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Versatile Automated Pyrolysis GC Combining a Filament Type Pyrolyzer with a Thermal Desorption Unit

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Keywords

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Abstract

This paper describes an automated pyrolysis system for gas chromatography (GC) based on a filament type pyrolyzer combined with a commercially available thermal desorption instrument, onto which the pyrolysis module is installed. Automated sample introduction for both pyrolysis and thermal desorption is performed using a commercially available autosampler.

For pyrolysis of solid, liquid, or melting samples the use of different types of sample holders is investigated, for example cup-type holders for liquid samples. A special design has been developed that enables accelerated gas phase transport to help reduce the formation of secondary pyrolysis products. Sample holder design and complete flow path heating are essential design aspects in order to maximize recovery and minimize carry-over, enabling the system to reliably perform automated analysis of batches of different sample types. These aspect are discussed.

The cryo-trap function of the thermal desorption system used enables splitless transfer to the GC/MS of the formed pyrolysis products. An example is presented, in which water containing macromolecule residue in the ppm range is introduced into the pyrolysis module. The water is then removed using a solvent vent step and pyrolysis performed immediately afterwards, enabling quantification of the macromolecules by chromatographic determination of their pyrolysis products.

Introduction

Pyrolysis GC is used to obtain structural information of macromolecules by GC analysis of their thermal degradation products. A recently developed pyrolyzer was used for this study. The basis of the instrumental set-up is the GERSTEL Thermal Desorption Unit (TDU), equipped with a pyrolysis module that fits into the cavity of the TDU, into which thermal desorption tubes are normally placed. One advantage of this design is the possibility of easily switching between normal TDU operation and pyrolysis operation. As an interface to the GC column (or if needed as a cryogenic trap for focusing or concentration of substances) a GERSTEL Cooled Injection System (CIS), PTV-type inlet, is used. Automation of all processes, such as transporting desorption tubes and pyrolysis sample holders to and from the TDU as well performing liquid injections into the CIS are performed using a GERSTEL Multi Purpose Sampler (MPS).

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Figure 1a: GC/MS system equipped with a Thermal Desorption Unit (TDU), Pyrolysis Module (PYRO), and MultiPurpose Sampler (MPS) used for automation of all sample introduction techniques.

In fig. 1b the PYRO module is shown with transport adapters. Transport adapters are needed to load samples held in quartz sample holders from the autosampler tray into the pyrolyzer. During pyrolysis, the transport adapters also serve as carrier gas conduits. The heart of PYRO is a platinum filament. Pyrolysis temperatures can be set from 350 to 1000 °C, a temperature calibration at the sample point ensures an accurate temperature control. To enable compensation for effects of changes in the resistance of electrical connections over time, the filament is connected using a four conductor set-up. Since PYRO is a filament based pyrolyzer, it can perform temperature ramping from 0.02 to 100 °/sec in addition to standard pulsed pyrolysis.

Figure 1b: Pyrolysis Module (PYRO) shown with transport adapters and sample holders.

Experimental

Analysis Conditions

TDU	splitless
	50 °C; 720 °C/min to 275 °C (1.5 min)
Pyrolysis	pulsed
PTV	split 1:50 or 1:100
	270 °C (hot interface use) or
	-50 °C; 12 °C/s to 280 °C (3 min)
Column	30 m HP-5MS (Agilent)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics	He, constant flow = 1 mL/min
Oven	30 °C (4 min); 10 °C/min to 320 °C (7 min)

Results and Discussion

Sample Holder Design

Four different sample holders were tested; these are shown in figure 2. For solid samples, a quartz glass tube type sample holder with a plug of quartz wool can be used (type A). For liquid or melting samples, vial type sample holders are needed to retain liquid sample material (type B). A vial type design makes sample introduction easier, but the long diffusion path for the volatile pyrolysis products can lead to band broadening or discrimination if no cryogenic focusing is used. In order to avoid such effects two different vial type sample holders were developed with a venting slit on the side. This design significantly shortens the analyte diffusion path and reduces peak broadening by improving the purge profile. Additionally, the venting slit allows the carrier gas to flow more uniformly through the sample holder. The sample can be placed inside the sample holder in two different ways: 1) At the bottom below the slit (type C), leaving only a short diffusion path from the sample to the venting slit and thus to the carrier gas flow path, or 2) on a small plug of quartz wool above the venting slit (type D) allowing efficient transfer of degradation products to the GC, while retaining melting sample or excess liquid sample in the cavity.
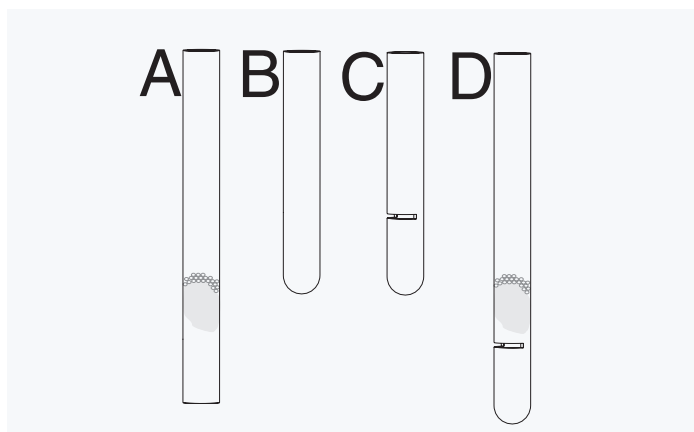
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Figure 2: Different designs of sample holders (explanation see text).

The pyrograms shown in Figure 3 illustrate the chromatographic effects of the two principal sample holder designs. Both chromatograms result from pyrolysis of polybutadiene at 450 °C; for the upper, the tube type sample holder with quartz wool was used; for the lower, the vial type sample holder with venting slit was used. From both pyrograms the main information can be seen, butadiene monomer and dimer as well as higher units can be identified, but the monomer peak in the upper chromatogram is much sharper due to the straight carrier gas flow path in the sample holder and the absence of unswept void volume.
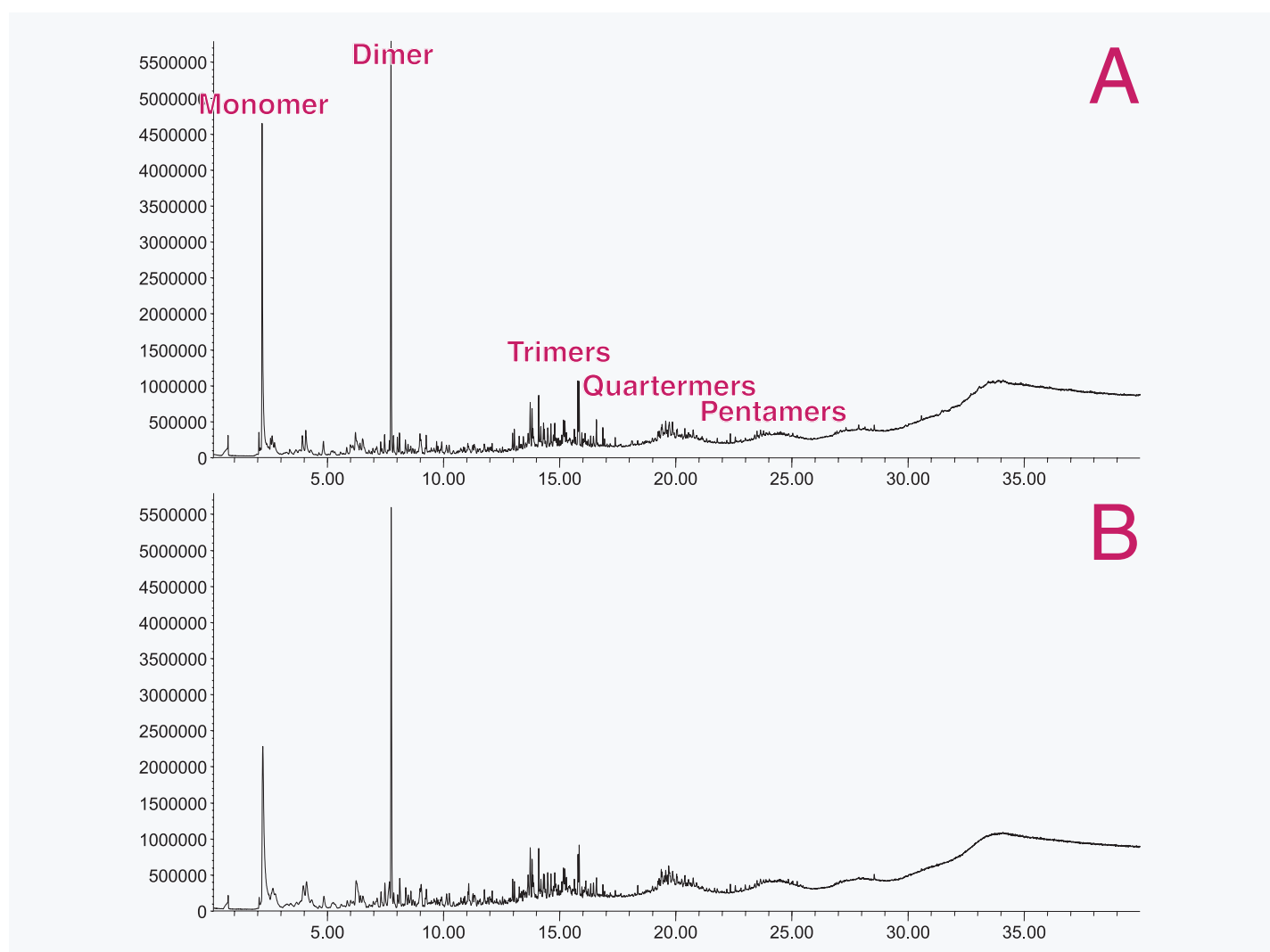

Figure 3: MSD TIC stacked view of two pyrograms resulting from pyrolysis of polybutadiene at 450 °C; top: Sample placed onto quartz wool in a tube type sample holder (type A), bottom: Sample placed into a vial type sample holder with venting slit (type C).

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A short and well designed analyte flow path with a uniform temperature profile is needed in order to avoid memory effects, which are often an issue in pyrolysis instrumentation. Pyrolysis of particles of pure compounds, such as polymers, leads to the introduction of large amounts of pyrolysis products, both into the pyrolysis unit and subsequently into the chromatographic system, which is frequently overloaded. The PYRO instrument design addresses these issues as can be seen from the results shown in fig. 4. Polypropylene was pyrolyzed at 700 °C in the tube type sample holder. The pyrogram and the subsequent blank run are shown in overlay mode. The same sample transport adapter was used for the two runs, only the disposable quartz sample holder was replaced. In the polypropylene pyrogram, the homologous series of degradation products up to C40 and higher can be seen. The blank run shows no memory effects from the sample introduction system, only a couple of broad, late eluting peaks, most likely resulting from high boiling compounds introduced to the column in previous runs. Had this been a case of carry-over from the inlet, the peaks would not have been as wide. In this example, the temperatures of the inlet transfer system and GC oven were both set to 300 °C. For pyrolysis of this kind of sample an instrument configured with column back-flush could be beneficial since it could help remove high boiling pyrolysis products from the column.
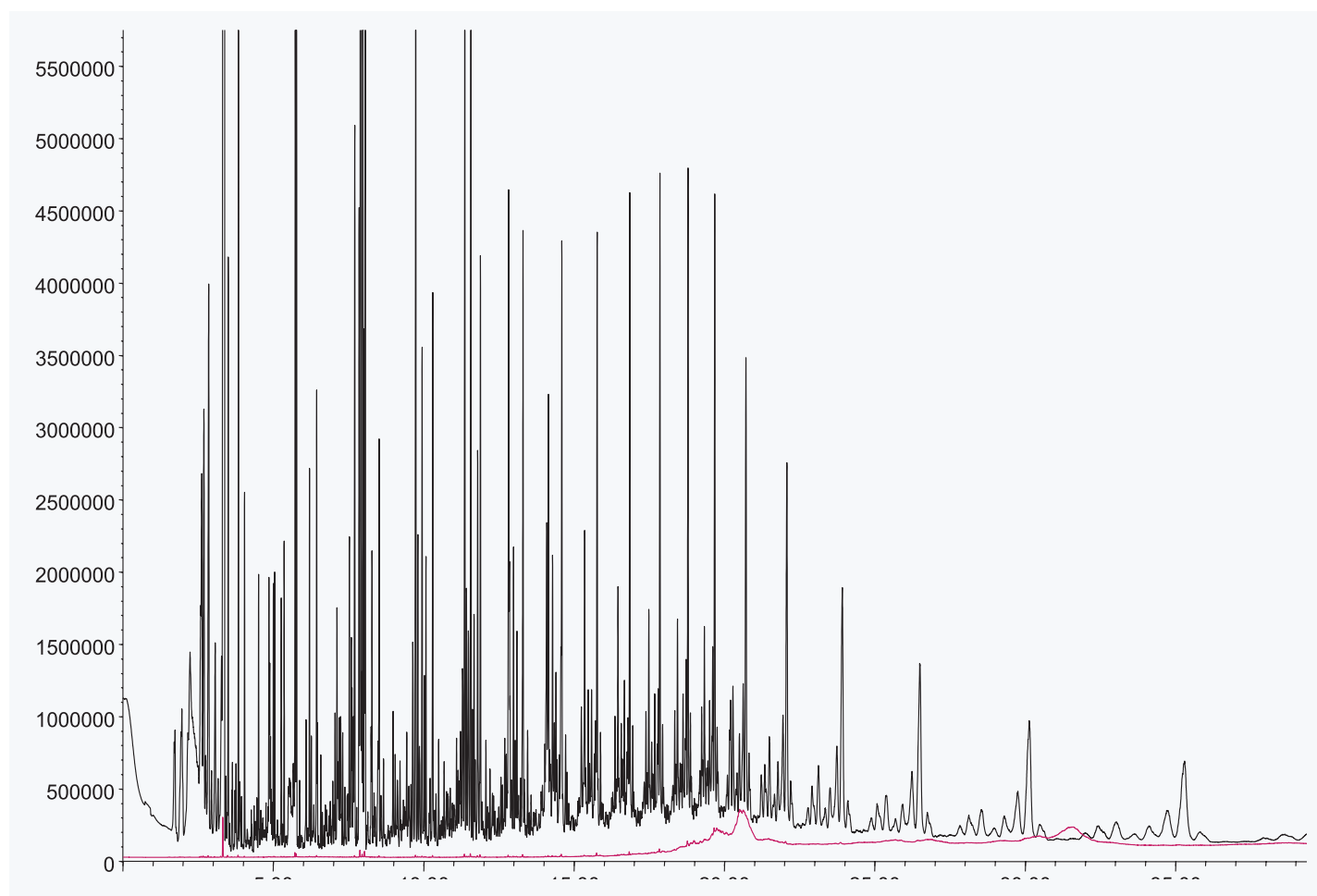

Figure 4: Pyrogram of polypropylene (Pyrolysis at 700 °C, split 1:50, FID) and a subsequent blank run (bottom trace).

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Fractionated Pyrolysis
Since it is the aim of pyrolysis GC to determine volatile degradation products of macromolecules it is important to distinguish between actual degradation products and previously adsorbed volatile organic compounds (VOCs). Consequently, a pyrolyzer should be able to perform both thermal desorption GC and pyrolysis GC in independent runs.

Fig. 5 shows a chromatogram of pyrolysis products from a lyophilized sludge pyrolyzed at 700 °C. Besides other compounds, short chain fatty acids were identified. A first guess was that these compounds must originate from degradation processes because, given their volatility, they should have evaporated during the lyophilization step. In fig. 6, the top GC/MS chromatogram shows the

compounds released from the lyophilized sludge during thermal desorption at 275 °C; the bottom chromatogram shows the pyrolysis products formed at 700 °C from the same sample immediately following the thermal desorption analysis. The pyrogram doesn't show the short chain fatty acids even though these were present in the thermal desorption chromatogram. This indicates that the acids were in fact adsorbed on the matrix and were not formed by degradation of the macromolecules. Obviously, without the initial thermal desorption step, a pyrogram could have been interpreted incorrectly. Of course for a more detailed and more well-founded interpretation, a fractionation with higher resolution in terms of temperature steps (e.g. from 50 ° to 250 °C in steps of 50 °) should be considered.
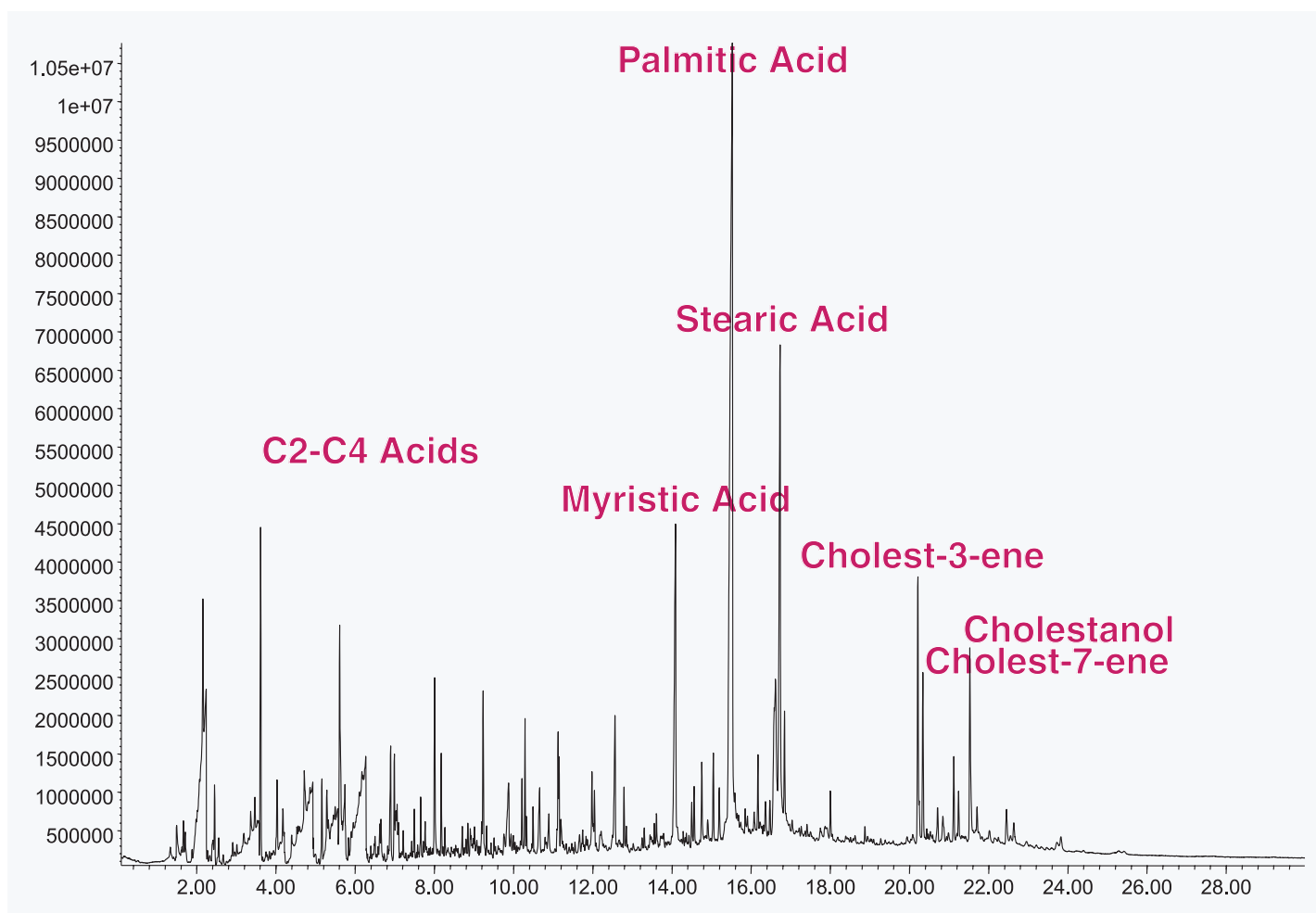

Figure 5: Pyrogram of a lyophilized sludge (700 °C, split 1:50, MSD).
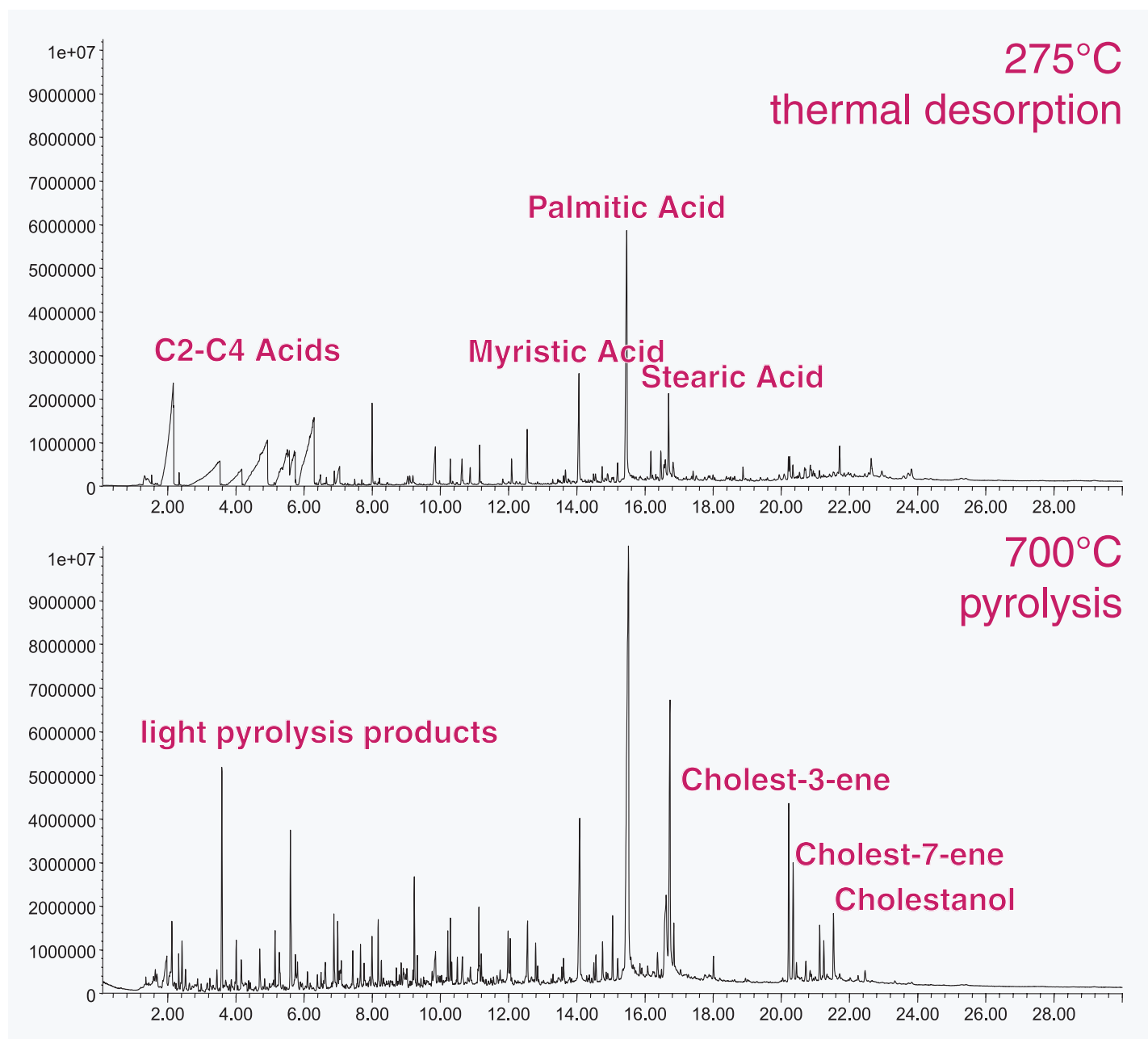
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Figure 6: MSD TIC chromatograms of a lyophilized sludge sample; top: After thermal desorption at 275 °C, bottom: Pyrogram resulting from pyrolysis of the same sample at 700 °C immediately after the thermal desorption step.

Sequential Pyrolysis

In contrast to the fractionated approach, sequential pyrolysis is performed by analyzing identical samples under different pyrolysis conditions, for example increasing the pyrolysis temperature, pyrolysis duration or varying the split ratio. Such a sequential procedure can be a great tool for optimizing a pyrolysis method and it may lead to more detailed information on the sample because at

lower temperatures there is less formation of secondary pyrolysis products. This means that in order to obtain information from primary pyrolysis of less stable compounds, the process may need to be performed at lower temperatures. If pyrolysis at low temperature does not lead to degradation of the more stable macromolecules in the sample, it must subsequently be performed at higher temperatures in order to get the information that is needed. Fig-

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ure 7 shows pyrograms of an acrylate glue obtained at different temperatures. At higher temperatures aromatic compounds are present in the pyrograms at increasing concentrations, indicating that secondary pyrolysis reactions are taking place. A pyrolysis temperature of 450 °C provides the most unadulterated view on the sample. Unfortunately, the major peaks in the chromatograms show signs of column overloading and peak broadening. In coming experiments, the sample size should be reduced and a polar column phase used instead of the HP5 MS column that was used in this case.
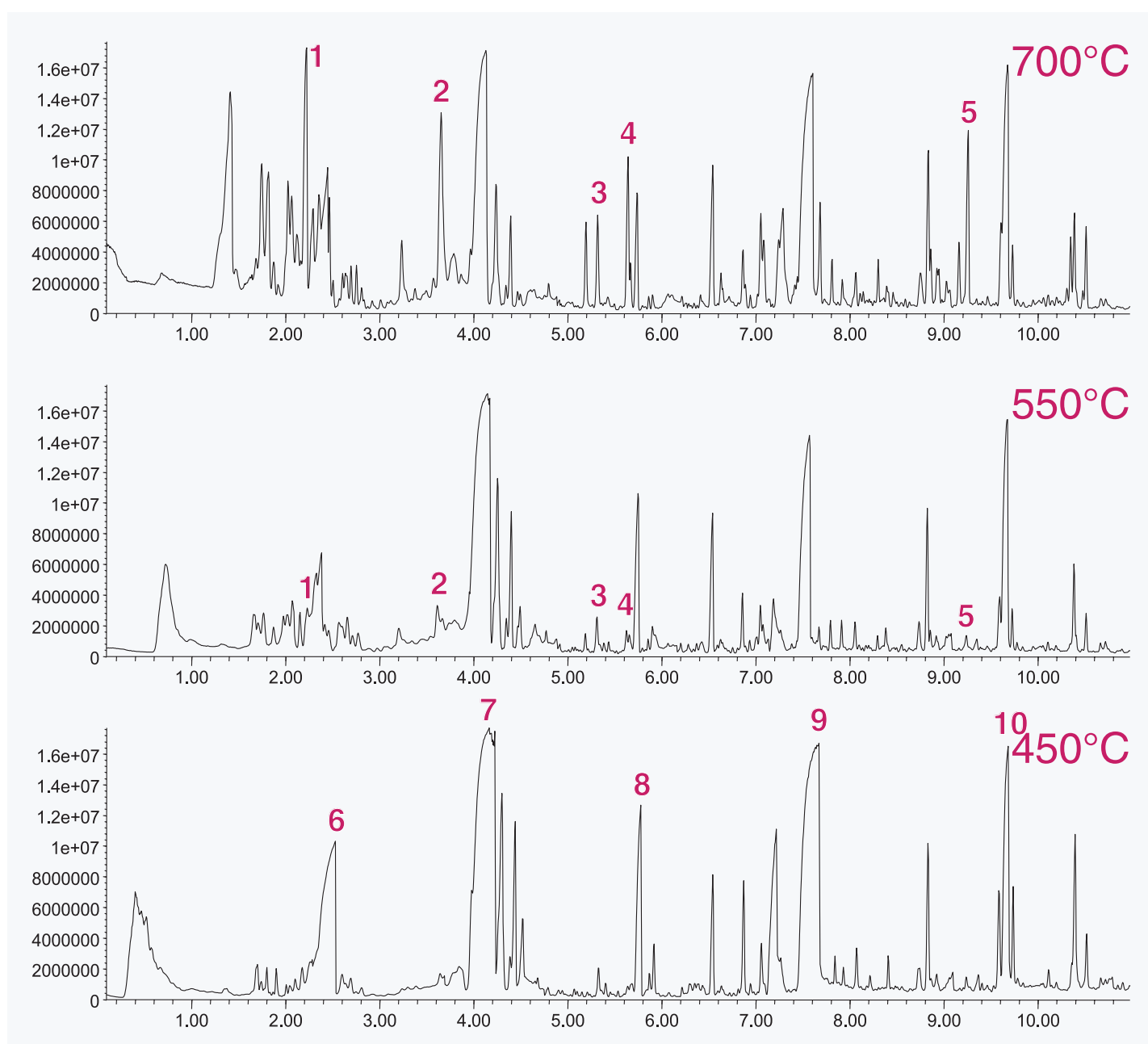

Figure 7: MSD TIC chromatograms resulting from pyrolysis of acrylate glue at increasing temperatures (450, 550 and 700 °C from bottom to top). [1) benzene; 2) toluene; 3) xylene; 4) styrene; 5) naphthalene; 6) 2-ethyl-1-hexene; 7) butylacrylate; 8) 2-ethylhexanol; 9) acetic acid, 2ethylhexylester; 10) 2-ethylhexylacrylate] At higher temperatures, aromatic compounds are present in increasing concentrations, indicating that secondary pyrolysis reactions are taking place.

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Pyrolysis of Trace Components

Normally pyrolysis is performed on almost pure solid or liquid compounds or on highly concentrated solutions. Instruments are therefore designed to work with high carrier gas flow rates and consequently high split ratios in order to avoid overloading the chromatographic system. The pyrolyzer used for this work is based on a thermal desorption system that can perform splitless analyte transfer and cryogenic focusing in addition to standard high split ratio operation. This added capability enables pyrolysis of macromolecules that are present only in trace concentrations. To test this approach aqueous solutions of a polyacrylamide coagulant at concentration levels of 1, 10 and 100 mg/L were prepared and 5 μL aliquots of each pipetted into vial type sample holders. The water was evaporated at slightly elevated temperatures and the polymer residue pyrolyzed at 800 °C. Analyte transfer from the pyrolysis module to the CIS was performed in splitless mode and the CIS kept cool in order to focus and concentrate volatile degradation products. In fig. 8, peak areas of the two main degradation products of the polymer as well as the combined peak areas of the degradation products are shown as a function of their concentration in aqueous solution. Although only single experiments were performed, it seems clear that there is a linear trend with correlation between peak areas and concentration. This indicates that pyrolysis of trace amounts of this polymer from aqueous solution can be performed reproducibly and automatically and that this could also be used as a basis for quantification.
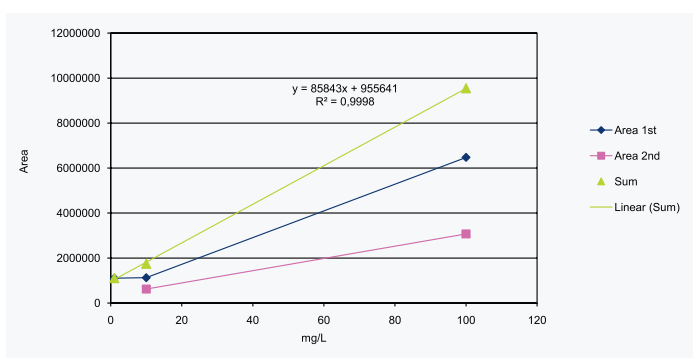

Figure 8: Quantitative pyrolysis of a coagulant residue in water. A 5 μL sample of a spiked solution was dried externally and the polymer residue pyrolyzed at 800 °C followed by splitless transfer of the degradation products and focusing in a cryotrap (CIS) prior to GC/MS determination using an MSD in SIM mode.

Solvent Venting

For the application example above a 5 μL aliquot of an aqueous solution was transferred to a pyrolysis sample holder and dried externally. This involves additional manual steps, which many laboratories are keen to avoid. The Thermal Desorption instrument used for the PYRO system has pneumatic and temperature programming capabilities that enable direct solvent venting. This means that the instrument can dry the sample prior to pyrolysis using solvent venting at slightly elevated temperatures. In order to test this capability a comparison of external drying and water removal with a solvent vent step was performed, the results of which can be seen in figure 9.
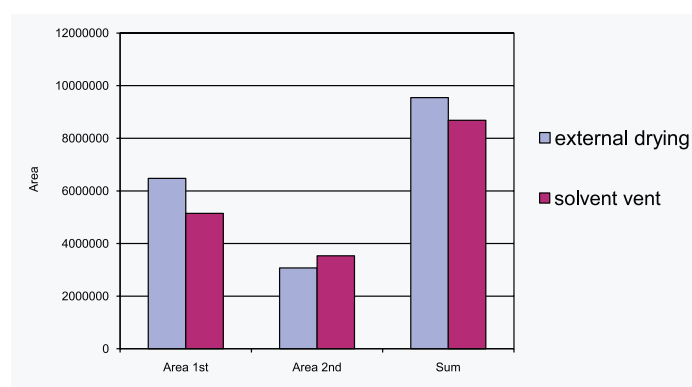

Figure 9: Comparison of peak areas and the peak area sums of pyrolysis products of a coagulant residue in water obtained by using external sample drying and solvent venting respectively. 5 μL aliquots of spiked solution were dried externally or using a solvent venting step in the Thermal Desorption unit (7.5 min, 90 °C, 50mL/min). Pyrolysis was performed at 800 °C, followed by splitless analyte transfer and focusing in a cryotrap (CIS). Chromatographic data were obtained using a GC/MSD system in SIM mode to determine the main degradation products.

The data shown in figure 9 demonstrate that using an automated solvent venting step gives results that are very similar to those obtained using external drying. In future applications, the effectiveness of such a solvent vent step for the removal of organic solvents will be investigated. This might be important, for example, when small amounts of highly adhesive or electrostatically charged particles have to be handled and inserted into sample holders. This task is more easily performed when such particles

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can be transferred to the sample holder using a solvent. Additionally, solvent venting can be helpful in order to reproducibly transfer exact amounts of polymers to sample holders. A defined small amount of polymer sample can be transferred more easily and reproducibly when a weighed in portion of the polymer can be dissolved and diluted in a solvent and a defined aliquot subsequently introduced into the pyrolysis instrument. The pyrolyzer presented here enables solvent removal from the sample by venting prior to pyrolysis.

Conclusion

A modular instrument design for pyrolysis GC is presented which is based on a filament type pyrolyzer in combination with a thermal desorption system and a GC autosampler used for sample introduction. Due to the modular design, the full functionality of the thermal desorption system, the PTV-type inlet, as well as the autosampler is preserved. This means that change-over between pyrolysis, thermal desorption, liquid injection, headspace sampling, or other analyte concentration techniques is easily performed. As can be seen from the results presented, the flexibility of the modular design is achieved entirely without compromising pyrolysis functionality and performance. All standard pyrolysis techniques such as pulsed, fractionated, and sequential pyrolysis are convincingly performed using the system presented here. Additionally, trace amounts of macromolecules in solution can be determined and quantification also seems realistic. Automated solvent venting effectively removes unwanted solvent prior to pyrolysis, potentially eliminating manual sample preparation steps and opening up new possibilities for highly accurate introduction of small amounts of polymer in solution.