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Technical Notes

Analysis of Consecutively Sampled Headspace and Liquid Fractions by Gas Chromatography/Mass Spectrometry

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An existing gas chromatograph/mass spectrometer (GC/MS) can be used to analyze gas and liquid fractions from the same system within a few minutes. The technique was applied to (a) separate and identify the gaseous components of the products of cracking an alkane, (b) measure trace levels of acetone in ethyl acetate, (c) determine the relative partial pressures over a binary mixture, and (d) identify nine unknown compounds for the purpose of disposal.

A number of researchers have been afforded some success employing GC/MS for headspace analysis with varied applications. Levermore et al.[1] suggest that the status of lubricating oil can be determined by analyzing the headspace above it by employing GC/MS. A variation of this type of methodology performed by Watson et al.[2] permits the analyses of selected volatile organic compounds present in cigarette tobacco, and another variation involves the analyses of volatile organic compounds emitted by growing oilseed rape plants.[3] Norman et al.[4] describe a combined GC/MS and GC-NPD (nitrogen phosphorus detection) method for the determination of phosphine residues in stored products and processed foods. Another variant reported by J. Schuberth[5] describes a methodology utilizing headspace analyses and mass spectrometry to overcome matrix effects when determining volatile organic compounds in blood and postmortem samples. Wenzl et al.[6] also reported a method of performing headspace mass spectral analysis that alleviates the problem of matrix effects when sampling solid samples, and yet another application of the headspace analyses involves the identification of chemicals that potentially could migrate into food samples when using dual-ovenable cookware.[7]

The impetus for the present work is our investigation of the cracking of alkanes and isomerization of alkenes by Lewis acidic ionic liquids, specifically systems containing an organic salt and aluminum chloride with the latter present at a mole fraction exceeding 0.5.[8] Preliminary studies[9] showed that C_4−C_7 branched-chain alkanes were the principal products of cracking C_8H_{18}−$C_{14}H_{30}$ *n*-alkanes; however, to obtain a clearer picture of these reactions over time, it was necessary to efficiently perform both headspace gas analysis and liquid analysis on samples of the hydrocarbon/ionic liquid reaction mixtures. We wished to know whether volatile hydrocarbons, saturated or unsaturated, were being formed and, eventually, the unsaturated/saturated distribution of the resultant products.

Ultimately, it would have been desirable to perform liquid and gas analyses on the two phases of a gas/liquid system simultaneously. Although this situation is impossible, a retrofit of an existing GC/MS system was designed to come close to this with the only time lag being that time necessary to equilibrate the gas chromatograph injection port and oven temperatures. Because of the excessive amount of time necessary to "cool" the injection port or GC oven relative to "heating" the same, it was advantageous to allow the components to cool and perform the headspace analysis first. Within a few minutes of setting the next parameters for the liquid analysis (<5 min), the instrument was armed for the liquid injection. The success of applying this technique to the system of primary interest suggested that it could have wider application, and we have given a few appropriate examples in this paper.

EXPERIMENTAL SECTION

All GC/MS analyses were performed using a Finnigan Mat Incos 50 mass spectrometer system. The instrument consisted of a Hewlett-Packard 5890 gas chromatograph directly interfaced to

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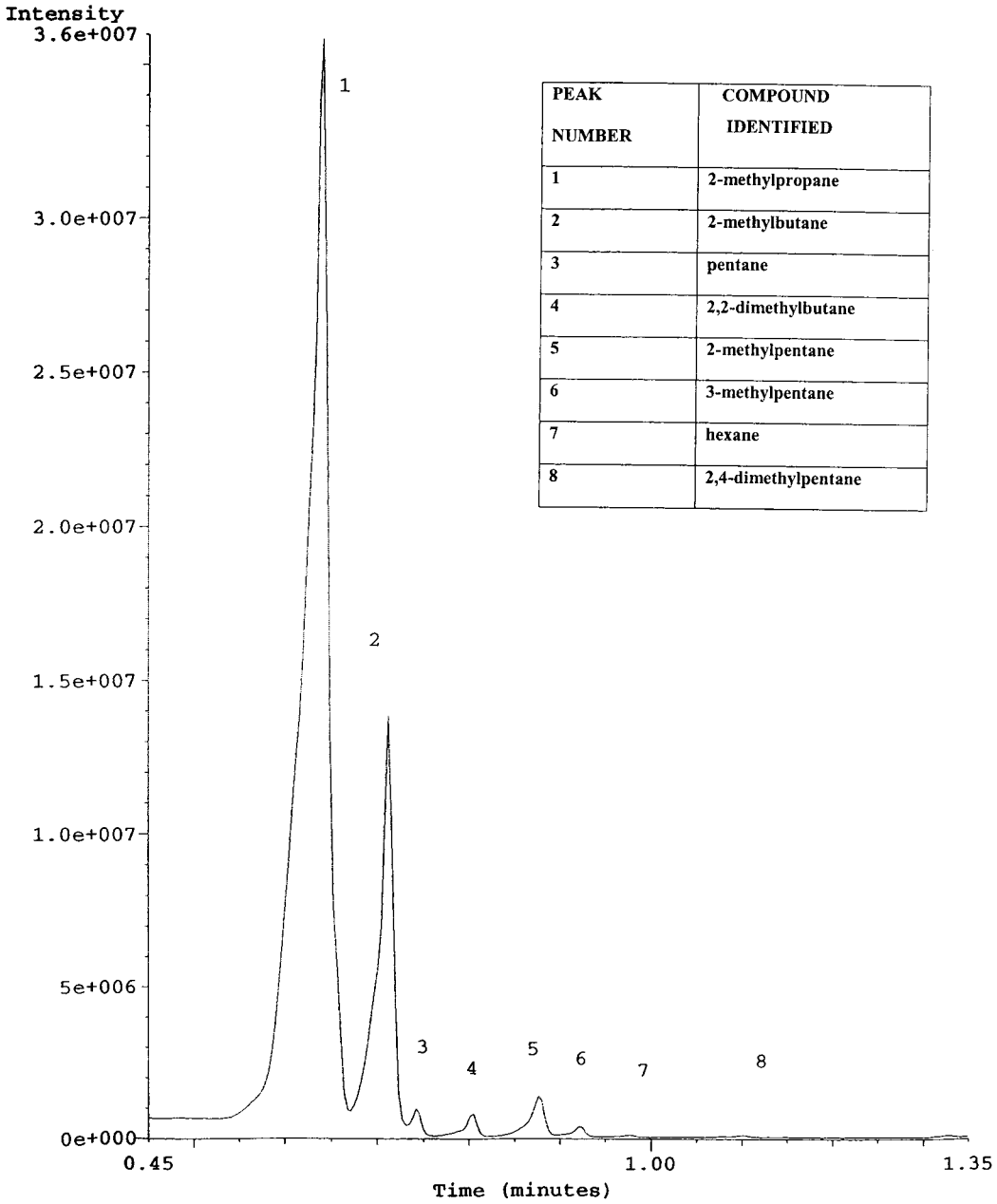


PEAK NUMBER	COMPOUND IDENTIFIED
1	2-methylpropane
2	2-methylbutane
3	pentane
4	2,2-dimethylbutane
5	2-methylpentane
6	3-methylpentane
7	hexane
8	2,4-dimethylpentane

Figure 1. Total ion chromatogram; headspace from the cracking of nonane.

an Incos 50 quadrupole MS via a heated transfer line/capillary interface. The GC was configured with a splitless injection port and a DB-5MS fused-silica capillary column coated with a 0.25-μm film of stationary phase (15 m × 0.25 mm i.d.; J&W Scientific, Folsom, CA). As little as 0.05 mL of the headspace could be conveniently sampled and injected employing a Becton Dickinson & Co. (Franklin Lakes, NJ) latex-free 1-mL tuberculin disposable syringe. There are many types of vials available that will accommodate a gastight septum for both the headspace and the liquid analysis. Our methodology employed 40-mL borosilicate vials with silicon/teflon septa in open cap screw tops (Chromatographic Specialties Inc., 300 Laurier Blvd, Brockville, Ont.). It is important to note that once the headspace is sampled, the syringe tip is not pulled out immediately from the sample vial septa, instead, it is allowed to remain with plunger withdrawn for about 8 to 10 s to ensure equilibrium. The splitless injection port was set at 40 °C for the headspace analyses while the GC oven temperature was maintained isothermal at 23−24 °C. The mass spectrometer was operated in the electron impact ionization mode with an electron energy of 70 eV. The ion source temperature was maintained at 180 °C for all analyses, and the capillary interface transfer line was held at 250 °C. Imperative to the headspace analyses was the ability to acquire data immediately following the gas injection with no solvent delay. This situation was necessary in order to capture and record all volatiles eluted. The mass spectrometer could also be adjusted to acquire data continuously for hours if subsequent injections were necessary. As an example, one run could include running a complete set of calibration standards, unlimited replicate injections of unknowns, and appropriate quality control samples, all without any additional adjustment of the mass spectrometer. All analyses could be undertaken in the total ion chromatogram or the selective ion monitoring mode. The helium

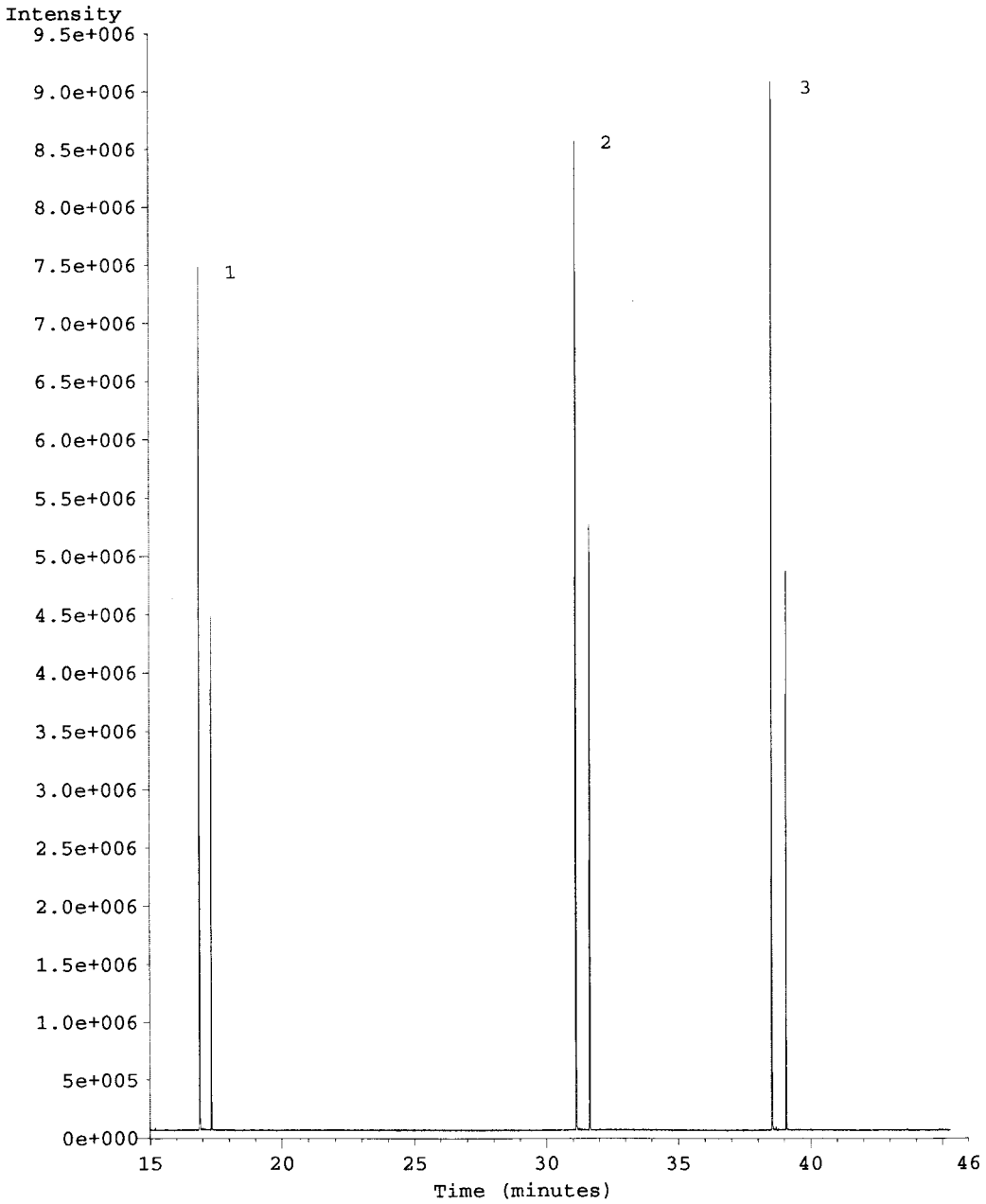


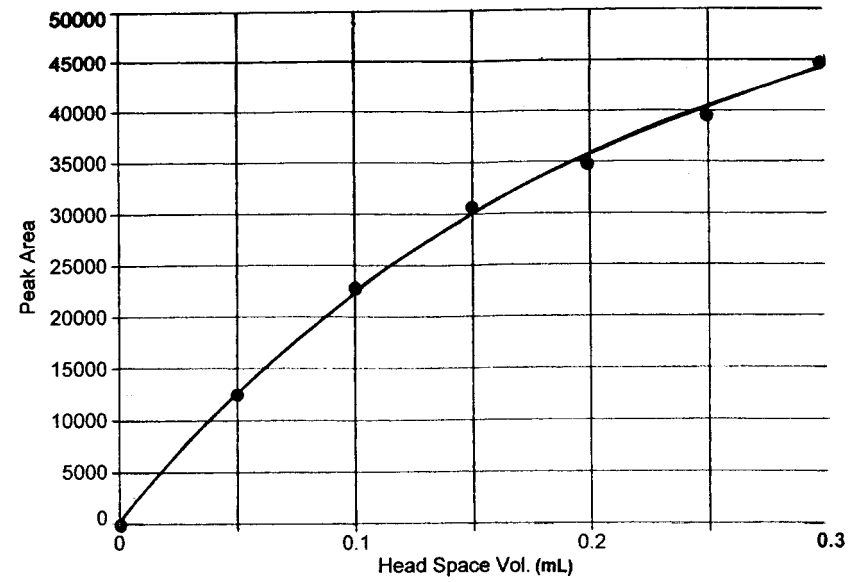
Figure 2. Total ion chromatograms for precision determination.

carrier gas was maintained at a column head pressure <0.5 PSI. The original Data General data handling system (sold with the Finnigan Incos 50 mass spectrometer) was replaced/upgraded with the ProLab Resources 2050-1-150 Vector/Two Data System upgrade (ProLab Resources, Inc., 2923 Market-place Drive, Suite 102, Madison, WI 53719).

RESULTS

1. Identification of Components; Cracking of Hydrocarbons. The ability of the system to reliably identify the resolved total ion chromatograms (TICs) can be observed in Figure 1. This TIC is the result of a 0.20-mL headspace injection from the cracking of nonane. All eight peaks observed were accurately identified with the existing library database. Note that the entire TIC was acquired in ~0.5 min. Immediately following the headspace analysis, the instrumentation was retrofitted to accommodate the analysis of the liquid portion of the sample. In this particular case, the corresponding TIC resulted from a 2-μL injection of the liquid portion of the same sample.

2. Trace Analysis of Acetone in Ethyl Acetate. An estimation of the precision afforded for the headspace analyses in the development of this methodology can be seen in Figure 2. This TIC is representative of the convenience of being able to perform unlimited headspace analyses (if necessary) without the bother of having to re-download the same method for the purpose of running a replicate sample. Figure 2 is the resultant TICs for three of nine replicate 0.3-mL headspace injections of a sample vapor containing detectable amounts of air (first injection peak in each pair) and ethyl acetate. The precision afforded within a run was performed on the nine air peaks. The percent relative standard deviation for the air TICs was calculated to be 1.1%.



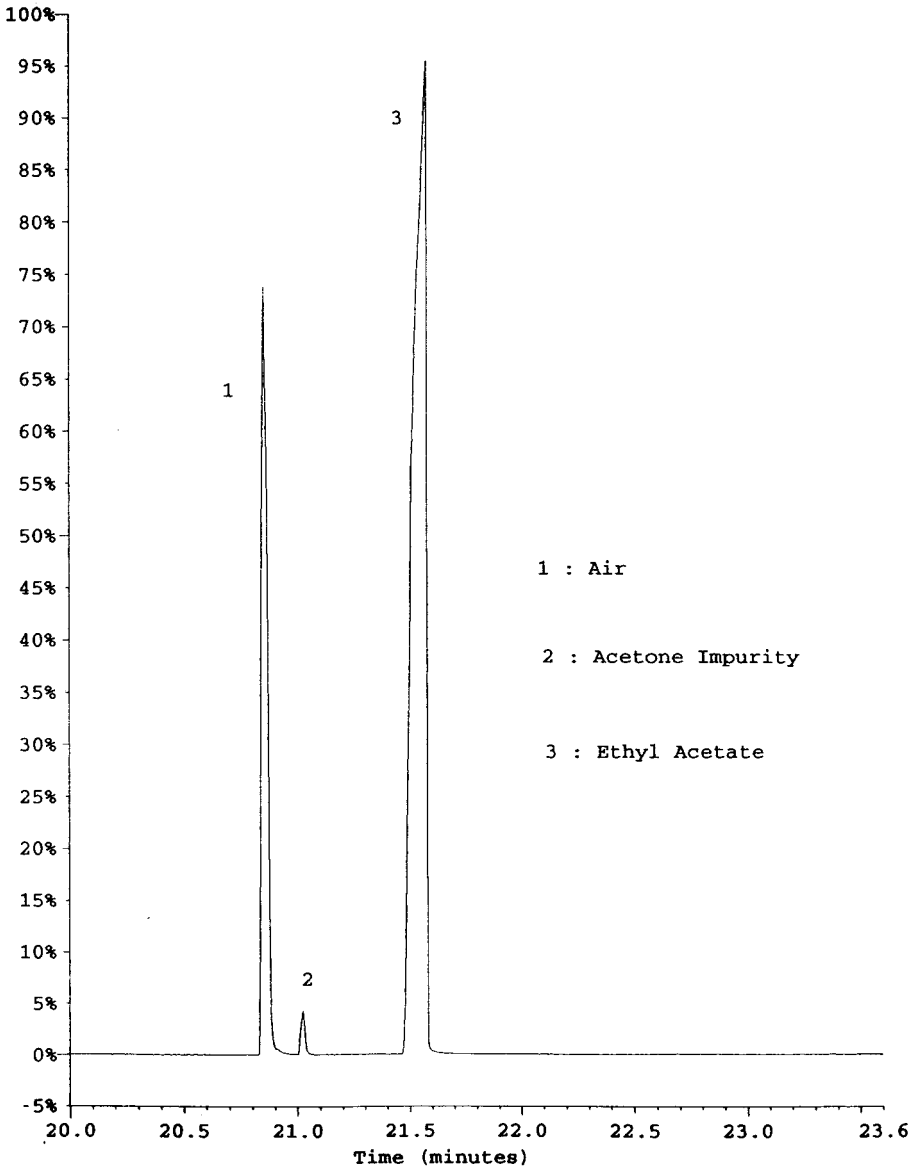


Figure 3. Headspace total ion chromatogram and plot of the respective peak areas found for the total ion chromatograms of acetone as a function of their headspace volumes.

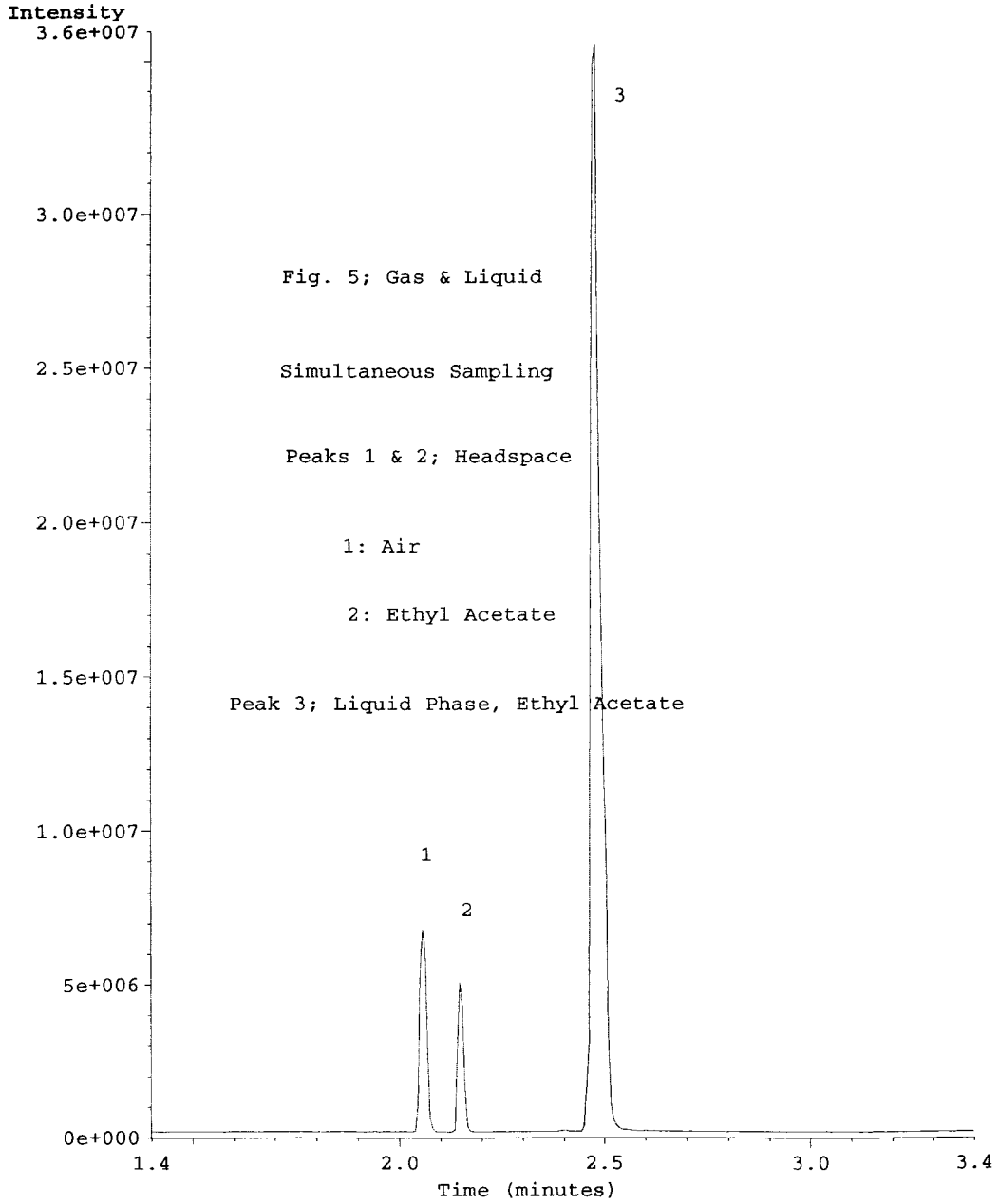


Figure 4. Total ion chromatogram of both the gas and the liquid ethyl acetate (without alteration to GC oven or injection port temperatures).

It was discovered during the course of the methodology development for the headspace analyses that one of the solvents employed had been previously contaminated. Analytical reagent grade ethyl acetate was found to contain more than just a trace of acetone. Volumes of 0.05, 0.10, 0.15, 0.2, 0.25, and 0.30 mL were injected into the gas chromatograph with the resultant areas for the acetone peaks recorded. Figure 3 shows a TIC for one of the headspace injections along with a plot of the respective peak areas found for the TICs of acetone as a function of their headspace volumes.

In an additional trial, an attempt was made to try to analyze the simultaneous sampling volumes (headspace and liquid) of a volatile compound. Figure 4 is the resultant TIC of both the gas and the liquid ethyl acetate *without having to change GC oven or injection port temperatures.* Peaks 1 and 2 are the resultant TICs for a 0.1-mL injection of the headspace, with peak 1 identified as air, and peak 2, the ethyl acetate vapor. Peak 3 is the resultant TIC for a 0.4-uL injection of the liquid portion of the ethyl acetate. Once the gas sample is injected, the previously sampled liquid portion can be injected almost immediately. The time between the initial injection and the complete recording of the last peak was ~0.5 min.

Table 1. Partial Pressures of a Chloroform–Acetone Mixture at 25 °C

mole fraction chloroform	0.32	0.48
A, mean TIC counts chloroform	2.54×10^4	5.67×10^4
B, mean TIC counts acetone	10.53×10^4	8.69×10^4
A/B	0.24 ± 0.04	0.65 ± 0.06
A/B[a]	0.28	0.66

[a] See ref 10.

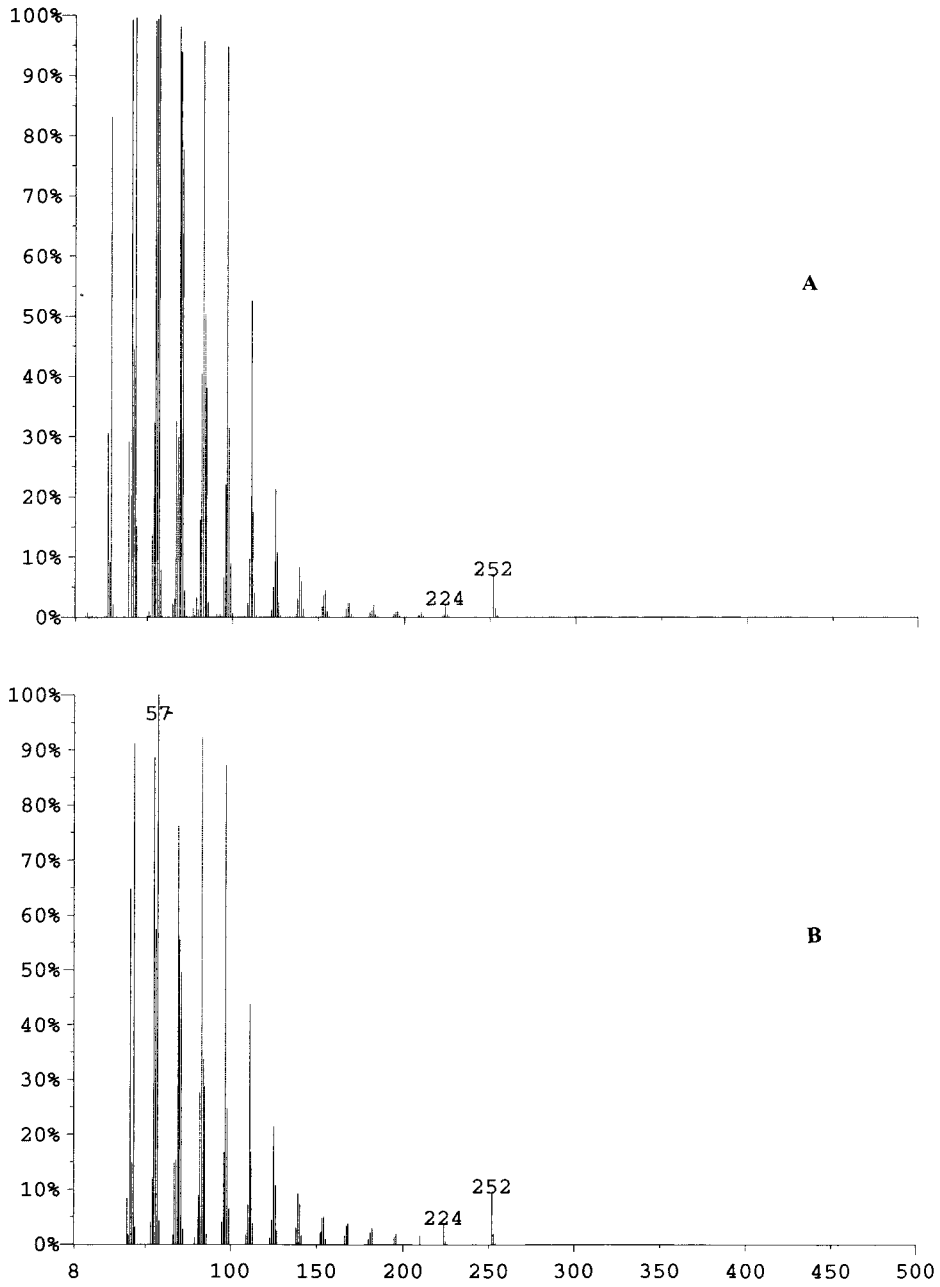


Figure 5. Mass spectrum and library search; identification of "unknown" 1-octadecene employing headspace methodology: (A) unknown analyzed, (B) library match.

3. Vapor Pressure Studies. An additional attempt was made to employ data received from typical headspace analyses for the purpose of approximating a correlation for partial pressures of a binary mixture of volatile components. The ratios of the respective volumes of headspace for chloroform and acetone were determined and compared with previously determined data. Replicate solutions containing mole fractions of 0.32 and 0.48 chloroform (99.8%, lot C1651, Fisher Scientific, Nepean, Ont. Canada, K2E 7L6) in acetone (HPLC grade, Catalog no. 27,072-5, 99.9+%, Aldrich, Milwaukee, WI, 53233) were analyzed, and the TICs (0.1-mL injections) for acetone and chloroform, respectively, were resolved, identified, and integrated. Table 1 indicates good agreement between the partial pressure ratios and those obtained previously.[10]

4. Identification of Volatile Compounds with No Background Information. In the previous examples, we had some idea of the compounds being analyzed. However, Occupational Health and Occupational Hygiene agencies are constantly plagued with the task of identifying volatile compounds in unlabeled containers. Nine unlabeled containers were submitted for possible chemical identification of their "odorous" contents. Exactly the same type of headspace analysis was performed for possible identification of these unknowns, and all nine unknowns were identified within 1 h. One, which had been "on the shelf" for 15 years, was identified from a 0.2-mL gas sample as 1-octadecene (see Figure 5).

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CONCLUSION

The significant feature of the present developed procedure is the ability to convert an existing instrument from gas to liquid analyses very quickly (<5 min). In the event that constituents are sufficiently volatile, the conversion is not necessary as long, because sample volumes are controlled so as not to burn out the source filament. In this case, the liquid analysis can be performed immediately following the headspace run. If an enhancement in sensitivity is a requirement in the procedure, the scan mode of the spectrometer can immediately be switched from total ion monitoring to selected ion monitoring (SIM). Although the existing methodology employed consecutive sampling, it actually lends itself to monitoring proportions of constituents in the vapor and liquid phase if "sampled simultaneously". It is, of course, acknowledged that for some sample solutions, specialized GC columns must be employed for the desired resolution. An additional consideration for future work will include the technique of employing stable isotope dilution[11] for an accurate determination of concentrations in the gas and liquid analyzed.

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