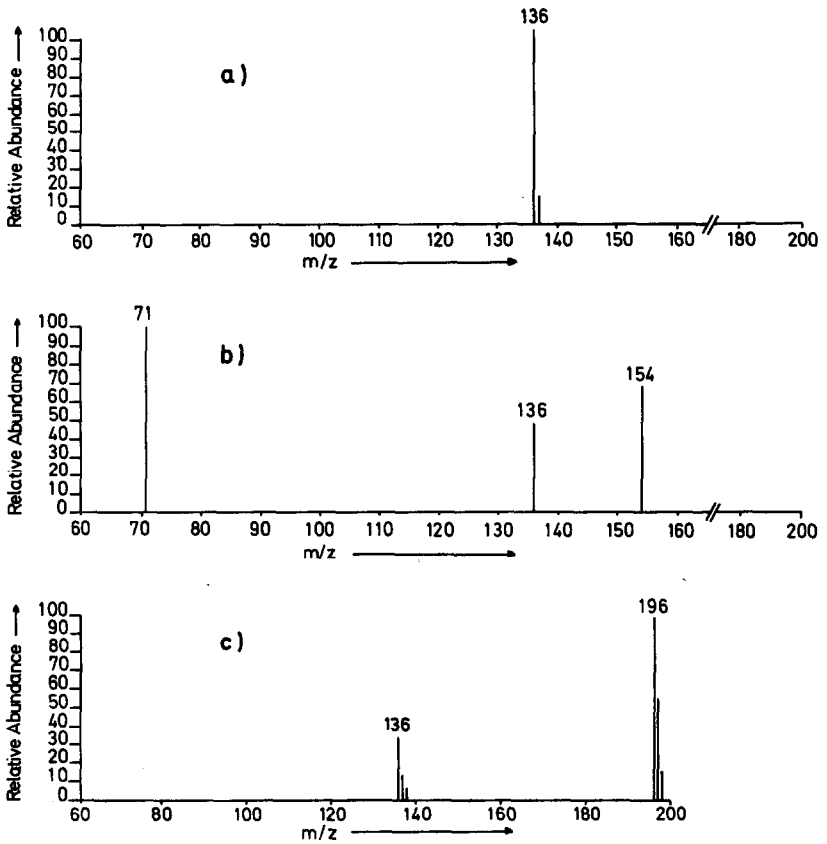

Fig. 4. Examples of FI mass spectra obtained from New Mexico purple sage perfume after GC separation: (a) limonene (MW 136), (b) linalool (MW 154) and (c) linalyl acetate (MW 196).

Particularly striking is the information gained at the base line level where many probable molecular ion spikes are apparent. In the case of the corresponding EI spectra, many molecular ions would no longer be visible, only the major low mass range fragments being found. Such rapid GC–FI profiles can provide pointers to the presence of trace components which if cannot be detected by correlation in EI profiles can be looked for after isolation procedures. In particular, the background spectra are free of signals.

The known sensitivity disadvantages of FIMS can thus be offset by increasing the sample amount. Additional sensitivity may be achieved by scanning over a more limited mass region, *e.g.* *m/z* 100–300 for such essential oils.

The clear advantage over CIMS is that the spectra consist mainly of molecular ions and cannot be influenced to a great extent by instrumental conditions such as source pressure, reactant gas and its purity. Many components in essential oils fail to produce unambiguous molecular weight information in their isobutane CI spectra[9]. Owing to its higher sensitivity, CIMS is certainly a more suitable technique in cases where sample amount is limited. A direct comparison of GC–FIMS and various GC–CIMS techniques remains to be carried out.

TABLE I

TENTATIVE IDENTIFICATIONS OF SAGE OIL COMPONENTS BASED UPON EI MASS SPECTRA

Approximate retention indices are calculated by reference to literature[8] values for limonene, linalyl acetate and diethyl phthalate on a similar liquid phase.

GC Peak		I_{EI}*	I_{FI}	*FI mol. wt. peak (m/z)*	*Tentative identification*	$I_{Lit.}$**
Number	*$Time_{EI}$ (min:sec)*					
1	5:55	1010	1014	108	Benzyl alcohol	1033
2	6:14	1033	1034	136	Limonene	1030
3	6:57	1085	1087	154	Linalool	1092
4	7:05	1095	1097	122	Phenyl ethyl alcohol	1104
5	7:41	1139	1137	150	Benzyl acetate	1144
6	8:24	1191	–	–	α-Terpinol	1185
7	8:40	1211	1206	156	Citronellol	1215
8	9:05	1241	1239	196	Linalyl acetate	1246
9	9:24	1265	1262	–	–	–
10	10:23	1336	1329	151	2-Aminobenzoic acid methyl ester	–
11	11:43	1434	1428	192	α-Ionone	1416
12	12:32	1494	1490	206	α-Isomethyl ionone	1471
13	12:47	1512	1512	103	–	–
14	13:08	1538	1535	208	Isoamyl salicylate	1528
15	13:32	1567	1568	222	Diethyl phthalate	1565
16	13:58	1574	1579	208	*n*-Amyl salicylate	1557

* CpSil 5 phase.
** OV-101 phase.

The FI method in combination with a thick-film column having high capacity while maintaining chromatographic resolution provides a very rapid molecular ion fingerprint of such samples as essential oils where sample amount is not normally severely limited. Further developments in thick-film technology[10] should increase this potential.

ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg and the Umweltbundesamt, Berlin (F.R.G.).

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