# Note

# Ion profiling approach to detailed mixture comparison

# Application to a polypropylene off-odor problem

R. A. SANDERS* and T. R. MORSCH

*The Procter and Gamble Company, 6071 Center Hill Road, Cincinnati, OH 45224 (U.S.A.)*

Determining the relevant differences between two very similar samples (one which performs well and one which does not) is a request that analytical chemists encounter frequently. In a food product development analytical laboratory, the requests come in the form of questions such as these: why does this product taste rancid, while this other one tastes fresh? Baked goods from this package taste fine; but the same food from this other package has an off-flavor —why? We have frying oils made by the same process —why is one cloudy but the other is clear?

Answering such questions in a scientific manner often requires detailed comparisons of the molecular composition of the products involved. One makes the assumption that, once key differences are revealed, the different components can be identified, and the identifications will lead to an understanding of the chemistry which caused the differences.

The ability to reveal differences between volatile mixtures has long been an important capability of capillary gas chromatography (GC). Minor differences are revealed due to the high chromatographic resolution achievable, and mass spectrometry (MS) or IR spectroscopy is used to identify those differences. Though this procedure is sometimes successful, it often fails due to co-elution or near co-elution. Minor, but significant, differences are obscured by major, innocuous components. Another approach, which is a variation of the scheme described, has been much more successful in identifying minor differences between samples in this laboratory. Differences are located by systematically examining ion profiles reconstructed from scanning GC–MS analyses of the comparative samples. The mass spectrometer is used to locate the differences, rather than merely identify differences revealed by chromatography. In this mode, the mass spectrometer can be more sensitive than a flame ionization detector; and, more importantly, the uniqueness of most mass spectra suggests that at least one reconstructed ion profile will reveal a minor difference even when extensive peak overlapping occurs. A careful review of such profiles, whether visually or with pattern recognition techniques, often reveals significant aspects that are not visible in the normal chromatographic profile, even after their discovery. A similar approach has been used for metabolic profiling for several years[1]. A key difference is that the metabolic profiles focus only on target compounds known to be related to biological function. We illustrate that the ion profile approach can be quite effective even when the target compound is not known.

The display of ion profiles can take a variety of forms. The most common procedure is to display a particular $m/z$ (nominal mass) over a particular retention window. This can be done sequentially and viewed rapidly by eye, or a peak detection algorithm may be used in an automated version which produces hardcopy only for ion profile segments which are different in the two samples. Alternatively, one can use the accurate mass measuring capability of high-resolution mass spectrometers to obtain ion profiles specific for a particular fragment formula, *e.g.*, one may search for $[CH_3CO]^+$ of methyl ketones in the presence of $C_3H_7^+$ despite the fact that both have nominal $m/z$ 43. A more rapid approach than either of these is to display mass profiles in a three-dimensional plot with relative abundance and retention time. Careful (often tedious) review of such three-dimensional plots can reveal differences, but this display format does not readily reveal minor differences among the vast amount of data displayed. Illustrations of all these presentations are included in this work.

The ion profiling approach is illustrated with the determination of the cause of an irritating off-odor in some polypropylene sheets. The headspace compositions of heated polypropylene from acceptable and unacceptable sheets were compared, first by capillary GC, and then by ion profiling GC–MS. The offending component, revealed by ion profiling, was invisible to capillary GC. Once discovered by ion profiling, it was identified from its mass spectrum as 2-(ethylthio)propane even though it was present at a level less than 200 ppb* and co-eluted with a hydrocarbon under the analysis conditions. By monitoring the off-odor in resins and sheets, the source of the compound was found and the batches of contaminated polypropylene were pinpointed. Subsequent processing changes and analytical monitoring protect against recurrence.

EXPERIMENTAL

*Identification of off-odor in polypropylene sheets*

Headspace analyses were achieved through the use of an injector/trap device[2] which preserved chromatographic integrity during syringe injections of 1–10 ml of sample headspace. Condensable components are trapped initially onto a 15 cm × 1 mm I.D. quartz tube at −120°C while air passes out of the system through a vent. The contents of the quartz trap are then transferred to the head of 30 m × 0.32 mm, DB-5, fused-silica capillary column (J&W Scientific, Rancho Cordova, CA, U.S.A.) which is inserted through a second liquid nitrogen cooled trap (−140°C). In this way, large and repeated injection volumes may be made while preserving the high-resolution characteristics of the chromatography through thermal focusing.

Approximately 1 g of polypropylene sheet cuttings were placed in a headspace sampling vial (*ca.* 5 ml volume) and incubated for 30 min at 90°C. Using a gas-tight, 5-ml syringe, approximately 1 ml of headspace was withdrawn from the vial and injected onto the first trap.

The gas chromatograph was a Hewlett-Packard 5890, programmed from 50°C (5 min hold) to 110°C at 5°C/min, then from 110°C (no hold) to 220°C at 15°C/min. The GC–MS transfer line, a 1-m length of deactivated, uncoated fused-silica, coupled the GC column directly to the ion source of a Kratos MS-30 mass spectrometer,

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* Throughout this article, the American billion ($10^9$) is meant.

operated in the dual-beam mode. The mass spectrometer resolution (10% valley) was about 1000 and the scan rate was 1 s/decade (cycle time of 2.5 s). Under these conditions, the MS-30 makes mass measurements accurate to within 15–20 ppm. Electron ionization mode was chosen for these analyses.

### Quantitation of off-odor in polypropylene resin

Following identification of ethyl isopropyl sulfide, the need for routine monitoring in numerous polypropylene resin and sheet samples demanded a more rapid method that utilized less sophisticated instrumentation than that described above. For the low chromatographic resolution required in this GC–MS method, direct syringe injections (without thermal focusing) into the injection port of the Hewlett-Packard 5890 gas chromatograph sufficed. A Hewlett-Packard 5970B mass selective detector was used to monitor $m/z$ 89 and 104. The injection mode was splitless (purge off time 0.5 min) and the gas chromatograph, with a 30 m × 0.32 mm DB 1701 column, was programmed from 40°C to 70°C at 5°C/min. The GC–MS interface was direct, the column terminating in the mass spectrometer ion source. With a vacuum at the column outlet, a column head pressure of 2.5 p.s.i. produced a carrier gas (He) flow of 2.4 ml/min. The dwell time for each mass monitored was 50 ms and the electron multiplier bias potential was 2800 V.

Sample preparation was similar to that described above except that samples for quantitative analysis were incubated at 110°C for at least 2 h. The detection limit (*ca.* 1 ppb) and sensitivity were determined by spiking blank resin with known amounts of ethyl isopropyl sulfide. Response linearity from 1 to 100 ppb and a precision of 20% relative standard deviation were established, values which were quite acceptable for the screening function of the method.
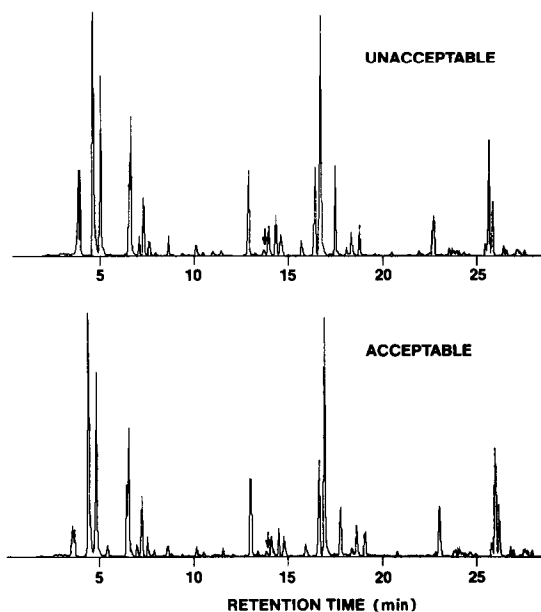


Fig. 1. Headspace gas chromatographic profiles of acceptable and unacceptable polypropylene sheets.
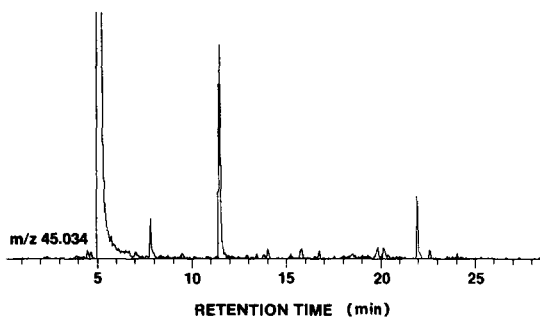
Fig. 2. Accurate mass ion profile for the $[C_2H_5O]^+$ fragment.

RESULTS AND DISCUSSION

Reconstructed total ion chromatograms from acceptable and unacceptable sheets are shown in Fig. 1. These chromatograms are very similar to the GC–flame ionization detection (FID) chromatograms, and reveal no significant differences in the headspace compositions of the two samples. Peak intensity differences were investigated, but were found to be due to slight level variations in innocuous, saturated hydrocarbons. Olefin levels varied somewhat between acceptable and unacceptable samples, but there were higher levels of the sometimes pungent olefins in acceptable sheets than in unacceptable ones. All major GC peaks were identified and found to be logical polypropylene residual volatiles or processing solvent residues. Some sol-
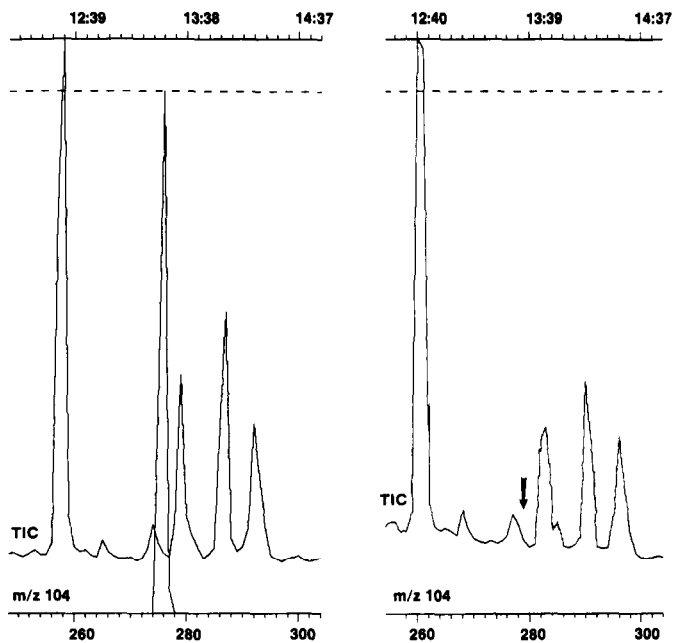


Fig. 3. $m/z$ 104 and total ion current (TIC) profiles for acceptable (right) and unacceptable (left) polypropylene sheets. Arrow denotes region where $m/z$ 104 is conspicuously absent.
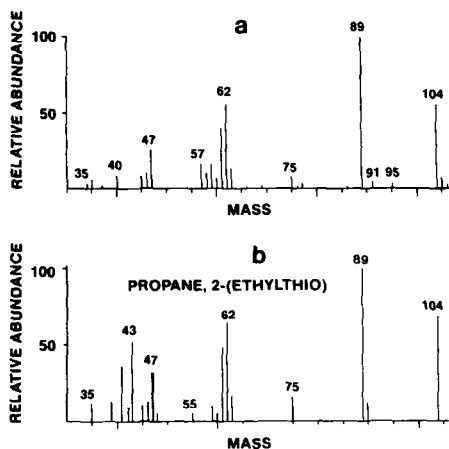
Fig. 4. Electron impact mass spectrum of component giving $m/z$ 104 response (a). The 2-ethylthiopropane reference spectrum (b) was the best match retrieved in a search of the National Bureau of Standards' library.

vent residues were pinpointed by reconstructing the ion profile for the $[CH_3CH(OH)]^+$ fragment at $m/z$ 45.034, shown in Fig. 2. Accurate mass measurement permitted pinpointing of minor oxygen-containing components in the presence of the hydrocarbon bulk. These profiles led to identification of isopropanol (5 min retention time) and isopentanol (11.5 min retention time) as the major non-hydrocarbon components of the volatile composition, but their aroma types and thresholds did not match the observed off-odor; and they were equally abundant in acceptable and unacceptable sheets.

Accurate mass ion profiling was used to search for logical polypropylene oxidation products: $m/z$ 30.011 for formaldehyde, $m/z$ 44.026 for other short chain
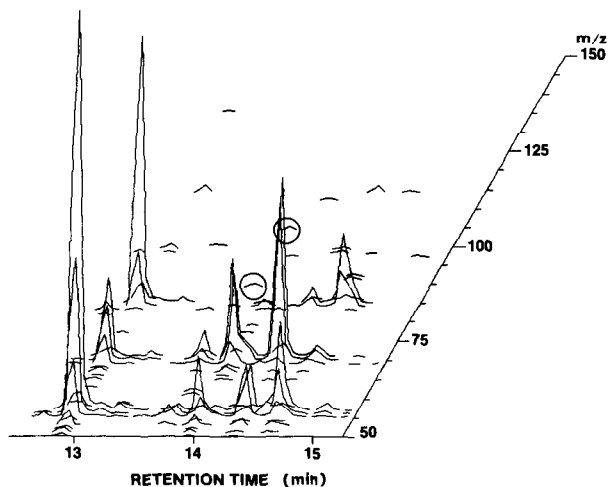


Fig. 5. Three-dimensional display of headspace GC data from unacceptable polypropylene sheet. Circled regions indicate responses at $m/z$ 89 and 104 due to ethyl isopropyl sulfide.
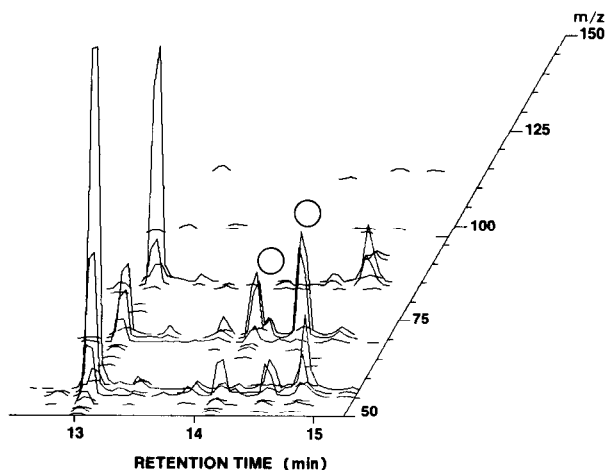
Fig. 6. Three-dimensional display from an acceptable sheet. Circled region indicates absence of ethyl isopropyl sulfide.

aldehydes, and $m/z$ 43.018 for methyl ketones. No polypropylene oxidation products were detected in acceptable or unacceptable samples.

Mass profiles were obtained for numerous odoriferous compounds previously encountered: toluene, styrene, acrolein, etc. Finally, while searching for styrene at nominal $m/z$ 104, a significant difference between the two samples was observed. The nominal $m/z$ 104 profile in the $C_8$–$C_9$ hydrocarbon region for acceptable and unacceptable sheets is shown in Fig. 3. The $m/z$ 104 component co-elutes with a $C_8$ hydrocarbon (see arrows in Fig. 1) and is invisible to GC–FID. Yet, its presence is obvious even in casual observation of the ion profile. Subtraction of the hydrocarbon interference resulted in the mass spectrum shown in Fig. 4a. A search of the National Bureau of Standards' library revealed an excellent match (Fig. 4b) which was 2-ethylthiopropane, *i.e.* ethyl isopropyl sulfide. The identification was confirmed by retention time and MS comparison with authentic ethyl isopropyl sulfide (available from ICN Pharmaceuticals, Plainview, NJ, U.S.A.).
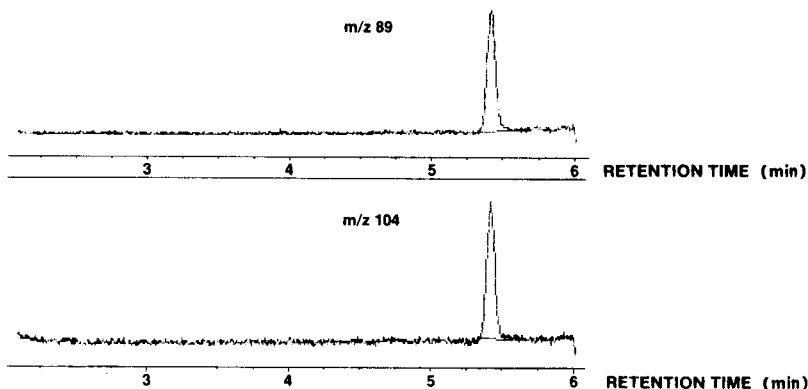


Fig. 7. Selected-ion-monitoring results from quantitative headspace analysis of a polypropylene resin spiked to contain 10 ppb of ethyl isopropyl sulfide.

Figs. 5 and 6 are three-dimensional plots of retention time ($x$-axis), abundance ($y$-axis), and mass ($z$-axis). The $m/z$ 89 and 104 peaks are circled in Fig. 5 (unacceptable sheet). The circled region in Fig. 6 denotes the $m/z$ 89 and 104 regions where the absence of ethyl isopropyl sulfide is revealed. It is clear, however, that other differences between the samples tend to obscure the relevant components, and this three dimensional mapping approach was revealing only through hindsight.

A screening program was begun to determine the relation between ethyl isopropyl sulfide level and perceived off-odor. For this purpose, the quantitative procedure described in the Experimental section was employed to analyze several hundred resin and sheet samples. Fig. 7 shows a chromatogram resulting from injection of the headspace over a resin (previously found to be free of analyte) which had been spiked to contain 10 ppb of ethyl isopropyl sulfide. The screening procedure established a strong correlation between measured ethyl isopropyl sulfide levels and sensorily determined off-odor levels. The worst sheets contained ethyl isopropyl sulfide at levels as high as 200 ppb. Sheets and resins without the irritating, oily odor were free of ethyl isopropyl sulfide at the 1-ppb detection limit. The presence of ethyl isopropyl sulfide in odorous resin eliminated focus on subsequent processing steps (such as extrusion), and monitoring of that analyte in all production lots of polypropylene resin assures absence of the off-odor in future sheet receipts.

CONCLUSIONS

The sole use of MS to identify components revealed by GC or as a selective detector for target components ignores one of the most powerful capabilities of GC–MS; the ability to discover minute differences between very complex samples. In this regard, GC–MS is much more powrful than GC alone. Three approaches to making detailed GC–MS comparisons were illustrated in the solution of a polypropylene off-odor problem: sequential nominal mass profiling, accurate mass profiling, and three-dimensional plots. All are amenable to atuomated implementation. Perhaps the most effective means of implementing these approaches in a routine fashion is to incorporate time-resolved MS data into pattern recognition algorithms already developed for GC profiling.

REFERENCES

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