HEWLETT PACKARD

GC/IR/MS Analysis of Some Minor Components in Coriander Oil

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IRD Application Brief

HP 5965B IRD
HP 5970B MSD

IRD89-4

IRD Productivity Profile

Industry
Flavors and Fragrances

Chemicals
Sabinene, alpha Phellandrene
Solvents

Sample Matrix
Essential Oil

Analysis
Identification of Components

Introduction

Coriander oil, used extensively in seasonings and perfumes, is obtained by the steam distillation of the partially dried ripe fruits of Coriander sativum L. The major areas of cultivation are the U.S.S.R., Poland, and Hungary, as well as many additional countries with temperate climates. The oil is pale yellow with the odor of linalool, its major component (60-80%). Other components are mainly terpene hydrocarbons such as alpha pinene, gamma terpinene, camphor and para cymene. There are many other minor components.[1] To illustrate the utility of combined GC/IR/MS in the area of essential oil analysis, two of these minor components of Russian coriander oil were examined and their identities confirmed at a high confidence level. Also several residual contaminants were found.

Results

The examination of Russian coriander oil, see Figure 1, by combined GC/FTIR/MS was performed using the series configuration where all of the column effluent is sent first through the flow cell of the IRD and then a portion of the flow cell effluent, ca. 15%, is sent to the MSD. This arrangement gives similar chromatographic sensitivities. A more thorough discussion of these operational considerations is documented elsewhere.[2]

The first ten minutes of the coriander oil chromatograms are shown in Figure 2 along with the peak assignments. The differences in signal size in the MSD's total ion chromatogram and the IRD's total response chromatogram are apparent. By having both MS and IR data it is much easier to identify these components. The early components appear to be solvent residues from the oil preparation. Aromatic C-H absorption is observed in the IR spectra of the peak at 7.4 minutes while a strong m/z 91 ion is observed in the mass spectrum, strongly suggesting the presence of toluene. Oxygen, nitrogen, water, and ethanol all have ions less than m/z 33 (the lower mass limit used here) and hence are not seen on the Total Ion Chromatogram (TIC).

The major components of Russian coriander oil are noted on the chromatograms in Figure 3 and in Table 1. To illustrate the qualitative capabilities of the combined IRD/MSD, peak 3 at 17.3 minutes and peak 6 at 19.0 minutes were chosen. These peaks were not identified by Chialva and Gabri.[3] It can be seen in Figure 4 that the TIC/Total Response Chromatogram (TRC) response of peak 3 is fairly similar but the IR response is relatively weak for peak 6, however, a good infrared spectrum was obtained.

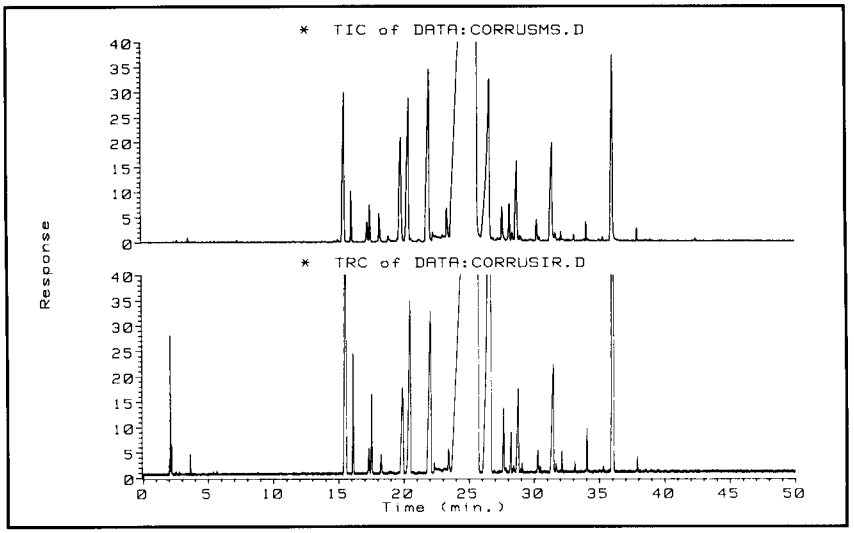

Figure 1. TIC and TRC of Russian Coriander Oil

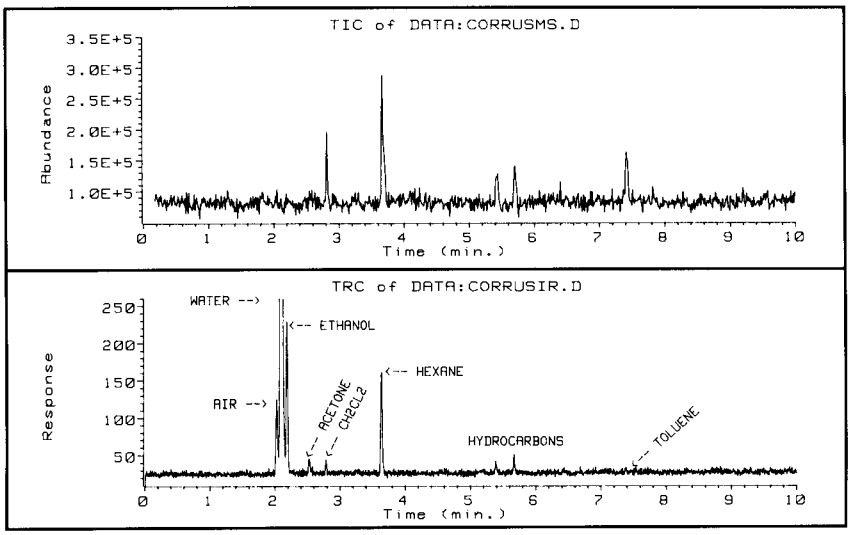

Figure 2. TIC and TRC of the first ten minutes

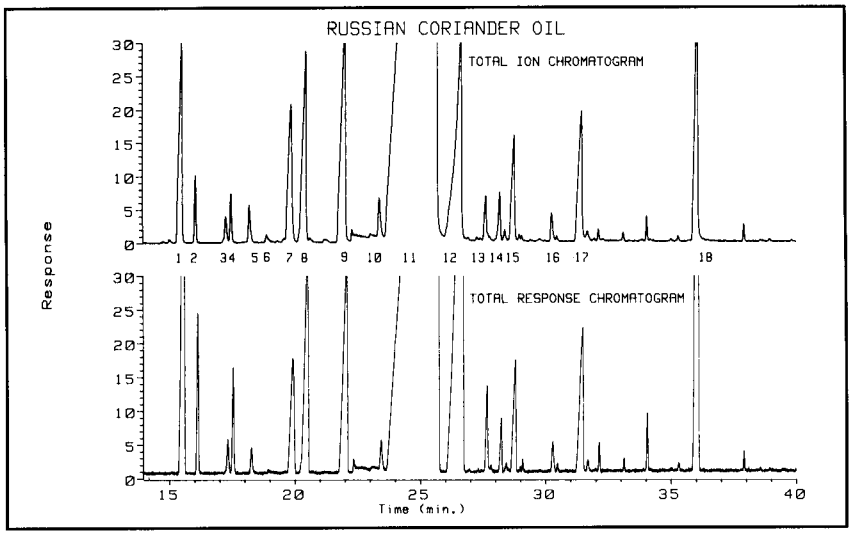

Figure 3. Major peaks of Russian Coriander Oil

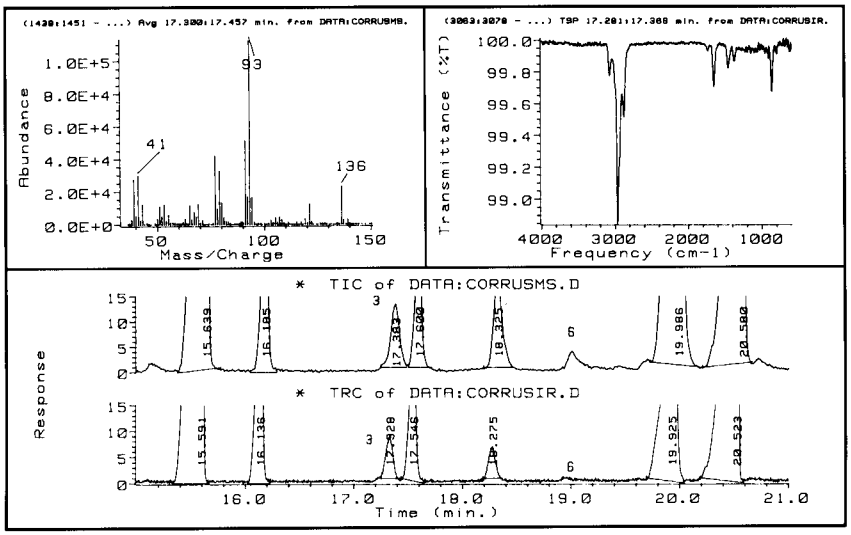

Figure 4. Expanded portion of chromatograms with mass and infrared spectra of peak at 17.3 minutes

The infrared and mass spectra of peak 3 are shown in Figure 4. The IR spectrum was searched against the 2000 entry Robertet Flavor and Fragrance Vapor Phase IR Library and the mass spectrum was searched against the 43000 entry NBS Library. Sabinene was the only common hit from both hit lists. Similarly the spectra for peak 6 are shown in Figure 5. The combined library search indicated the compound to be alpha phellandrene. This is indeed exceptional considering that the IR spectrum represents ca. 3 nanograms and the mass spectrum ca. 1/2 nanogram.

Table 1. Major components of Russian Coriander Oil, after Ref. 3. Peaks 3 and 6 identified in this work

Peak no.	Compound
1	alpha pinene
2	camphene
3	sabinene
4	beta pinene
5	myrcene
6	alpha phellandrene
7	para cymene
8	limonene
9	gamma terpinene
10	linalool oxide b
11	linalool
12	camphor
13	borneol
14	linalool oxide d
15	alpha terpineol
16	nerol
17	geraniol
18	geranyl acetate

The HP 5965B has the capability to view infrared spectra and up to four selected wavelength chromatograms in real time. Figure 6 is an example of a selected wavelength chromatogram (SWC) that shows the infrared absorption from 1748 to 1761 cm^{-1} indicating the that those components are esters. The peak at 36.0 minutes is indeed an ester, geranyl acetate. Further IRD/MSD work on coriander oil will utilize the power of selected wavelength chromatography to help identify the minor components.

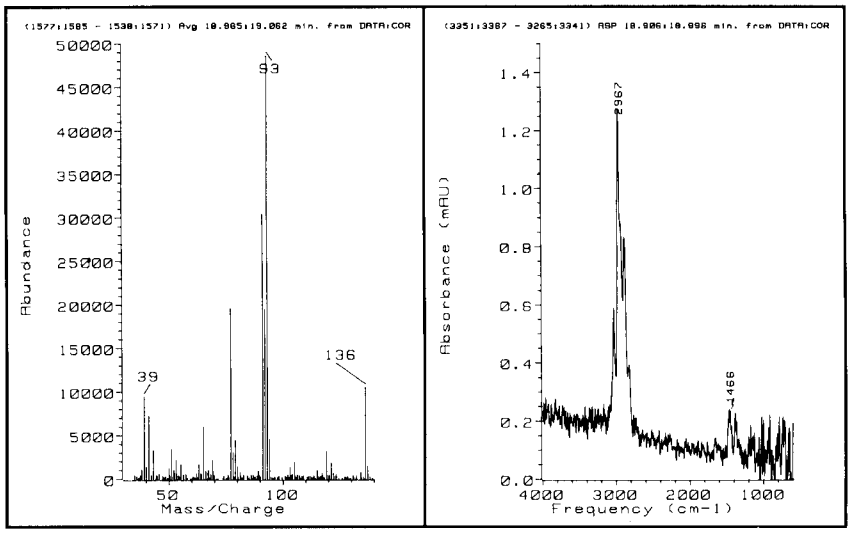

Figure 5. Mass spectrum and infrared spectrum of peak at 19.0 minutes

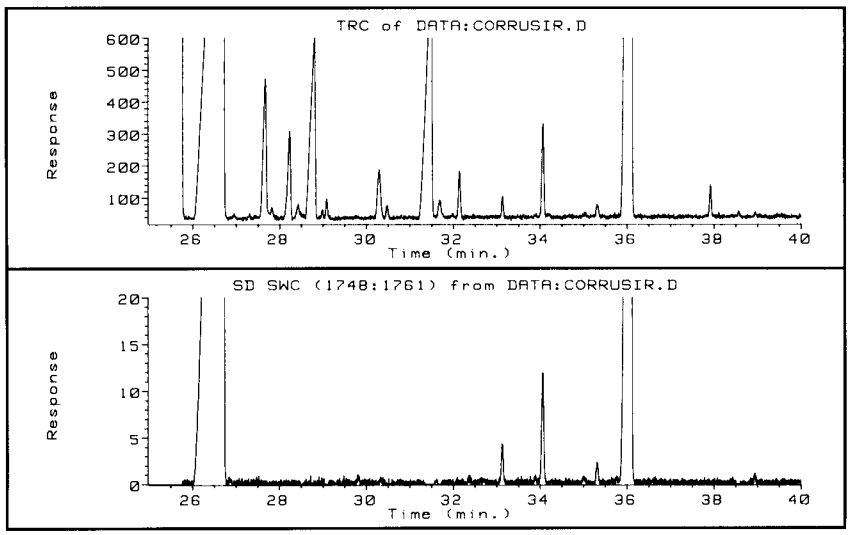

Figure 6. Later portion of TRC and second difference SWC for the Ester region

Conclusion

The combined IRD/MSD system has been shown to be a powerful tool in the low level identification of trace components in coriander oil. The combined instrument provides a higher confidence result than either IR or MS technique alone.

References

1. J. Tashinen and L. Nykanen, Acta Chem. Scand. B29, 425–429, 1975

2. R. Leibrand and W. Duncan, Int. Lab., 46–52, July/August 1989

3. F. Chialva and G. Gabri in P. Sandra and C. Bicchi, "Capillary Gas Chromatography in Essential Oil Analysis", p. 136–137, Huethig, Heidelberg, 1987

Conditions

Gas Chromatograph

Column

50m x 0.32mm id HP-1 (methyl silicone)
0.52 micrometer film

Carrier gas

Helium @ 25psi; 2.0 mL/min

Oven

40°C (2 min) to 120°C at 3°C/min
120°C to 200°C at 5°C/min, hold 6.33 min

IRD Parameters

Light pipe: 250°C
Transfer lines: 260°C
Optical Resolution: 8 cm^{-1}, wide band MCT detector
Scan rate: 3 scans/sec

MSD Parameters

Mass range: 33–300 daltons
Scan rate: 1.6 scans/sec (4 samples)