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Comparison of the Sensitivity of Static Headspace GC, Solid Phase Microextraction, and Direct Thermal Extraction for Analysis of Volatiles in Solid Matrices

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Headspace, Solid Phase Microextraction, SPME, Thermal Desorption, Herbs, Coffee, Tea, Polyethylene

ABSTRACT

The analysis of volatiles in solids is a common analytical problem. Examples include volatile aroma compounds in foods and plant materials (coffee, tea, and herbs), residual fragrances from soaps and fabric softeners on textiles, and volatiles in polymer resins, films and plastic products.

Several techniques are available that allow direct analysis of the volatiles in a variety of solid matrices with little or no sample preparation. Static headspace GC (HS-GC) is probably the most commonly applied technique for analysis of volatiles in solids. Direct thermal desorption (TDS), sometimes referred to as dynamic headspace analysis, and Solid Phase Microextraction (SPME) are alternative techniques that can now be automated. The relative sensitivity of these techniques, and the strengths and limitations of each when applied to a variety of solid matrices should be con-

sidered when choosing the most appropriate approach for a new analysis. Until now a direct comparison of these techniques for a variety of samples on equivalent instrumentation has been difficult to find.

Samples from the classes mentioned above were analyzed using HS-GC, SPME and TDS sample introduction into the same HP 6890 GC instrument. Column and detector conditions were maintained the same for all sample introduction methods. Generally, sensitivity of static headspace sampling was 10-50x lower than SPME sampling. Direct Thermal Extraction was found to be 50-100x higher sensitivity than SPME sampling. Besides sensitivity, advantages and limitations of the three sample introduction techniques for dealing with various sample types (low vs. high boilers, wet samples) should be considered before choosing an analytical approach.

INTRODUCTION

The analysis of volatiles above solid encompasses a wide variety of analytical problems, which can be approached using any of a number of analytical techniques. Traditional approaches can include some type of extraction of the solid material, usually using solvents compatible with GC analysis. Besides the fact that extractions are time consuming, solvents can selectively extract analytes (sometimes desirable, often not), may interfere with determination of some compounds, and disposal is costly.

Direct methods are available for analysis of volatiles that avoid solvent use. Static headspace, SPME and Direct Thermal Extraction can all be used to determine volatiles above solids and can all be automated. Choosing the best analytical technique for a given analysis requires considering a number of issues.

Sample Matrix. Sample matrices can range from relatively simple (fillers such as silica gel, titanium dioxide or carbon black), to moderate (formulations such as resins, films or soaps) or even very complex natural products (coffee, tea, and foods). Inhomogeneous matrices may necessitate larger sample sizes to assure representative samples are analyzed. The presence of significant water levels in a sample can limit the strategies used to recover volatiles, restricting the ability to cold trap without freezing the GC inlet.

Analyte Range. The particular analytical problem may require analysis of a single or limited number of analytes, for example measuring antioxidants or plasticizers in a resin formulation. In this case selectivity in the sample preparation can be an asset. More complex problems may require that a technique accurately profile a wide range of related materials, such as the hydrocarbon profile from a plastic film. Analysis of extremely complex samples, for example profiling the volatiles from natural products or essential oils can require adequate sampling and detection of compounds varying greatly in both boiling point and structure. In these cases, a technique that accurately reflects the relative proportion of each analyte rather than providing selectivity for specific analytes is preferred.

Furthermore, the sensitivity necessary for adequate detection of target analytes can vary dramatically from gross profiling of volatiles to ultra trace analysis depending on the application. Often, trying to estimate which technique may provide appropriate sensitivity can be the first step when beginning method development.

It is the purpose of this paper to illustrate with examples the relative sensitivity of Static Headspace, SPME and Direct Thermal Extraction for analysis of volatiles in solid matrices. Particular advantages and limitations of the three techniques are highlighted for different sample types.

EXPERIMENTAL

Instrumentation. All analyses were performed on a single GC (6890, Agilent Technologies, Little Falls, USA) with Flame ionization detection (Figure 1). The GC was equipped with a Thermal Desorption unit with autosampling capacity (TDS 2 & TDS A, Gerstel GmbH & Co.KG, Mülheim an der Ruhr, Germany) and a Multipurpose sampler with Headspace and SPME capability (MPS 2, Gerstel). Column and detection conditions were kept constant throughout the study. Inlet conditions were only varied as necessary to accommodate the requirements of each sample introduction technique. Sample was introduced into the column in the splitless mode for highest sensitivity except where noted in the figures.

Sample Preparation. Solid samples were weighed into 20 mL headspace vials or thermal extraction tubes as appropriate. Samples were preheated at 60°C for 15 minutes prior to both Headspace and SPME analysis. No preheating was done before analysis by direct Thermal Extraction.

Fresh basil contained too much water to allow direct cold trapping of volatiles in the inlet. The sample was therefore first extracted in a Gerstel Thermal Extractor unit, trapping volatiles onto a Tenax TA air sampling tube. The adsorbent tube was then thermally desorbed in the TDS and analytes were focused in the inlet by cold trapping as described below.

Sample introduction conditions were optimized to provide the highest sensitivity for

Figure 1. Instrument configuration used for the study.

each technique. Sample sizes of 10-25mg were used for all techniques to directly compare sensitivity unless inadequate signal was obtained. In these cases, sample size was increased to levels necessary to obtain detectable signal.

Analysis conditions.

Column	30 m HP 5 (Agilent), $d_i = 0.25$ mm, $d_f = 0.25$ µm
Pneumatics	He, $P_i = 91.7$ kPa, constant flow = 1.2 ml/min
Oven	40°C (2 min), 10°C/min, 280°C (4 min)

Analysis conditions headspace.

Injection	1 ml (500 µl/s)
MPS 2	60°C (5 min)
PTV	0.5 min solvent venting (10 ml/min), 1.1 min splitless -50°C, 12°C/s, 290°C (5 min)

Analysis conditions solid phase microextraction.

| Fiber	PDMS, 100 µm
MPS 2	60°C (15 min), 10 min extraction
PTV	0.5 min splitless 220°C

Analysis conditions thermal extraction.

| TDS 2	splitless 20°C, 60°C/min, 60°C (7.5 min)
PTV	0.1 min solvent venting (45 ml/min), 1.1 min splitless -50°C, 12°C/s, 290°C (5 min)

RESULTS AND DISCUSSION

A variety of solid sample types were chosen to illustrate the relative sensitivity of Static Headspace, SPME and direct Thermal Extraction sample introduction techniques under mild sampling conditions.

Figures 2 and 3 show the comparison of the aromatic volatiles in dried and fresh basil. Herbs are used in cooking as a concentrated source of aromatic compounds to impart characteristic flavors and aromas to food. The volatile profile in the headspace above the herbs may provide indications of the quality of the dried material.
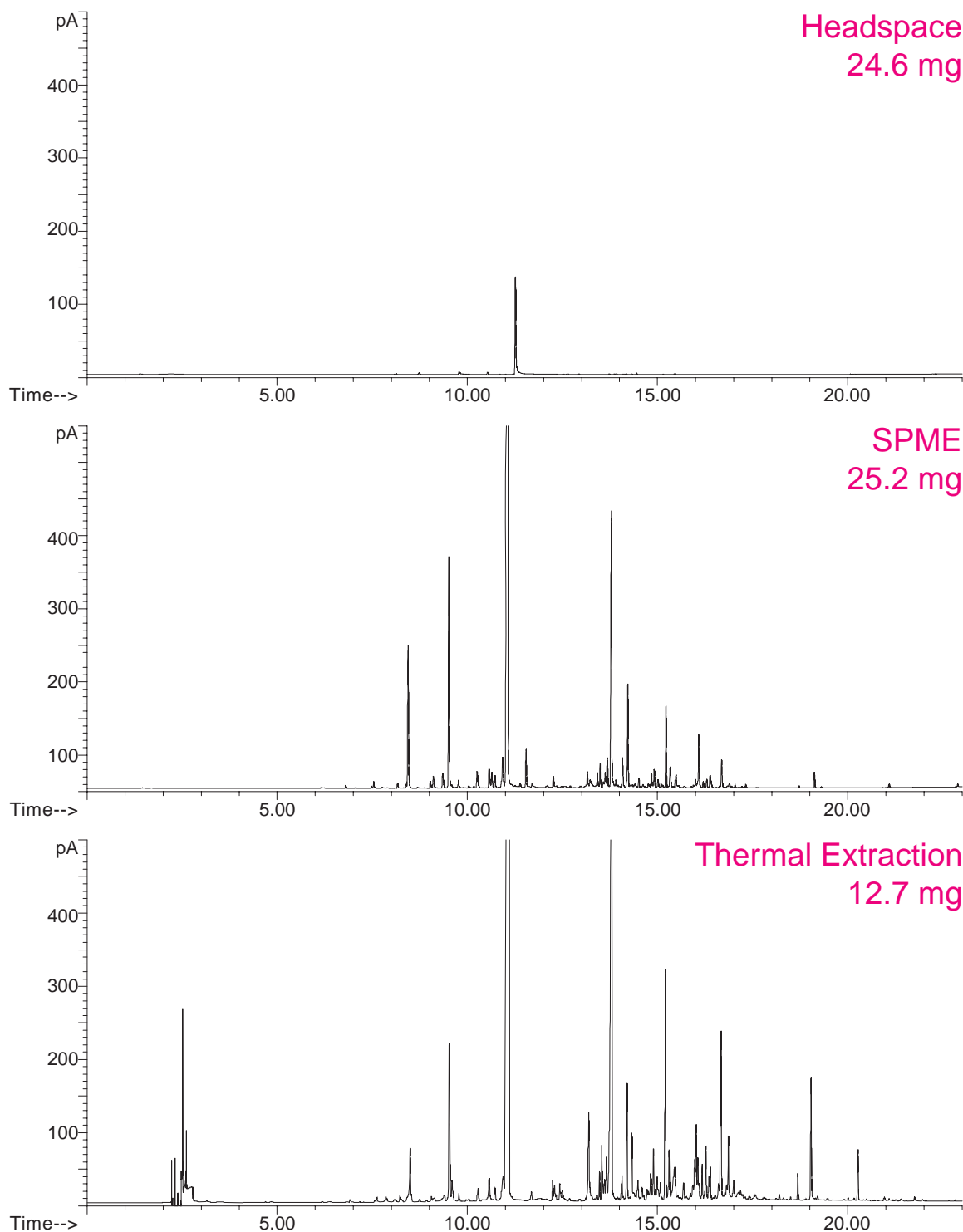
Figure 2. Volatile profiles from dried basil.

Static headspace analysis provides only limited information about the principle component present. SPME is able to provide 50-100x greater sensitivity with a similar sample size, and easily tolerates the water present in the fresh sample. Thermal Extraction provides still greater sensitivity, particularly in the higher boiling region. Note that in the fresh basil sample, direct Thermal Extraction with cold trapping resulted in water freezing in the inlet, preventing analysis. The fresh sample was therefore thermally extracted in an external device, trapping volatiles onto a Tenax TA adsorbent tube without retaining significant amounts of water. The adsorbent tube was then thermally desorbed at 280°C and analytes were trapped in the inlet as for the dried sample. A split ratio of 30:1 at the inlet was required to prevent overloading of the capillary column. Sensitivity appears to be 5-20x higher than SPME for this sample type.
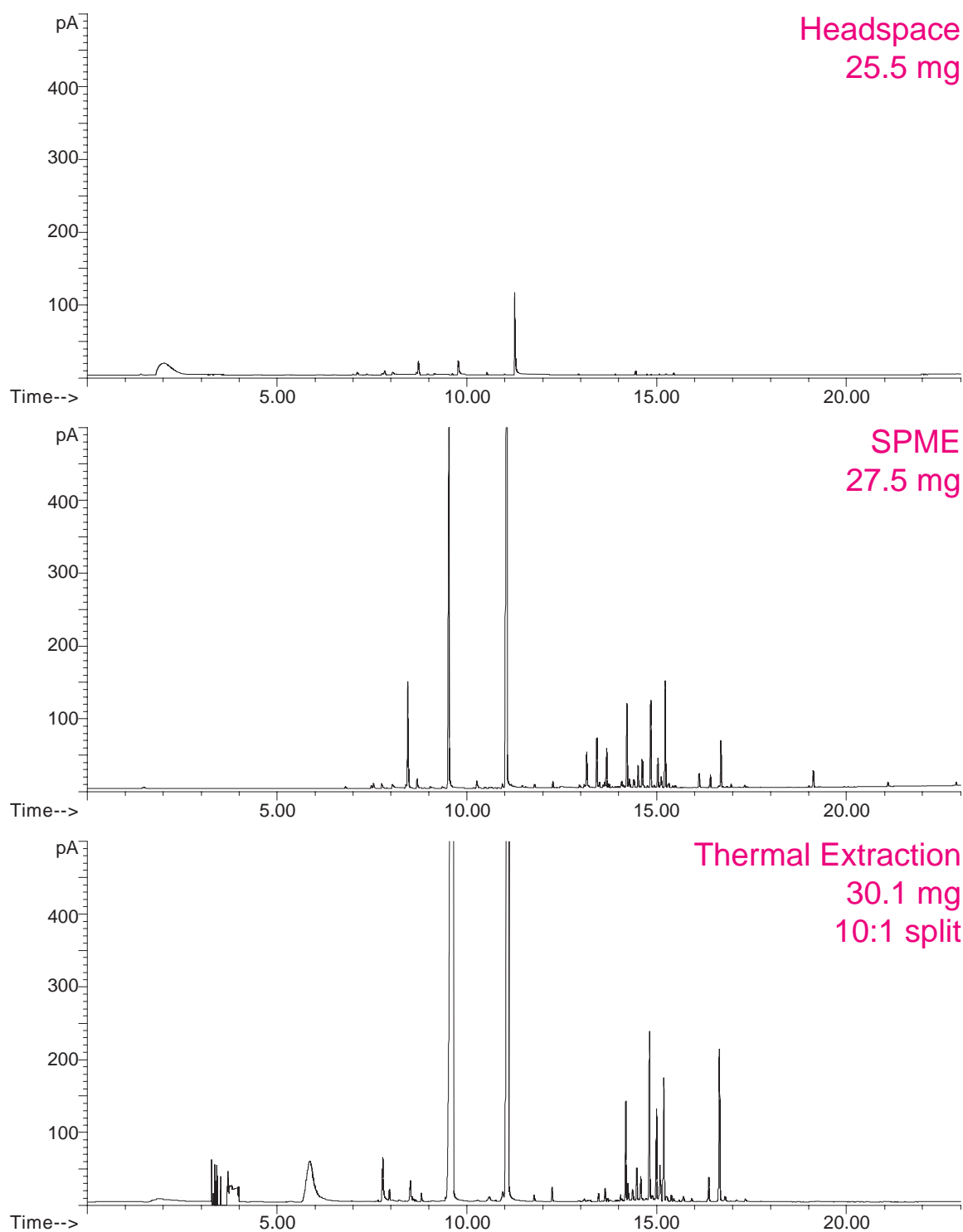
Figure 3. Volatile profiles from fresh basil.

Figure 4 shows a comparison of the volatiles from a dried herbal tea formulation. Herbal teas contain a variety of dried plant materials to produce particular flavor and aroma profiles, and are therefore quite inhomogeneous. Adequate volatile profiling may be useful as a QC tool to verify correct formulation blending.

Headspace analysis provides some information about the lower boiling major components, but completely misses a late eluting major component. SPME provides a reasonably complete profile of the range of compounds present with at least 50-100x higher sensitivity than Headspace GC. Thermal Extraction provides the highest sensitivity possible, detecting trace components with 20-50x higher sensitivity than SPME, particularly in the high boiling region. Smaller sample sizes (10-100mg) necessary for thermal extraction may limit the ability to obtain a representative sample, however.
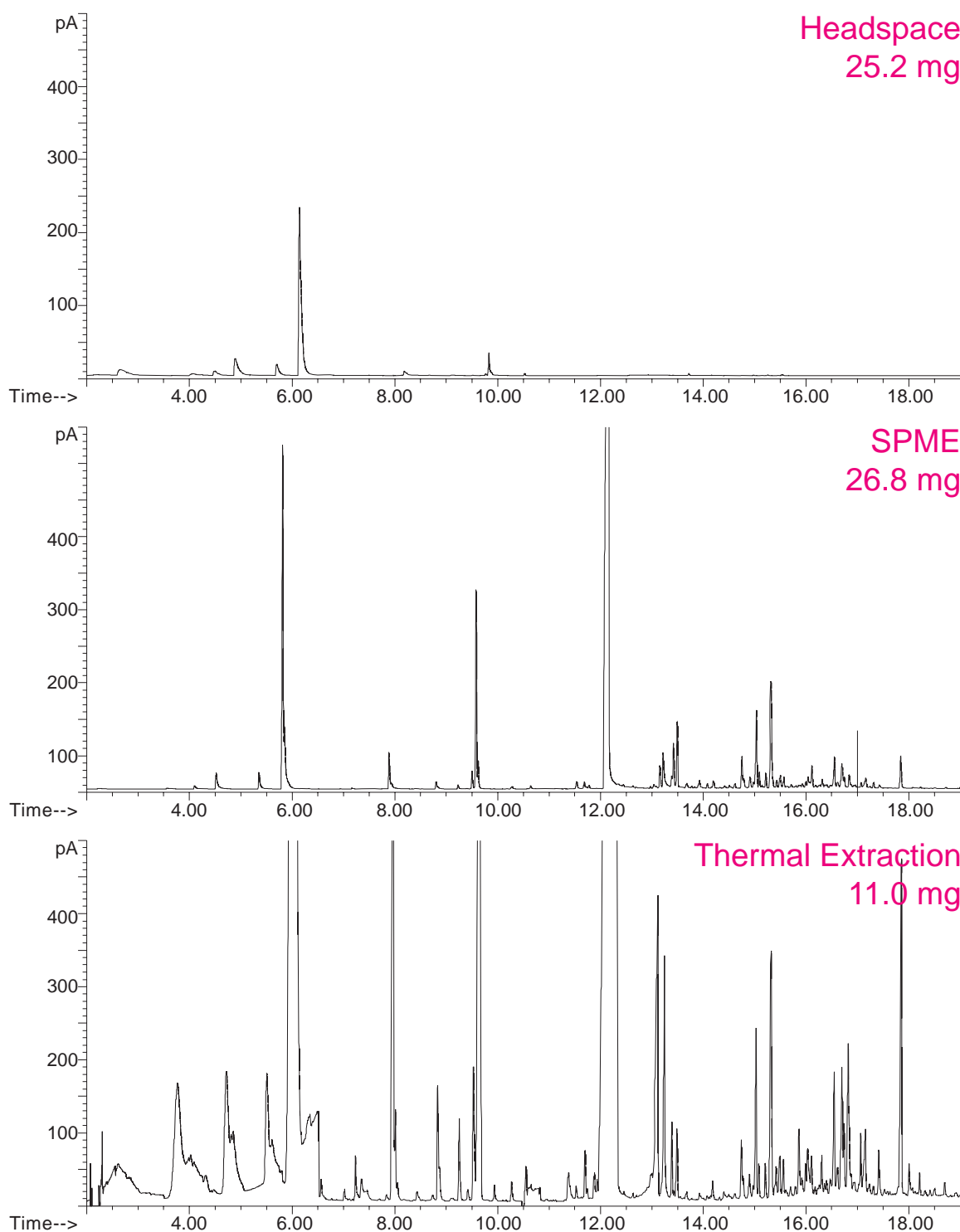
Figure 4. Volatile profiles from dry Cinnamon Apple herbal tea.

Figure 5 shows the profiles obtained from fresh white pine needles. The higher boiling compounds are present at levels undetectable by Static Headspace injection. The selectivity of the SPME PDMS fiber is an advantage for this sample type, since it is able to concentrate the higher boiling compounds providing dramatically improved sensitivity in the high boiling region compared to Static Headspace. Direct Thermal Extraction provides 2-5x higher sensitivity with 5x less sample compared to SPME.
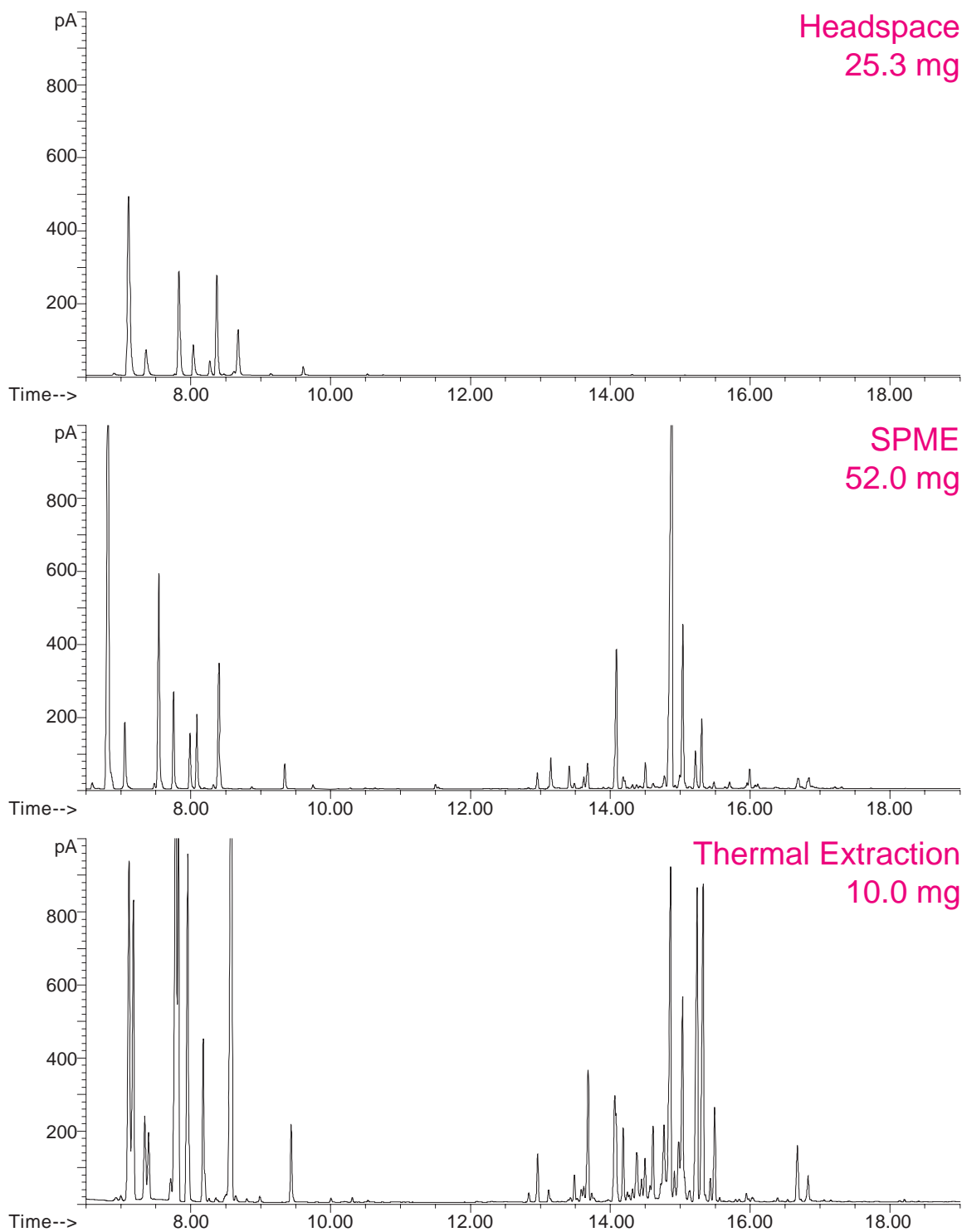
Figure 5. Volatile profiles from white pine needles.

Figures 6 and 7 compare the volatile profiles from a generic, instant coffee and a fresh ground, premium coffee. Even for large sample sizes (100-500mg) Static Headspace sampling is unable to provide any useful information about the volatiles in either sample. With large sample sizes, SPME is able to detect a range of volatiles in both samples, showing that the instant coffee has lost most of the low boiling compounds that probably contribute to aroma. Direct Thermal Extraction provides excellent sensitivity even with very small sample sizes, providing a wealth of information about the volatile aroma compounds present in fresh ground coffee. The large peak near 19 minutes is caffeine.
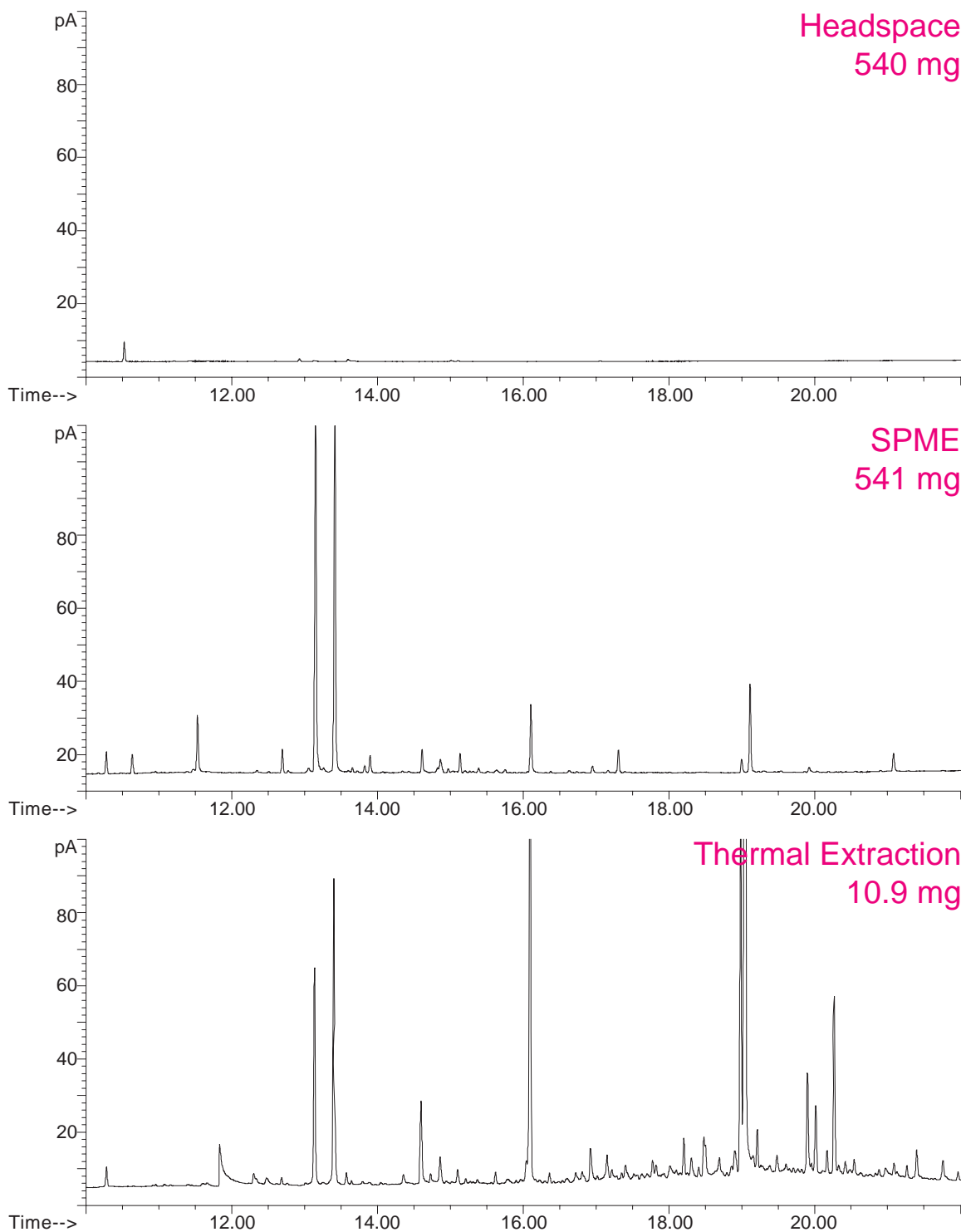
Figure 6. Volatile profiles from generic instant coffee.
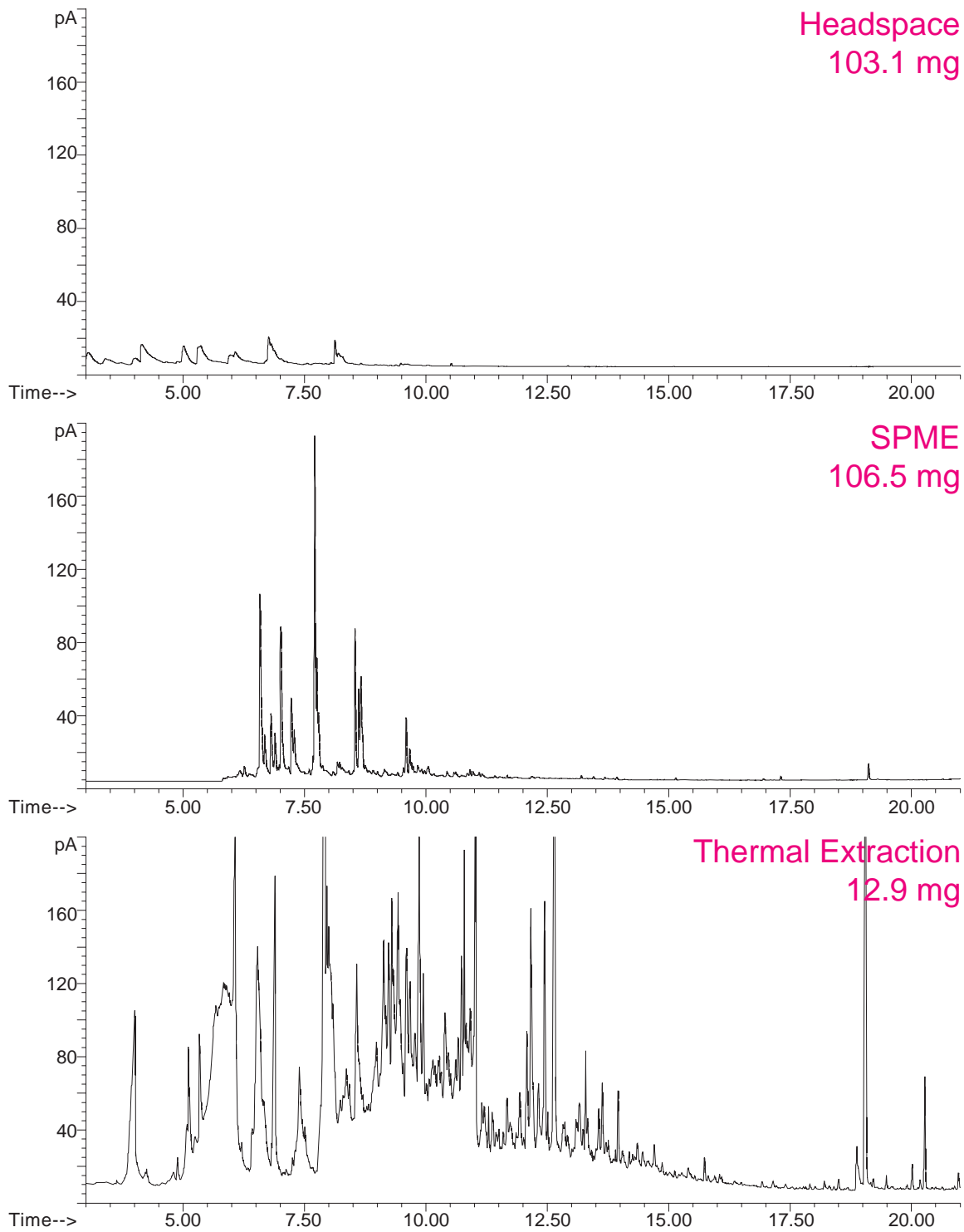
Figure 7. Volatile profiles from premium fresh ground coffee.

Figure (compares the sensitivity of Static Headspace and SPME for volatile hydrocarbons in a large sample (1 g) of polyethylene film used to package hard disk drives. Volatiles depositing on the surface of disk drives have been implicated in contributing to hard disk failure. Although SPME provides some information about the hydrocarbons present, Direct Thermal Extraction of a small film sample provides over 100x higher sensitivity and is clearly the method of choice for this sample type.
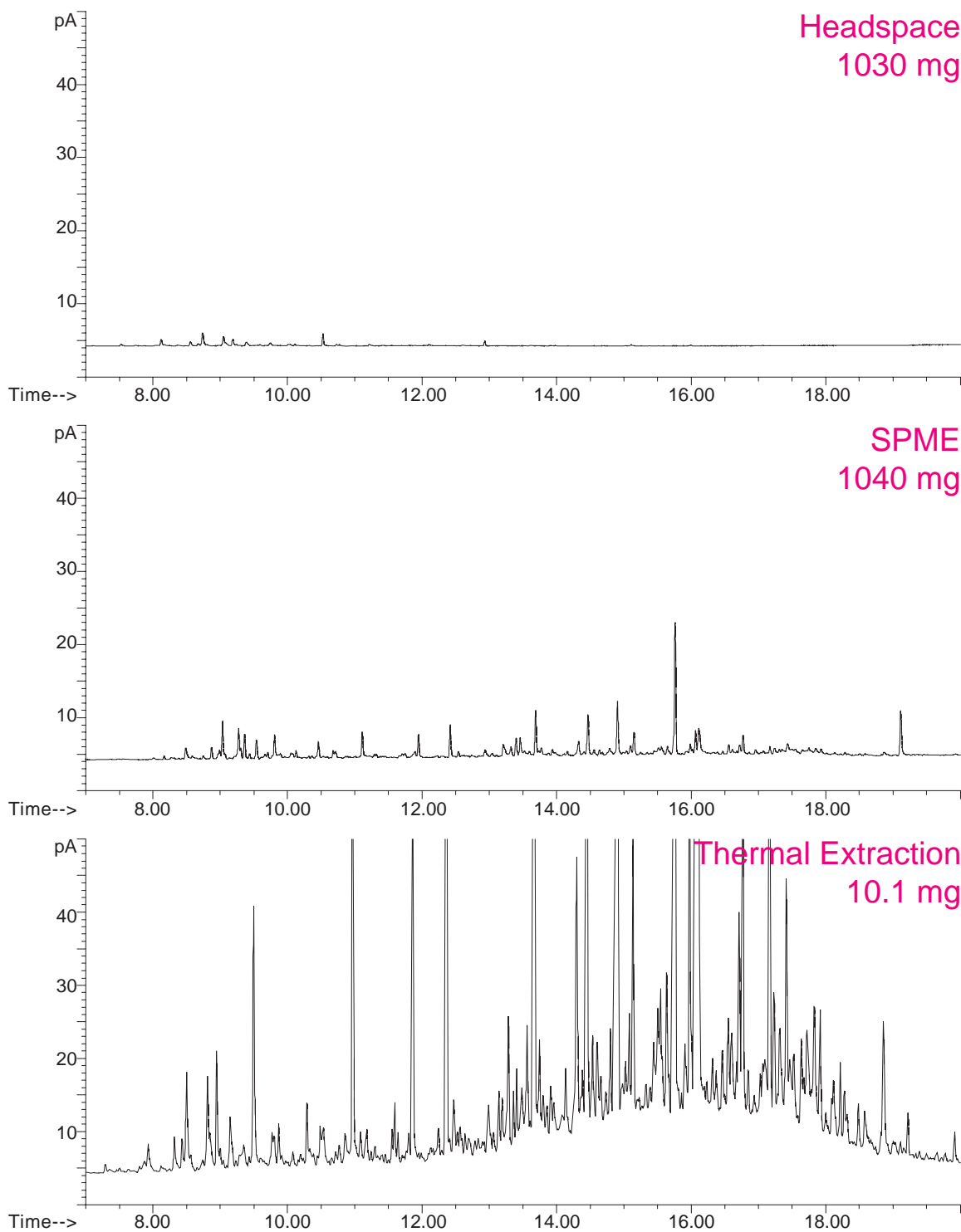
Figure 8. Volatiles from polyethylene packaging film used for hard disk drives.

CONCLUSIONS

The comparisons shown here provide a starting point for estimating the relative sensitivity of three sample introduction techniques available for automating analysis of volatiles in solid matrices. Static Headspace analysis is clearly the least sensitive technique, but for some sample types may provide adequate sensitivity if gram quantities of sample are available. Headspace sampling is also relatively tolerant of water content of the sample.

SPME was evaluated using only the 100 μm PDMS fiber. Additional selectivity available with other phases was beyond the scope of this study. SPME was found to provide 10-50x higher sensitivity than Static Headspace analysis over a wide range of analytes. It also is a convenient technique for sampling above samples containing high water levels.

Direct Thermal Extraction is capable of providing very high sensitivity for volatiles in a wide variety of sample types. Sensitivity is approximately 50-100x higher than SPME and 500-5000x higher than Static Headspace sampling. SPME and Static Headspace may be tolerant of samples containing high water levels, whereas volatiles from Direct Thermal Extraction must be trapped onto Tenax TA adsorbent resins in the inlet liner to eliminate water interference. Due to the very high sensitivity of Direct Thermal Extraction, small sample sizes (10-100mg) are used which may produce variable results with inhomogeneous samples.

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