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Quantitative Determination of Trace Analytes in Solid Materials by Thermal Extraction GC

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ABSTRACT

Direct thermal extraction of solids has most commonly been used for qualitative identification of trace materials such as additives, impurities and residual monomer or solvents. The technique has many benefits including reduced matrix interference, eliminating solvent extractions, and significant improvements in detection limits relative to liquid extraction techniques.

Many types of solid materials are amenable to quantitative analysis using direct thermal extraction. Samples must be homogeneous, so that the small amount of material needed for thermal extraction is representative of the whole. Samples must be able to fit into the relatively small (4mm ID) thermal desorption tube. Diffusional distances in the solid must be minimized, and surface area maximized to facilitate recovery of analytes from the solid matrix. This can be accomplished for example, by reducing the sample to small particle size, or analysis of polymers as thin films.

Key extraction parameters that must be optimized in-

clude desorption temperature, time and flowrate. In addition, trapping conditions in the inlet used to re-focus analytes prior to transfer to the column can be adjusted depending on the range of analytes present. Finally, for quantitation to be reliable the system must be calibrated using conditions similar to the thermal extraction conditions used for the sample.

Examples of optimized conditions for quantitation of residual hydrocarbons in polymeric packaging film and residual flavor components in recycled PET are shown. Techniques and equipment necessary for reliable calibration are also described.

INTRODUCTION

The analysis of trace volatiles in solids 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. Previous studies have shown that compared to static headspace and SPME, direct thermal extraction has the potential for 100-1000x lower detection limits for volatiles in solids.

The techniques and limitations associated with quantitative analysis by static headspace and SPME are well known. Quantitative analysis by direct thermal extraction of solids, however, has met with limited acceptance despite the fact that standard air sampling methods routinely use the analogous technique, thermal desorption, for quantitation from solid adsorbent tubes. If the known parameters affecting adsorbent tube performance can be applied to thermal extraction of solid samples, then reasonable strategies for quantitative direct thermal extraction methods can be developed.

First and foremost, the diffusional distances in the solid must be short to allow rapid transfer of volatiles from the sample to the gas stream carrying them into the GC inlet. This restricts appropriate sample form to finely divided powders and thin films. Sample must not contain active or catalytic surfaces that degrade analyte

at the temperatures necessary to thermally extract them from the solid. The majority of the sample matrix must be nonvolatile under the temperature conditions for extraction. It is acceptable, however, for the sample to melt during thermal extraction.

Finally, analyte recovery from the matrix should be complete, or at the very least well defined and reproducible if reliable quantitation is to be obtained. This requirement is relatively easy to test with modern, automated thermal desorption equipment. The purpose of this paper is to illustrate with two examples the process of developing and validating quantitative direct thermal extraction methods for trace volatiles in solid samples.

EXPERIMENTAL

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) equipped with flame ionization detection, a PTV inlet (CIS4, Gerstel) and a Thermal Desorption unit with autosampler (TDS2 & TDSA, Gerstel). Inlet trapping conditions were optimized for each sample type.

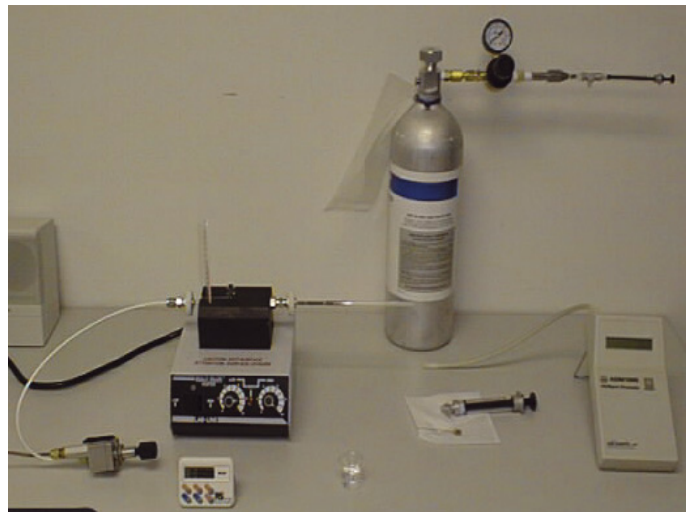


Figure 1. Gerstel TDS 2 ThermoDesorption System.

Sample Preparation. All samples (15-25mg) were weighed directly into conditioned glass thermal desorption tubes. Samples were then thermally extracted in the TDSA unit. Desorption conditions were optimized for each sample type and are given in the text.

Standard Preparation. For each study, five or six-point calibration curves were generated with each level prepared in duplicate. A decane standard was used to calculate total hydrocarbons present in the polyethylene films. External standard calibration curves for both sample types were set up by spiking standards onto

Tenax TA™ adsorbent tubes (4mm ID x 178mm) connected to a prototype heater block assembly (Supelco). A 10ul syringe was used to deliver each standard into a 50mL/min nitrogen flow through a glass bulb heated at 65° C in the heater block. Standards were then thermally desorbed in the TDS 2 unit at 280°C.



Analysis Conditions.

Column: 30m HP-5 (Agilent),
 $d_i = 0.25\text{mm}$, $d_f = 0.25\text{mm}$
 Pneumatics: He, $P_i = 91.7\text{ kPa}$,
 Constant flow = 1.2 mL/min
 Oven: 40°C (20 min), 10°C/min, 280°C

Polyethylene packaging film sample

TDS 2 splitless,
 20°C, 60°C/min, 100°C (30 min)
 PTV 0.2 min solvent vent (60 mL/min),
 split ratio 30:1
 -70°C, 10°C/s, 275°C (3 min)

PET sample

TDS 2 splitless,
 20°C, 60°C/min, 200°C (5 min)
 PTV 0.1 min solvent vent (45 mL/min),
 split ratio 30:1
 -70°C, 12°C/s, 280°C (3 min)

RESULTS AND DISCUSSION

Residual Hydrocarbons in Packaging Film. Plastic packaging films used for disk drives and other sensitive electronic applications are carefully monitored for residual volatile materials that can outgas and deposit on the device surfaces. Contamination due to deposited volatiles can lead to early failure of the device. Suppliers to the disk drive industry base many of their test methods on standard methods published by the International Disk Drive Equipment and Materials Association (IDEMA). These methods are designed to give a snapshot of the outgassing performance of a material under specified time and temperature conditions, and are not necessarily designed to sample all possible material that may outgas from a given material.

Figure 3 shows a chromatogram of the C10- C25 hydrocarbons found to outgas from 25mg of one such packaging film using thermal extraction conditions similar to conditions specified by IDEMA. The majority of the compounds identified in this chromatogram consist of straight and branched chain hydrocarbons, but antioxidants like BHT and BHEB were also found. We decided to optimize the key thermal extraction parameters for our thermal desorption system before attempting to quantify the level of residual volatile hydrocarbon in the packaging film. We held desorption temperature constant at 100°C to match current industry methods.

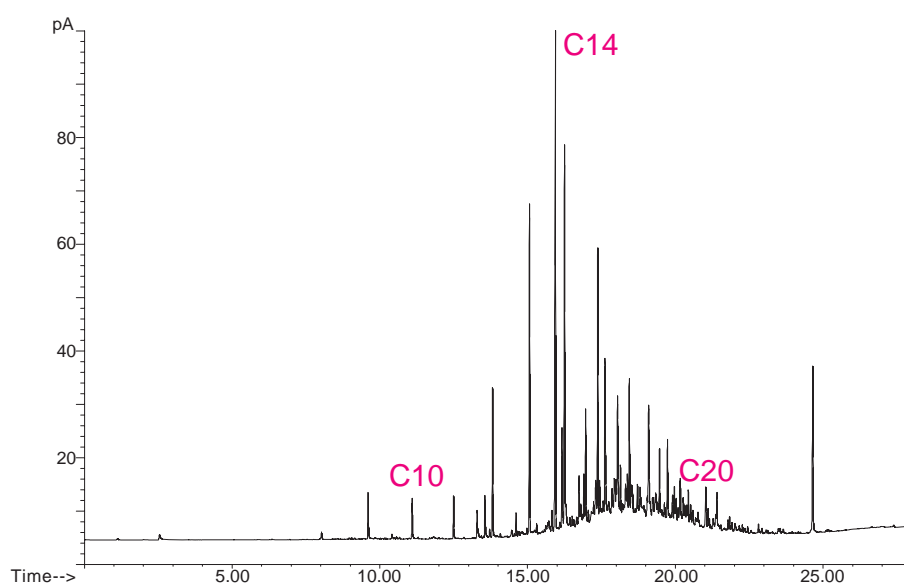


Figure 3. Residual hydrocarbons in packaging film.

The efficiency of the thermal extraction process can be influenced by numerous factors, but one of the most important parameters at any given temperature is gas flowrate during desorption. Figure 4 shows the peak area for seven hydrocarbons after 30-minute thermal extraction at 100°C with flowrates from 10 to 100 mL/min. Based on these results, we chose 60 mL/min desorption gas flow for all subsequent studies.

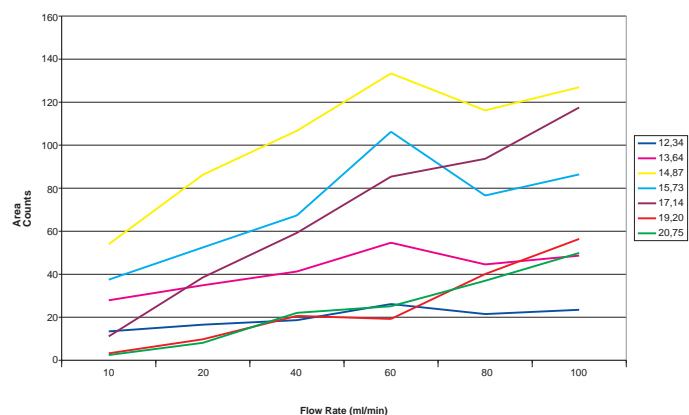


Figure 4. Polybag flowrate study.

We tested whether extraction time could be shortened and still provide reasonably complete recovery of the full range of hydrocarbons present in the film sample. Figure 5 shows the area counts recovered for seven of the major hydrocarbon peaks after 10, 20, 30 or 40 minute extractions at 100°C. For desorption times of more than 30 minutes, the earlier eluting, lower boiling hydrocarbons begin to break through the cold trap resulting in a decrease in peak area. The later eluting, higher boiling hydrocarbons, however, still show increases in peak area indicating they have not been exhaustively extracted from the film. This method is known to be only semi-quantitative, and is used to screen film samples to assure they do not contain inordinately high residual volatiles. Figure 5 illustrates that the high boiling hydrocarbons may be underrepresented using this sampling method.

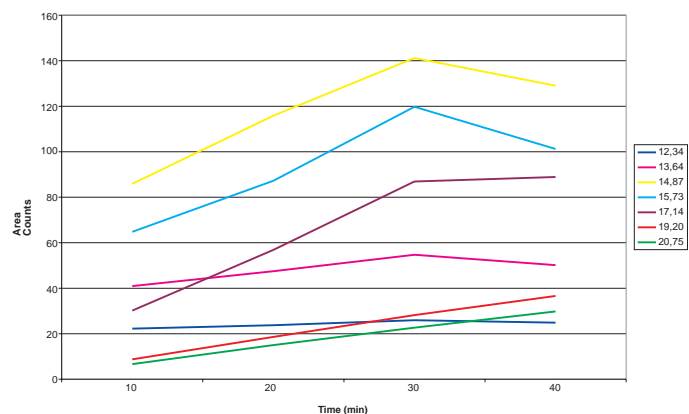


Figure 5. Polybag extraction time study.

To quantify the hydrocarbons present in the film, an external calibration curve was prepared using a decane standard spiked onto Tenax TA™ adsorbent tubes. The spiked adsorbent tubes were then thermally desorbed using the same conditions of time, gas flow and split ratio used for the sample. For accurate quantitation, it is important to maintain these parameters consistent between the standards and samples. Excellent linearity was obtained for decane calibration levels between 100 and 4000ng. Peak areas for all hydrocarbons were summed and using the decane response factor, the total hydrocarbon level was calculated.

In one packaging film the total extractable hydrocarbon level was found to be approximately 200 ug/g film. Precision, determined by comparing the peak area for 7 major hydrocarbon peaks in 5 replicate film samples, was acceptable for a semi-quantitative method with a %RSD of 6.52.

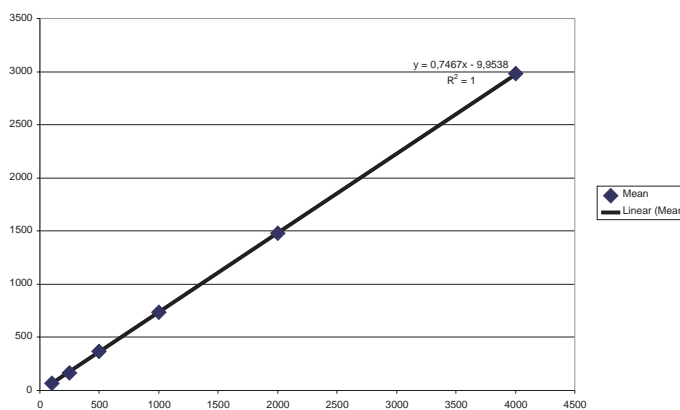


Figure 6. Decane calibration curve.

Residual Flavor Compounds in PET Bottles. Recycled plastics can contain a variety of impurities depending on the types of materials to which they have been exposed. Poly (ethylene terephthalate) (PET) is a commonly recycled material comprising a large fraction of the bottles used for consumer products, including soft drinks. The flavor components from soft drinks, most notably limonene, can be readily absorbed into the PET bottle and will be detectable in untreated recycled PET.

Figure 7 shows a typical thermal extraction chromatogram from 25mg of PET cut from the side wall of a soft drink bottle which had been rinsed three times with distilled water and air dried. Limonene, a major component in many fruit-based soft drinks, is the most prominent peak, whereas other flavor constituents are seen at much lower levels. For comparison, thermal extraction of an unused PET bottle shows no detectable limonene.

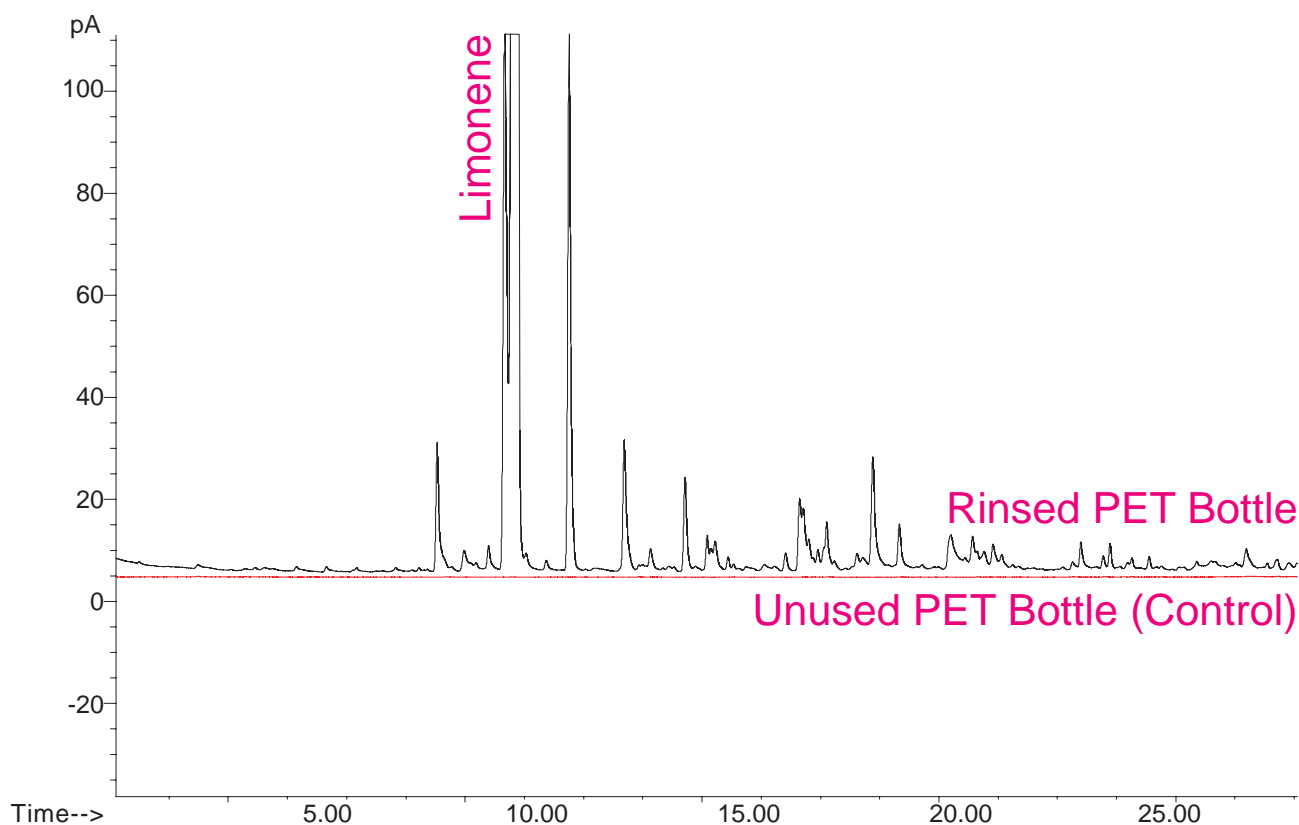


Figure 7. Residual flavor in PET.

To optimize the thermal extraction of limonene from the PET, desorption temperatures between 50°C and 200°C were tested. 25mg samples were first thermally extracted for 5 minutes at the test temperature (e.g. 50°C, 75°C, etc.). Samples were then reextracted at the maximum temperature (200°C) to see whether additional limonene could be extracted. The results shown in Figure 8 demonstrate that limonene extraction efficiency is very low below 75°C. Using extraction temperatures above 175°C essentially recovers all extractable limonene from the PET. For all subsequent studies a single thermal extraction at 200°C was used.

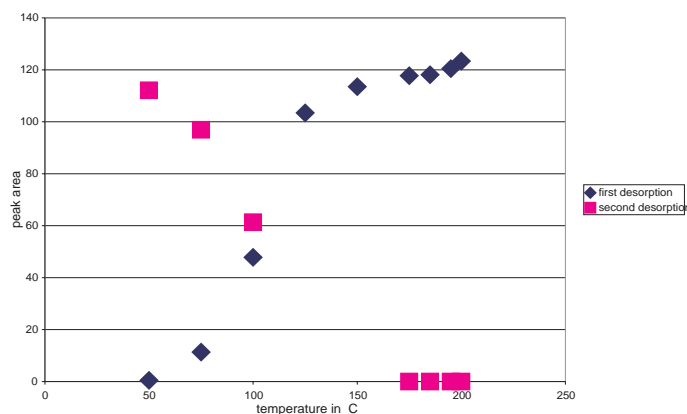


Figure 8. Limonene extraction curves.

To quantify the limonene present in the PET, an external calibration curve was prepared using a limonene standard spiked onto Tenax TA™ adsorbent tubes. For the two highest calibration curve points, the spiked adsorbent tubes were thermally desorbed using the same conditions of time, gas flow and split ratio used for the PET sample. To obtain the necessary sensitivity for the lower three calibration curve points, the inlet was set in the splitless mode. Excellent linearity was obtained for limonene levels between 1ng and 10ug, validating the use of different split conditions in the inlet for calibration (Figure 9).

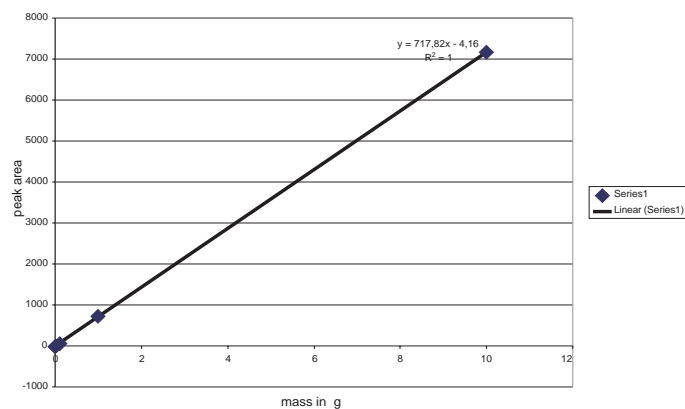


Figure 9. Limonene calibration curve.

In a single PET bottle the total extractable limonene level was found to be approximately 7 ug/g PET. Precision, determined by comparing the peak area for limonene in 10 replicate PET samples from the same bottle, was excellent, with a %RSD of 2.00. Based on the size of the limonene peak seen using a 30:1 split ratio, we estimate this direct thermal extraction technique will be able to detect limonene contamination in recycled PET at the low ppb level.

CONCLUSIONS

- Volatiles such as hydrocarbons or limonene in polymeric materials can be quantified in the ppm to ppb range by direct thermal extraction.
- Extraction temperature, flow, and time should be optimized to provide the most reliable conditions for quantitative analysis. Trapping conditions must be chosen based on the range of analytes to be quantified.
- Calibration is easily done by spiking standards onto adsorbent tubes developed for air sampling applications. Desorption flow, time and split ratio should match conditions used for sample analysis. Different inlet split ratios can be used to extend the dynamic range of the analysis if proper validation is done.



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