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Direct Thermal Extraction with Automated Liquid Calibration for the Quantification of Analytes in Solid Matrices

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Abstract
Direct thermal extraction is a sensitive technique for the analysis of residual compounds in solid matrices such as polymers, films, powders, and fibers. This approach can be used for both qualitative identification of unknowns as well as quantification of trace components.

Quantification of analytes is often performed based on off-line spiking of liquid or gaseous standards onto a thermal desorption tube containing a sorbent material. Instrument calibration can also be performed based on liquid introduction of standards into the gas chromatograph which usually involves removal of the thermal desorption system or moving the column from one injector to another.

In this study, a GERSTEL MultiPurpose Sampler (MPS 2) combined with a Thermal Desorption Unit (TDU) was configured to enable direct thermal extraction of solid materials combined with automated liquid calibration for unattended operation and high throughput. An optimized method for the analysis of residual solvents in tape samples was developed, illustrating the utility of this technique.

Introduction
In tape manufacturing operations, solvent based coatings and adhesives are applied to a continuous web of material. After

application, the material is passed through long tunnel ovens to evaporate solvents from the tape. Even after the drying process, some residual solvent remains in the final product. Although no regulatory standards exist for the amount of residual solvents in tape, the levels are closely monitored for process and quality control, as well as to reduce consumer exposure to solvents. This is especially important in the manufacture of medical grade tapes.

This study examines the direct thermal extraction of tape samples for quantification of residual solvents. Calibration of the instrument using external standards applied to Tenax-TA filled sorbent tubes and direct liquid injection is compared. Samples of medical grade tape and duct tape were purchased at a local store.

Experimental

Instrumentation.

GERSTEL MPS 2 robotic sampler with TDU and Automated TDU-Liner Exchange (ATEX) option, GERSTEL Cooled Inlet System (CIS 4), a PTV-type inlet, with LN_2 option, GERSTEL Modular Accelerated Column Heater (MACH), Agilent 6890 GC/FID

Analysis conditions.

TDU:	splitless 40°C, 720°C/min, 180°C (5 min) for sample 40°C, 720° C/min, 250°C (3 min) for liquid
CIS 4:	0.2 min solvent vent (100 mL/min) split 100:1 -120°C (0.2 min), 12°C/sec, 250°C (3 min)
GC Oven:	250°C, held for duration
MACH Module:	15 m Rtx®-1701 (Restek), MACH format di = 0.25 mm; df = 0.5 µm He, constant pressure (8.0 psi) 40°C (2 min), 20°C/min, 150°C (1 min), 100°C/min, 260°C (1.9 min)
Detector:	FID

Sample Preparation. The tape samples were placed on a Kimwipe. A single hole punch was used to punch out a 1/4“ circle. The samples were placed into a TDU microvial, then into an empty TDU tube.

Standards were spiked onto the fritted end of a Tenax-TA adsorbent tube. Dry nitrogen was blown through the tube at 50 mL/min for 3 minutes.

Results and Discussion

Figure 1 shows an ATEX configuration similar to the one used for this study. The GERSTEL universal syringe holder and ATEX gripper combination is able to transport thermal desorption tubes, while holding any of a variety of syringe sizes for liquid injection through the top of the TDU transport adapter. Figure 2 shows a close up of the TDU tube with microvial insert. The insert shows an exploded view of the transport adapter with septum top.

Figure 1. GERSTEL MPS 2 with TDU and ATEX option mounted on an Agilent 6890 GC.

Figure 2. Microvial, GERSTEL TDU-liner and septum top.

Two types of tape were examined in this study: Duct tape and medical grade tape. The tape was applied to a Kimwipe prior to punching out the samples. This allowed easier handling of the samples with no addition of background contaminants.

The extraction conditions, time, temperature, and vent flow, were optimized. Figures 3a and 3b show relative peak area versus vent flow and temperature. The optimum peak area occurs at an extraction temperature of 180°C and the optimum flow rate at 100 mL/min. The optimum extraction time was found to be 5 minutes.

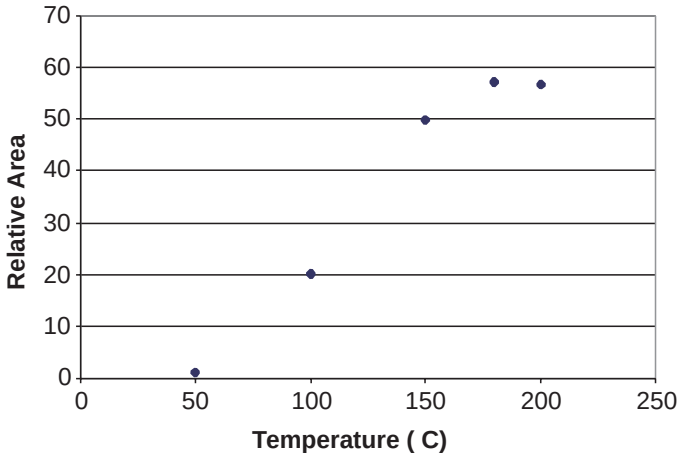

Figure 3a. Optimization of temperature.

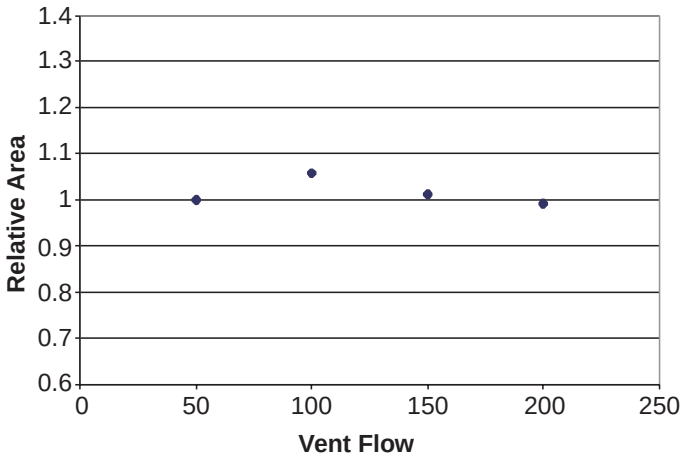

Figure 3b. Optimization of extraction flow rate.

Tape samples were first analyzed by thermal desorption GC/MS using a 30 m x 0.25 mm x 0.25 µm DB-5 column, in order to identify analytes of interest. Figure 4 shows a chromatogram resulting from thermal extraction of the medical tape. As can be seen, ethyl acetate is the dominant residual solvent.

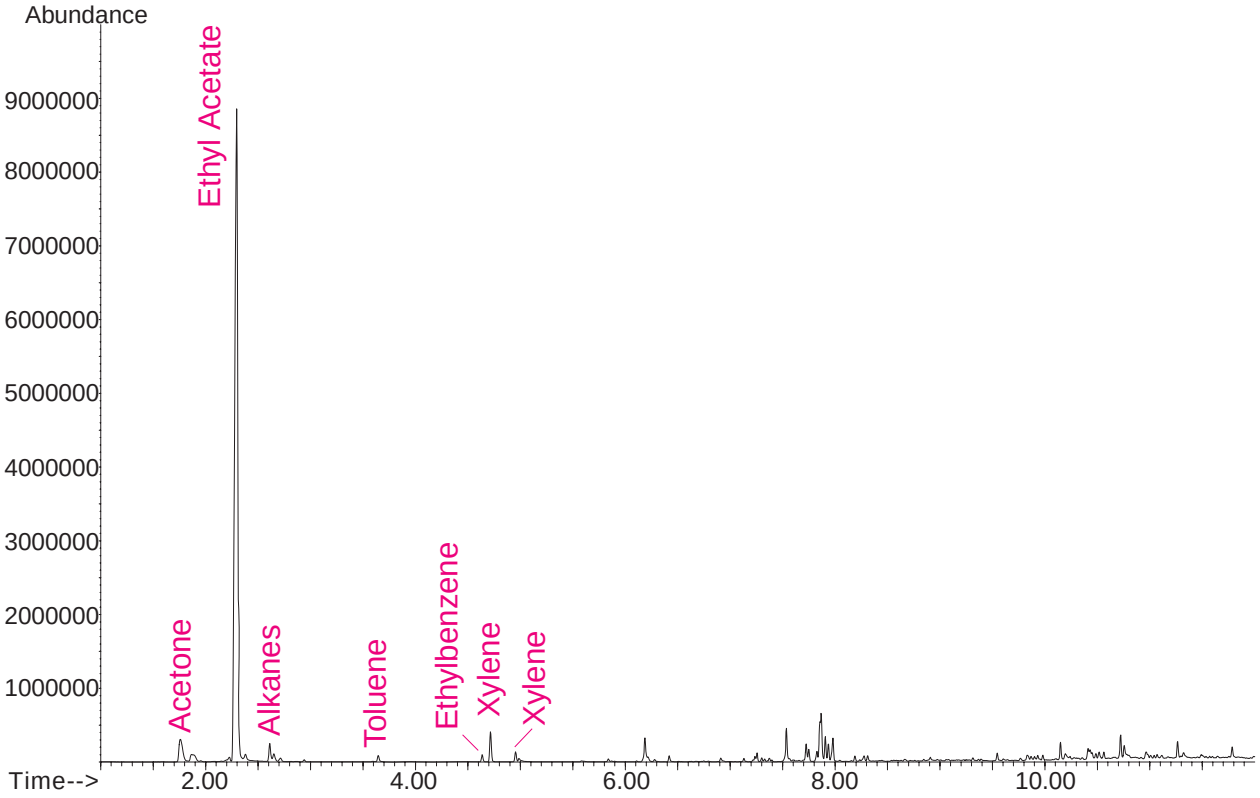

Figure 4. GC/MS Total ion chromatogram from thermal extraction of medical tape.

Figure 5 shows a chromatogram resulting from thermal extraction of the duct tape. As can be seen, toluene is the dominant residual solvent.

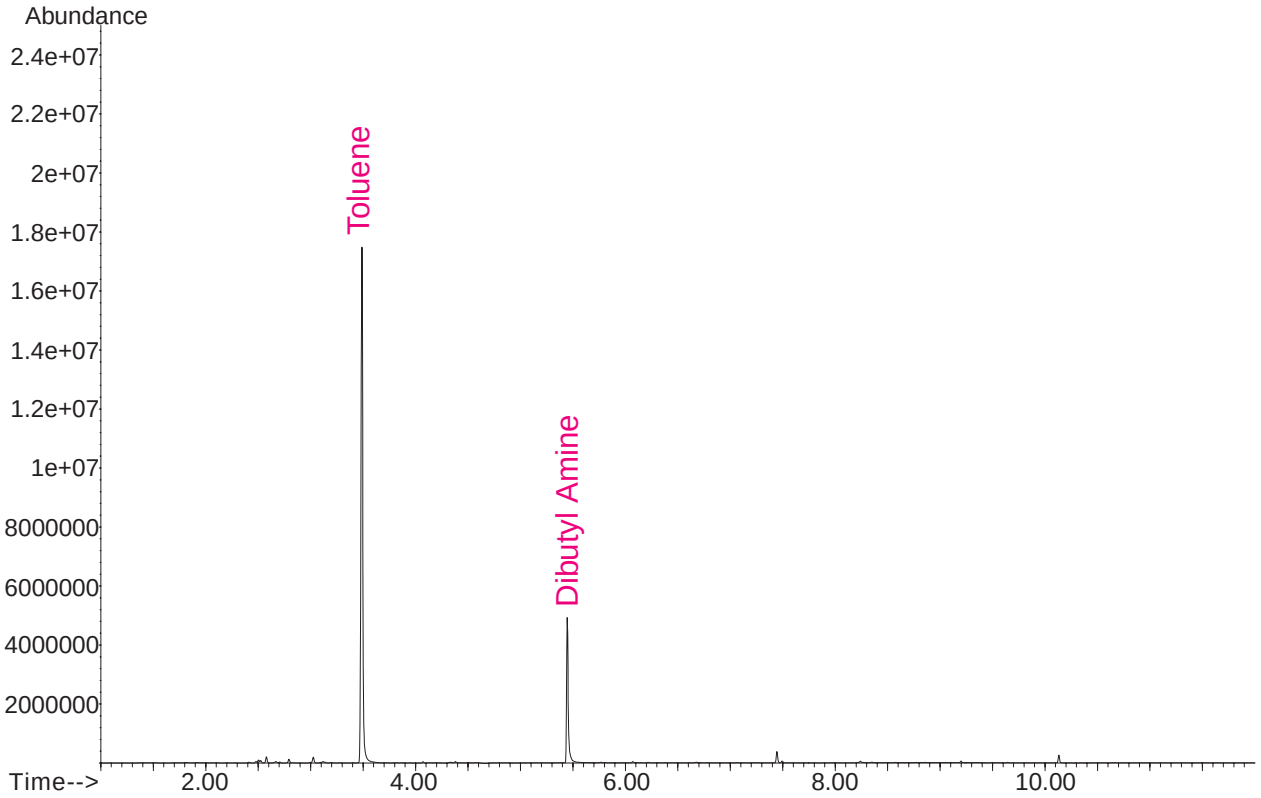

Figure 5. GC/MS total ion chromatogram from thermal extraction of duct tape.

Quantification of the residual solvents was conducted by thermal desorption GC/FID. The thermal extraction conditions used were 180°C for 5 minutes at a flow rate of 100 mL/min. A second extraction of both sample types found less than 1% of the original concentrations, proving an extraction efficiency of greater than 99%. A typical chromatogram resulting from thermal extraction of the medical tape is shown in Figure 6.

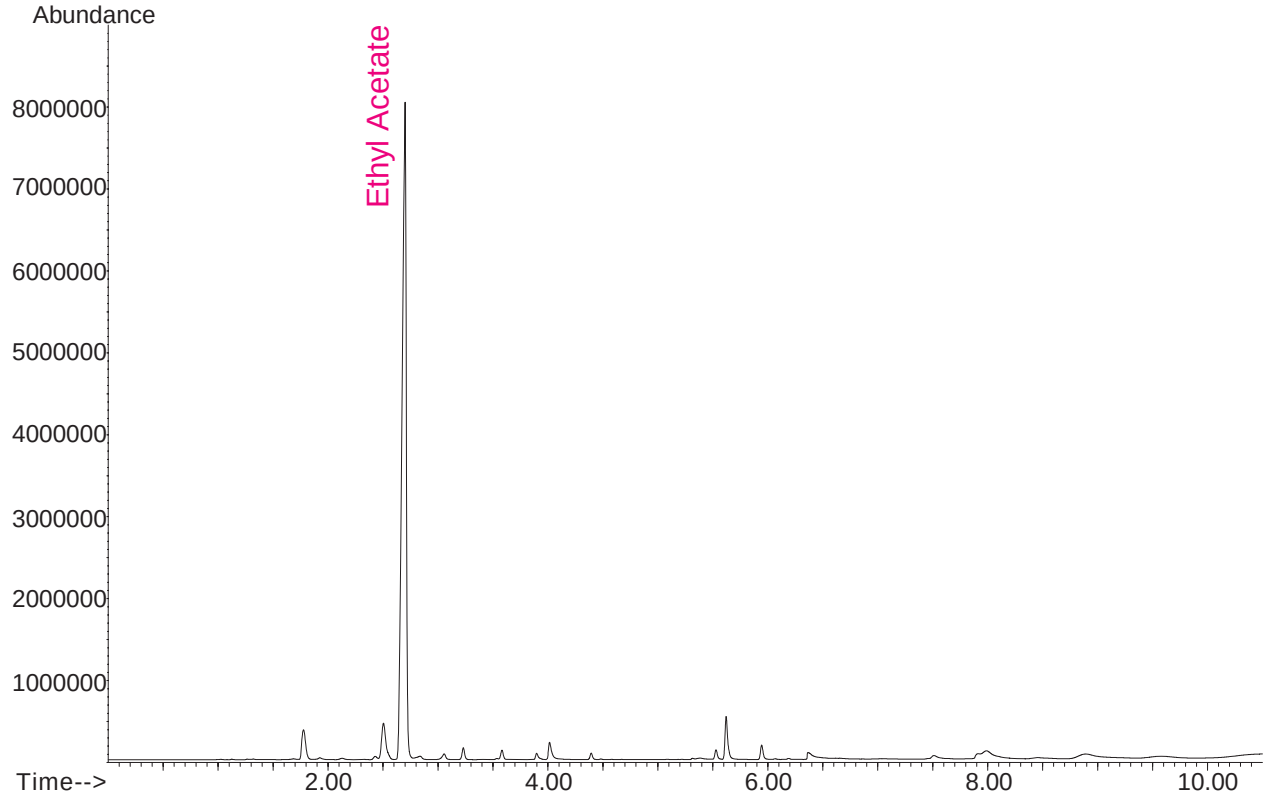

Figure 6. FID chromatogram from thermal extraction of medical tape.

Calibration curves were prepared by spiking standards on Tenax-TA tubes or by direct liquid injection of the same standards through the septum of an empty TDU liner. An empty TDU liner packed with deactivated glass wool provided the best results for liquid injection. A comparison of the two introduction techniques for calibration of ethyl acetate and toluene are shown in Figure 7.

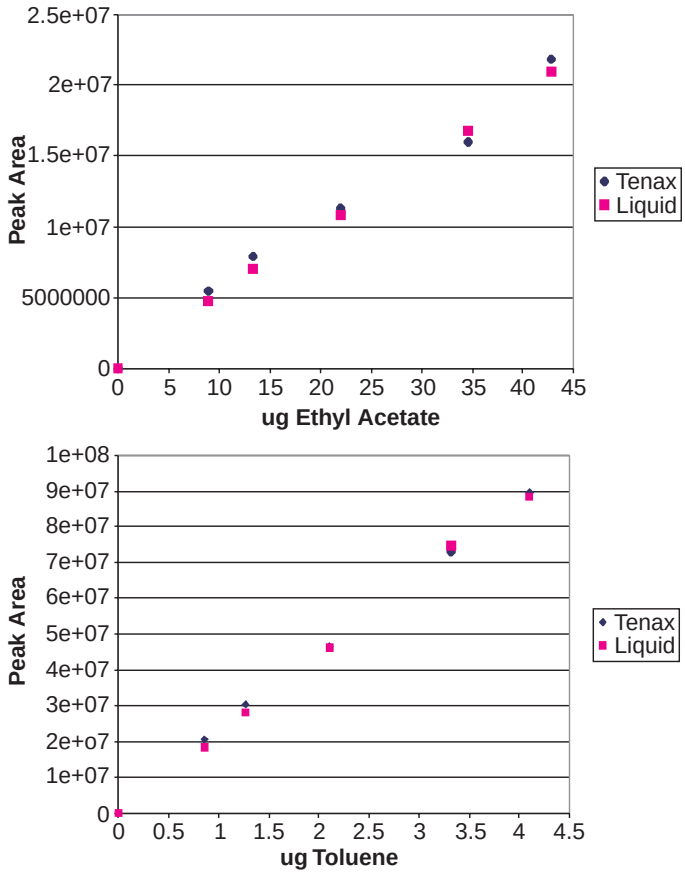

Figure 7. Calibration curves for ethyl acetate and toluene.

The curves show excellent agreement for the two introduction techniques. The correlation coefficients are all 0.999, except for the ethyl acetate calibration using Tenax which was 0.988. The automated liquid introduction enables complete automation of the calibration procedure.

Table 1 shows quantitative results for 5 replicates of each sample type using the liquid injection calibration curves. Excellent reproducibility is seen with RSDs less than 4%. The area of the sample is 0.0491 in^2 . This gives results of 362 µg/in^2 of ethyl acetate in the medical tape and 40.9 µg/in^2 of toluene in the duct tape.

Table 1. Quantitative results of 5 replicates.

	Ethyl Acetate [µg]	Toluene [µg]
Sample 1	17.9	2.06
Sample 2	18.7	1.99
Sample 3	17.2	2.05
Sample 4	18.0	1.93
Sample 5	17.0	2.00
Average	17.8	2.01
%RSD	3.96	2.50

Conclusions

Direct thermal extraction provides a fast and reproducible method for the analysis of residual solvents in tapes. The GERSTEL ATEX option enables liquid injection as well as thermal desorption of solids providing full automation of calibration, analysis of samples, and calibration checks. The TDU microvial provides a convenient container for the direct thermal extraction of solids. Typical sample sizes are 10-50 mg. This procedure can be applied to the analysis of other solid or liquid materials.

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