

GERSTEL AppNote 148

Rapid Automated Screening of Extractable Compounds in Materials for Food Packaging, Medical or Technical Purposes

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Keywords

LabWorks Platform, Extractables, Leachables, Food Packaging Materials, Medical Materials, Automated Sample Preparation, Liquid Injection, Thermal Desorption Unit (TDU), Gas Chromatography (GC)

Abstract

This application note describes two automated methods for screening of extractable compounds from materials for food packaging, medical or technical purposes, both performed using the GERSTEL LabWorks Platform. The first method is based on automated liquid extraction performed by the GERSTEL MultiPurpose Sampler (MPS), the second involves thermal desorption of the material in question in the GERSTEL Thermal Desorption Unit (TDU). Both methods are suitable for gaining an overview of the quality and emission potential of a material and therefore useful in the search for a suitable packaging material. The methods deliver comparable qualitative results.

Introduction

Methods to determine the purity of a material or, in other words, the potential of a material to emit unwanted compounds are of importance for many industries. For example: Packaging materials used in the pharmaceutical and food industries should not release harmful compounds or compounds which alter the product characteristics; materials used in medical or technical devices should not contaminate the processed media; equipment used for chemical analysis should not contaminate the sample and so on [1-4].

In packaging material analysis two terms play an important role: Leachables and extractables. The term "leachables" encompasses all compounds, which leach from a packaging material into the packaged product under normal storage or use conditions - as well as those formed in reactions between the packaging material and the product. The "extractables" found in a particular packaging material are those compounds which can be extracted from the material under extreme conditions, for example using solvent extraction. By determining the extractables in a material, the emission potential of the material can be characterized, which is useful for an initial differentiation between suitable and unsuitable materials. Most extractables can be determined by gas chromatography.

This application note describes two automated methods for screening materials for extractable compounds. These easy and fast methods are currently used to check the quality of materials used in GERSTEL analytical instrumentation. These are in-house methods that do not conform to any norm or legislation.

Method 1 employs a liquid extraction (LE) of the material with ethyl acetate at 45 °C for 4 hrs in an agitator followed by a liquid injection into a GC/MS. Method 2 relies on thermal desorption (TD) at temperatures between 100 and 200 °C, depending on the material, followed by GC/MS analysis.

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Experimental

Instrumentation

Analyses were performed with a GERSTEL LabWorks Platform on a 7890 gas chromatograph equipped with a 5975 Mass Selective Detector (Agilent Technologies, figure 1).



Figure 1: GERSTEL LabWorks Platform on Agilent 7890 GC and 5975 MSD used for the determination of extractables from materials.

Materials

Samples were taken from household articles like plastic bags for food storage, plastic food wrapping film and polymer storage boxes as well as from the laboratory (SPE cartridges, disposable syringe needles etc.).

The liquid extraction was performed in standard 1.5 mL vials (093640-046-00) fitted with magnetic silicone white/PTFE red caps (093640-091-00). The agitator was equipped with adapters for 1.5 mL vials (093631-002-00). Ethyl acetate and isopropanol p.a. quality were used.

Thermal desorption tubes with a glass frit (013742-005-00) were used for direct thermal desorption analysis of materials in the TDU.

Sample Preparation and Introduction

All materials were cut using scissors or scalpels that had been cleaned with isopropanol.

Method 1 (Liquid Extraction, LE)

Pieces of polymer film from bags or food wrap measuring approximately 1.5 x 1.5-3 cm and pieces of thicker plastic material from other samples measuring around 0.2-1 x 1-1.5 cm were cut, briefly rinsed with isopropanol to remove external contamination and placed in vials. 500 μ L of ethyl acetate, the extraction solvent, to which 2.5 μ g of d_{10} -phenanthrene has been added as internal standard, was added to each vial. Ethyl acetate was chosen since it is a "universal" extraction solvent and since it is compatible with GC analysis. The internal standard was added in order to enable the comparison of results generated on different instruments and at different times. Blank samples were prepared using the same chemicals and equipment.

The remainder of the analysis was performed automatically by the analysis system. The MPS placed the prepared vials into the agitator in which the packaging materials were extracted for 4 hrs at 45 °C and agitation speed 750 rpm. An aliquot of 1.5 μ L of each sample was injected into the GC/MS. The GERSTEL MAESTRO software controls the system such that several samples can be extracted in parallel, with overlapping extraction and GC analysis for highest possible throughput and efficiency (figure 2).

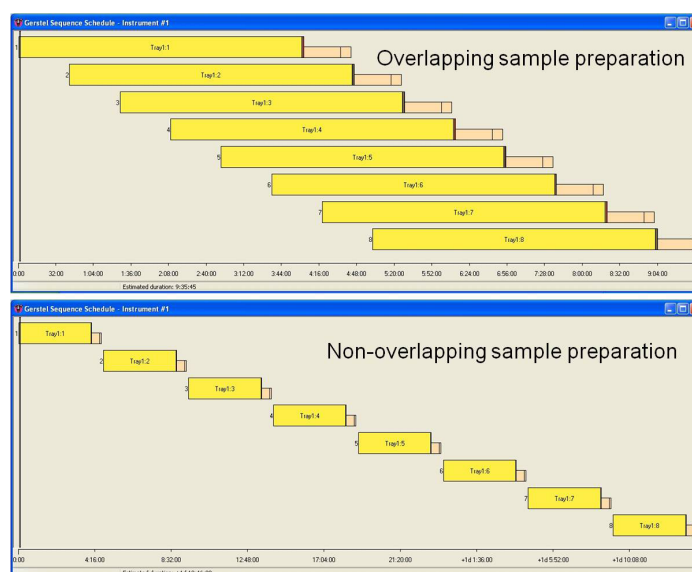


Figure 2: Runtime optimization through automatic multi-sample overlapping of extraction and chromatography under MAESTRO software control, illustrated in the form of the MAESTRO scheduler.

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The combination with liquid chromatography is possible by exchanging the extraction solvent following evaporation in the GERSTEL multi-position eVAPoration station (mVAP) and injecting the resulting solution into LC system through the injection valve.

In principle, it is possible to automate the addition of the extraction solvent using a 1 mL syringe mounted on a second autosampler tower. However, the syringe needle must penetrate the septum to add the solvent, which means the silicone layer could get into contact with the extraction solvent, increasing the danger of contaminating the sample with septum material i.e. silicone instead of only having the PTFE layer in contact with the extraction solvent.

Method 2 (Thermal Desorption, TD)

Pieces of material measuring around 0.3 x 1-1.5 cm were cut, cleaned with isopropanol, briefly left exposed to the air in order to dry, and placed in conditioned thermal desorption tubes.

The tubes were stored hermetically sealed on the MPS tray and automatically transported to the TDU. Following thermal desorption, analytes were refocused in the CIS, which was subsequently heated and the analytes transferred to the GC column. In order to avoid system contamination, the maximum desorption temperature for each sample was first determined by stepwise heating of the sample until it would begin to melt. The maximum desorption temperature was then set to 20 °C below the temperature at which the sample had started to melt. A blank chromatogram of each empty thermal desorption tube was recorded before using it.

Analysis Conditions LabWorks Platform- Method 1 (LE)

MPS (LE-Method)

Agitator	45 °C (4 h), 750 rpm
Syringe	10 µL
Inj. Vol.	1.5 µL

TDU (TD-Method)

Temperature	50 °C; 250 °C/min to 100-200 °C (1.6 min)
Pneumatics	Splitless

CIS (LE-Method)

Temperature	40 °C; 12 °C/s to 280 °C (20 min)
Pneumatics	Splitless
Liner	Baffled

CIS (TD-Method)

Temperature	-120 °C; 12 °C/s to 280 °C (20 min)
Pneumatics	Solvent Vent 30 mL/min, Split flow 20 mL/min @ 1 min
Liner	Packed with Glass beads

Analysis Conditions GC 7890

Temperature	50 °C (1 min); 18 °C/min to 325 °C (8 min)
Pneumatics	1.0 mL/min He, constant flow
Column	30 m Rxi-5ms (Restek) $d_i = 0.25$ mm, $d_f = 0.25$ µm

Analysis Conditions MS 5975

MSD	EI mode, full scan, 35-500 amu
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Figure 3: A sample extracted using method 1 (LE) inside a 1.5mL vial and a sample extracted using method 2 (TD) inside a TDU thermal desorption tube.

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Results and Discussion

Comparison of the results obtained using the two methods. Blank chromatograms of both extraction methods were highly satisfac-

tory, revealing no large peaks that could interfere with the analysis (figure 4).

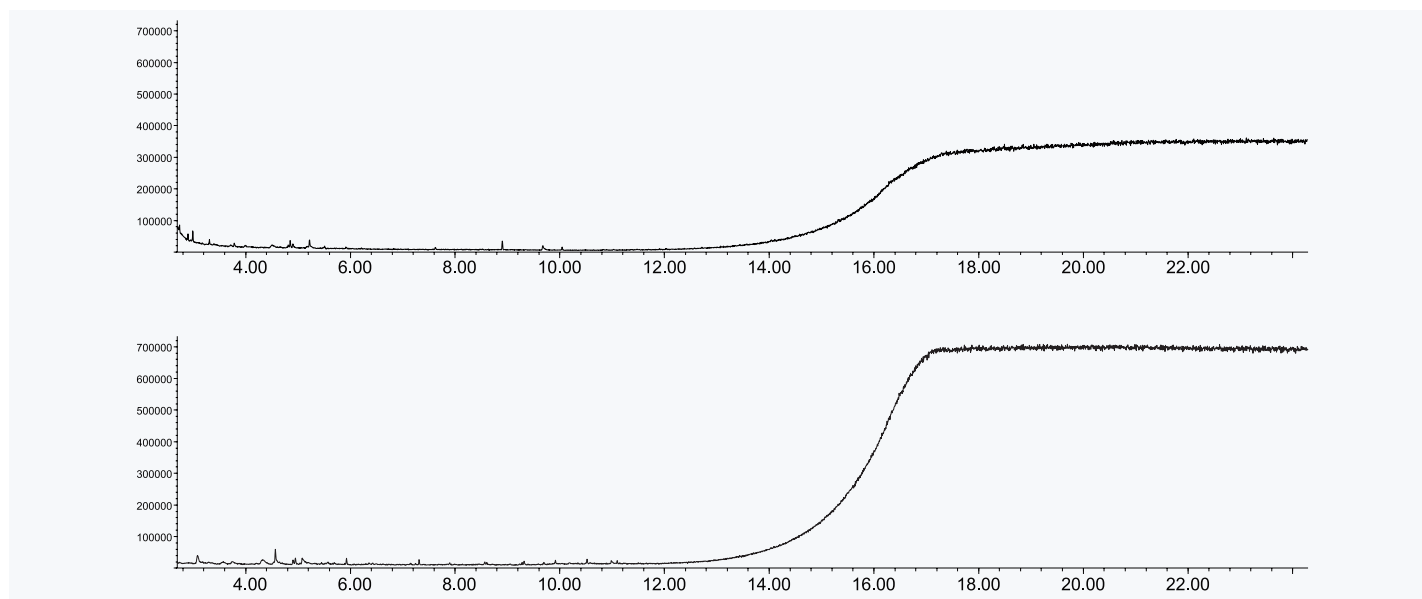


Figure 4: Blank chromatogram from method 1 (LE, top) and method 2 (TD). All peaks seen are small and do not interfere with the analysis.

Extracting a material for 4 hrs at 45 °C produces reliable results independent of the length of time the sample has been stored on the MPS tray before the extraction. This can be seen in figure 5 in which two chromatograms resulting from extractions of the same

material are shown: One sample of the material was extracted directly after it had been prepared, the other sample was prepared at the same time, but not extracted until it had spent ten hours in the MPS tray.

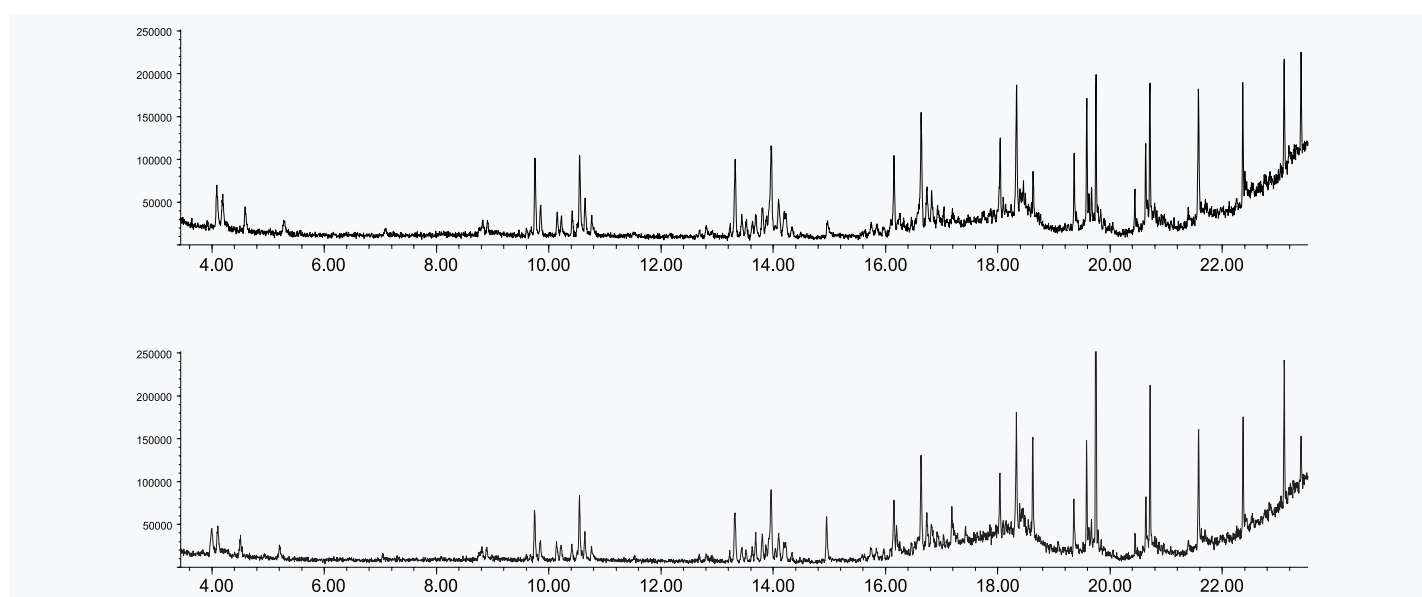


Figure 5: Extractables from a polymer lid extracted directly after adding ethyl acetate (top) and after 10 hrs in ethyl acetate. The results are the same, proving that the extraction method (four hours at 45 °C) is rugged.

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Figure 6 shows chromatograms resulting from extractions of a polymer lid of a plastic food storage container following method 1 (LE) and method 2 (TD). The same analytes, mainly branched n-alkanes, are extracted from the material by both methods giving the same chromatographic pattern. Under these conditions the

thermal desorption method, although performed with less sample, is much more sensitive (by a factor of 10-60) than the liquid extraction. However, high boiling compounds are extracted more efficiently by LE than by TD. Both methods are well suited to give an impression of the emission potential and quality of a material.

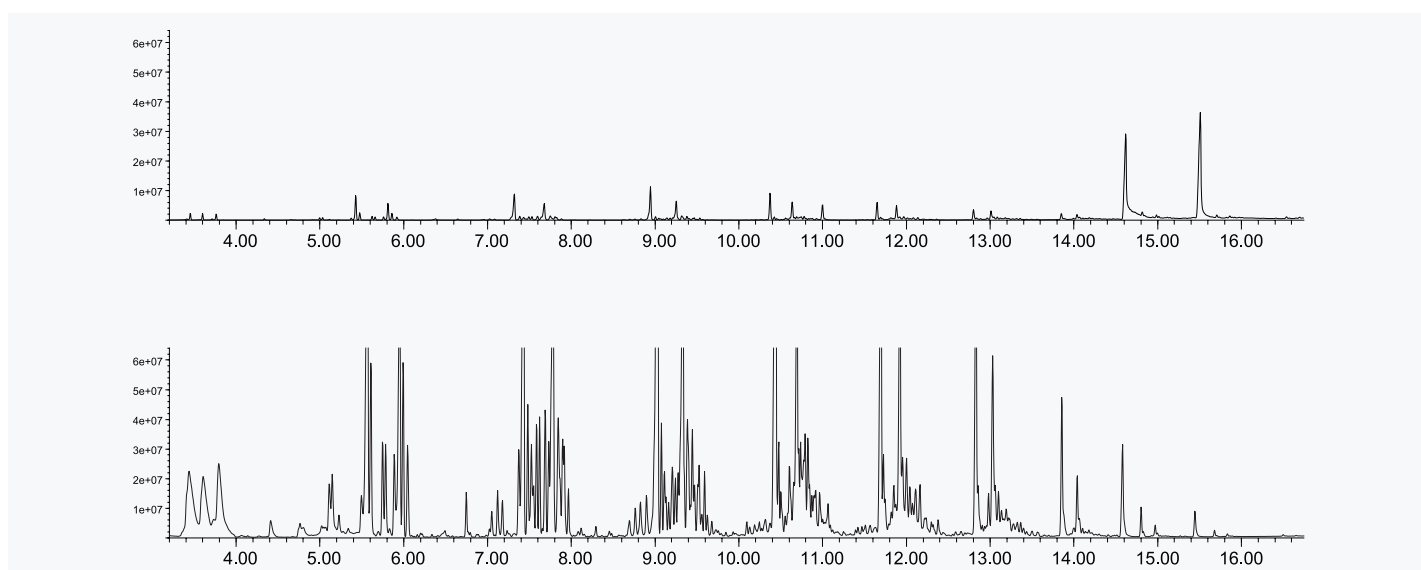


Figure 6: Extractables from the polymer lid of a plastic food storage box analyzed by method 1 (LE, top) and method 2 (TD). The same patterns are observed for both methods. The TD method is much more sensitive except when determining high boiling compounds.

By increasing the split ratio and reducing the desorption temperature of the TD method it is possible to adjust the compound signal intensities and to get comparable chromatograms from the

LE- and TD-based methods. This gives us two alternative analysis methods for a given material (figure 7).

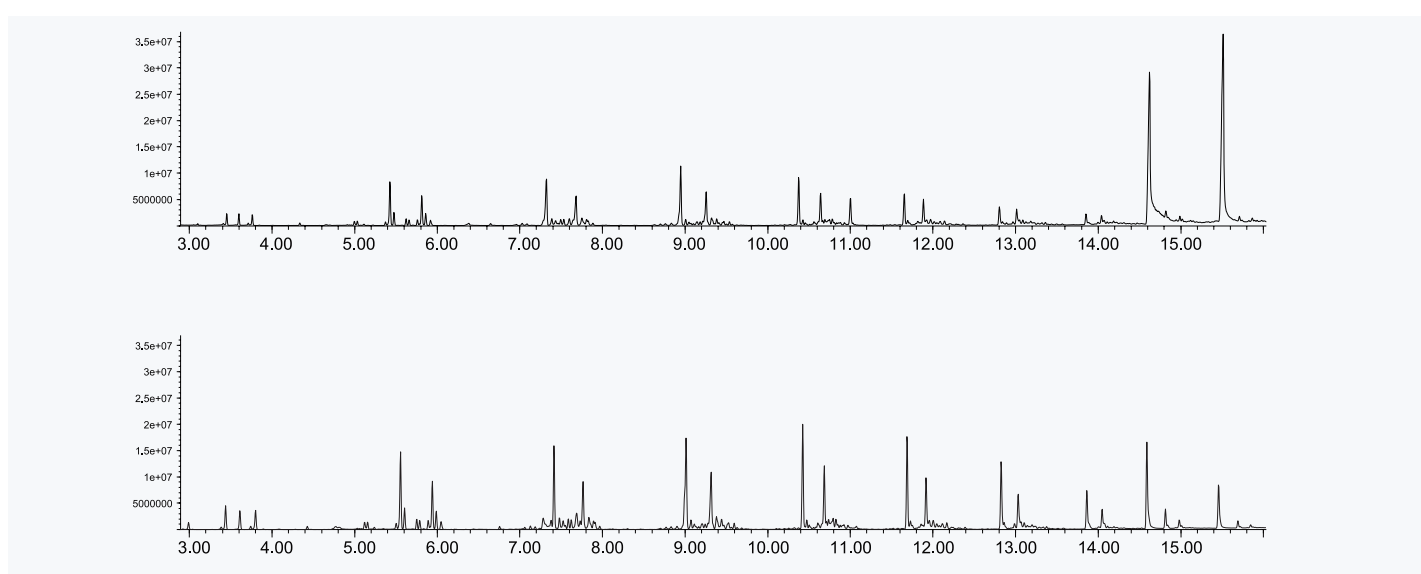


Figure 7: When the TD method parameters are adapted with lower desorption temperature and higher split ratio, the two methods give the same result for a given material and are therefore interchangeable except for the highest boiling compounds.

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Extractables Found in Samples [5]

Around 70 samples were analyzed using method 1 (LE). Generally, extractables in polymer materials are mainly monomers, oligomers or breakdown products from the polymer. Also additives like plasticizers, UV-protectants and catalysts can be found. In this section some interesting findings from the examined materials are discussed. As shown above both methods can be employed with similar results. Only chromatograms resulting from liquid extraction (LE) are shown and discussed here.

Most food packaging materials for single or multiple use are not

very clean. They often contain hydrocarbons, organic acid esters, organic acid amides, phenolic compounds and long-chain organic acids. In some samples, toxic monomers like organic isocyanates, endocrine disrupting chemicals (EDCs), such as bisphenol A and phthalates as well as other unwanted compounds, were found. Extractables profile examples are seen in figures 8-17.

Figure 8 shows an extractables profile from a film used for wrapping cheese. This profile is similar to those of many other olefine copolymers.

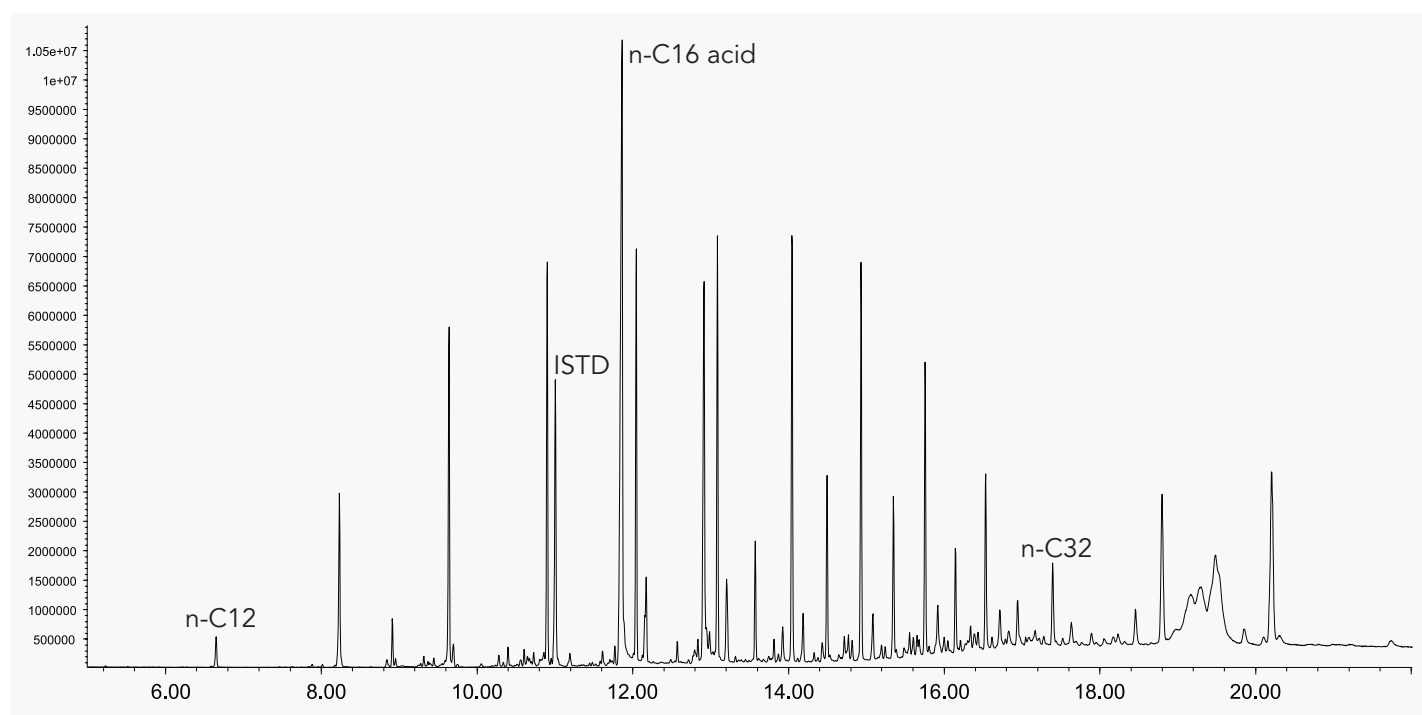


Figure 8: Extractables from a film used for wrapping cheese. Typical profile found for many olefine copolymers.

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Figure 9 shows a profile from a waxed paper. Such material is frequently used in the food industry and emits large amounts of long chain alkanes.

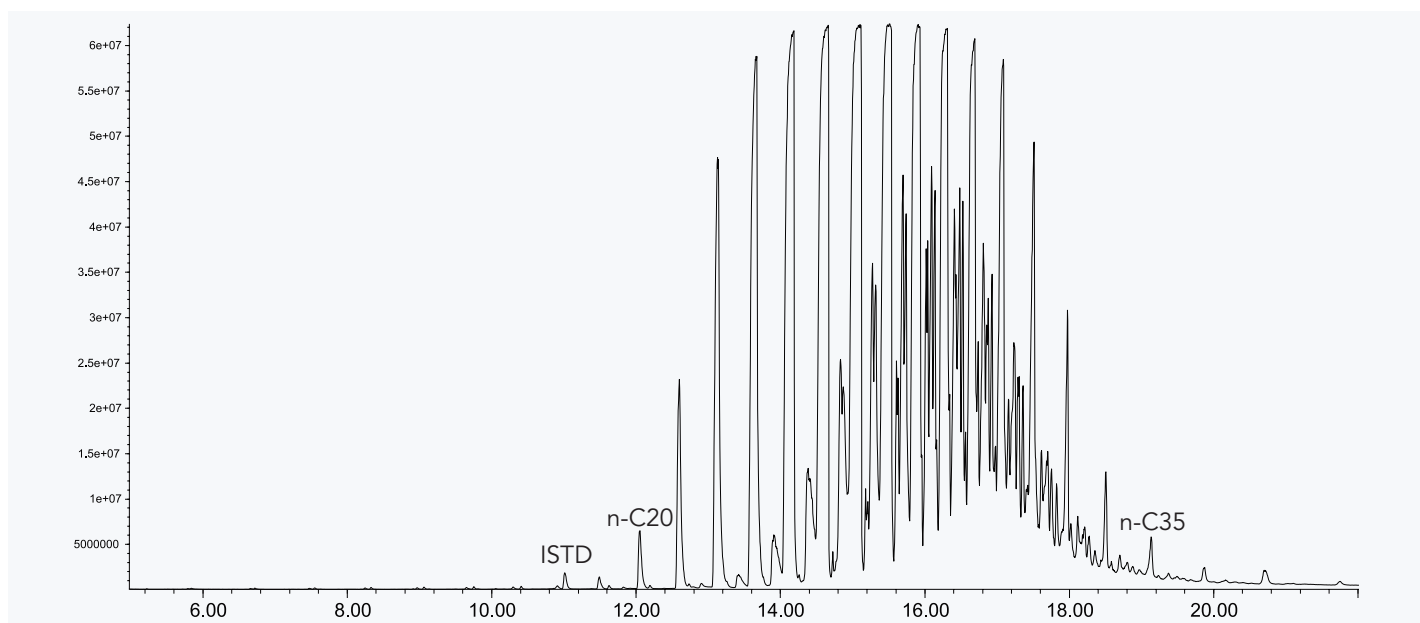


Figure 9: Extractables from a waxed paper used for wrapping sausage cold cuts.

Figure 10 shows a profile from a polymer film-based sausage packaging. Large amounts of compounds were found, including some that could affect the health of the consumer, such as di-

octylphthalate and diphenyl methanediisocyanate. Tributylacetyl citrate, a plasticizer used as substitute for phthalates was also detected.

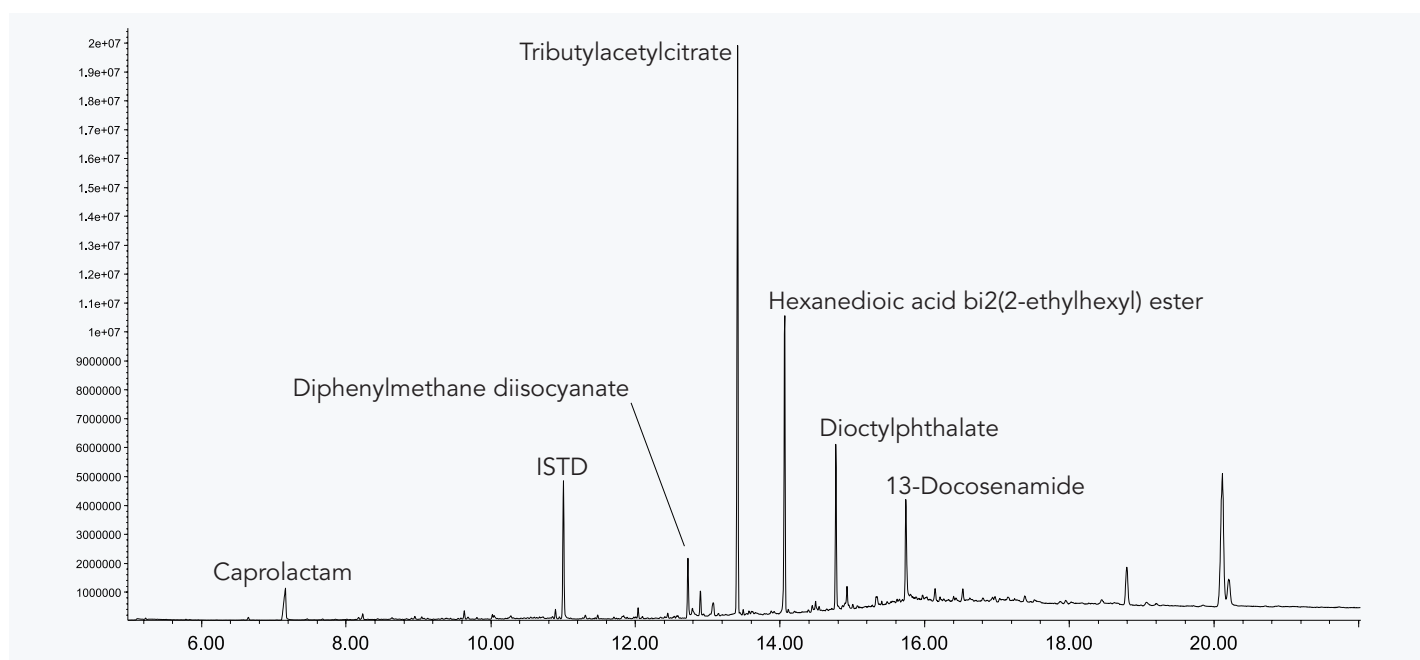


Figure 10: Extractables from polymer film-based packaging for sausages.

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Figure 11 shows the extractables profile of a microwave box. Among other compounds, drometrizole, a UV stabilizer, which,

according to the FDA, may be used in food packaging material, and bisphenol A, a known EDC, were found.

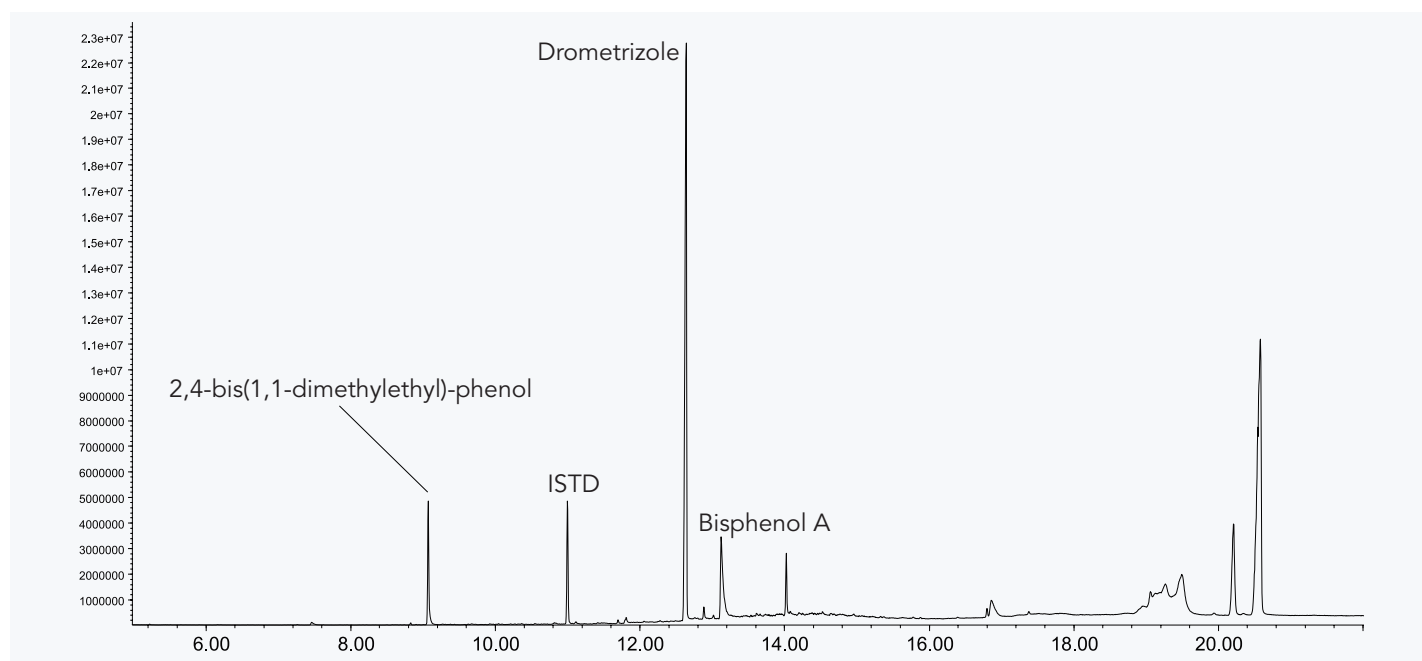


Figure 11: Extractables from a microwave box.

The manufacturer of a polymer foam used as seal in mineral water bottle closures (figure 12) has apparently substituted phthalate plasticizers with more "modern" substances such as tributylacetyl-

citrate and 1,2-cyclohexanedicarboxylic acid diisononyl ester. The latter was present in significant amounts. These compounds are also found in toys.

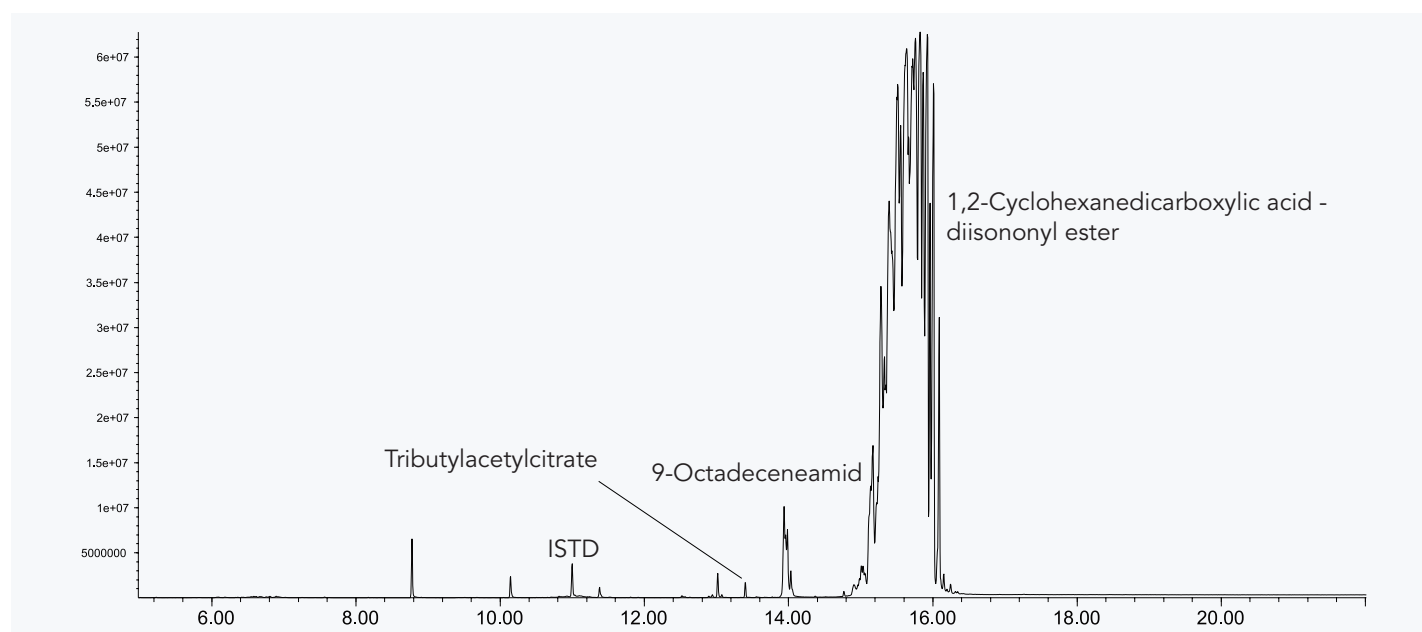


Figure 12: Extractables from a polymer foam used as seal in mineral water bottle closures.

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The toxic monomer toluene diisocyanate was found in a film-based closure used for packaging of fresh food (figure 13).

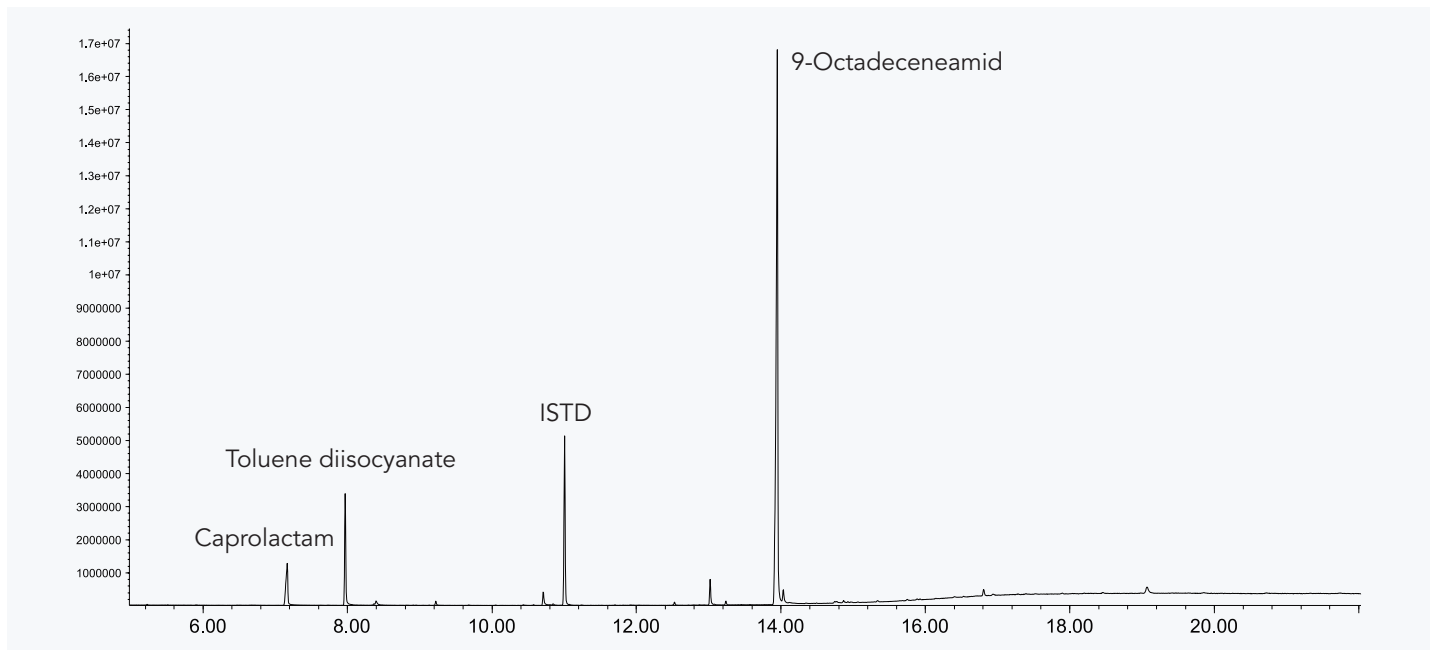


Figure 13: Extractables from a film-based closure used for packaging fresh food.

The lid of a microwave box, which was examined was of very high quality and emitted almost no compounds (figure 14). Unfortunately the only significant peak seen was dichlorobenzene, which

may in fairness have been introduced as a contamination during transport since 1,4-dichlorobenzene is generally used as a moth repellent on clothes.

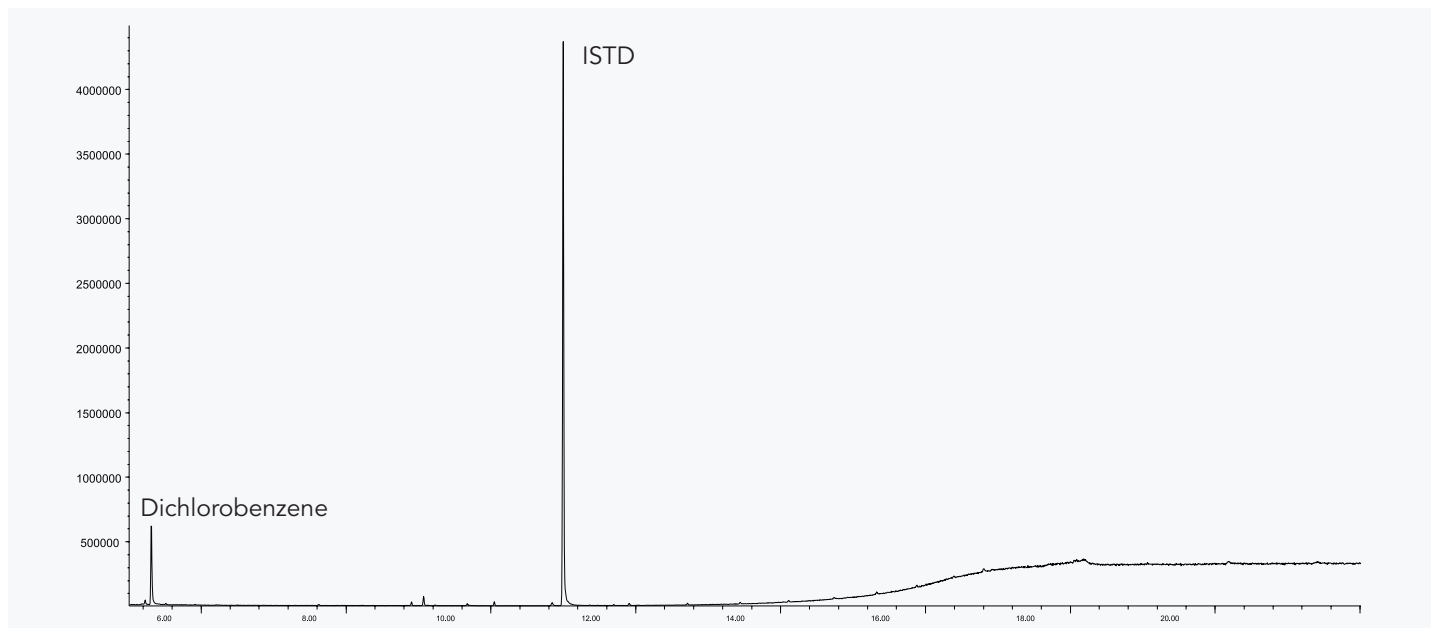


Figure 14: Extractables from a lid of a microwave box.

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Only a few packaging materials were found to be “clean”, one is shown in figure 15.

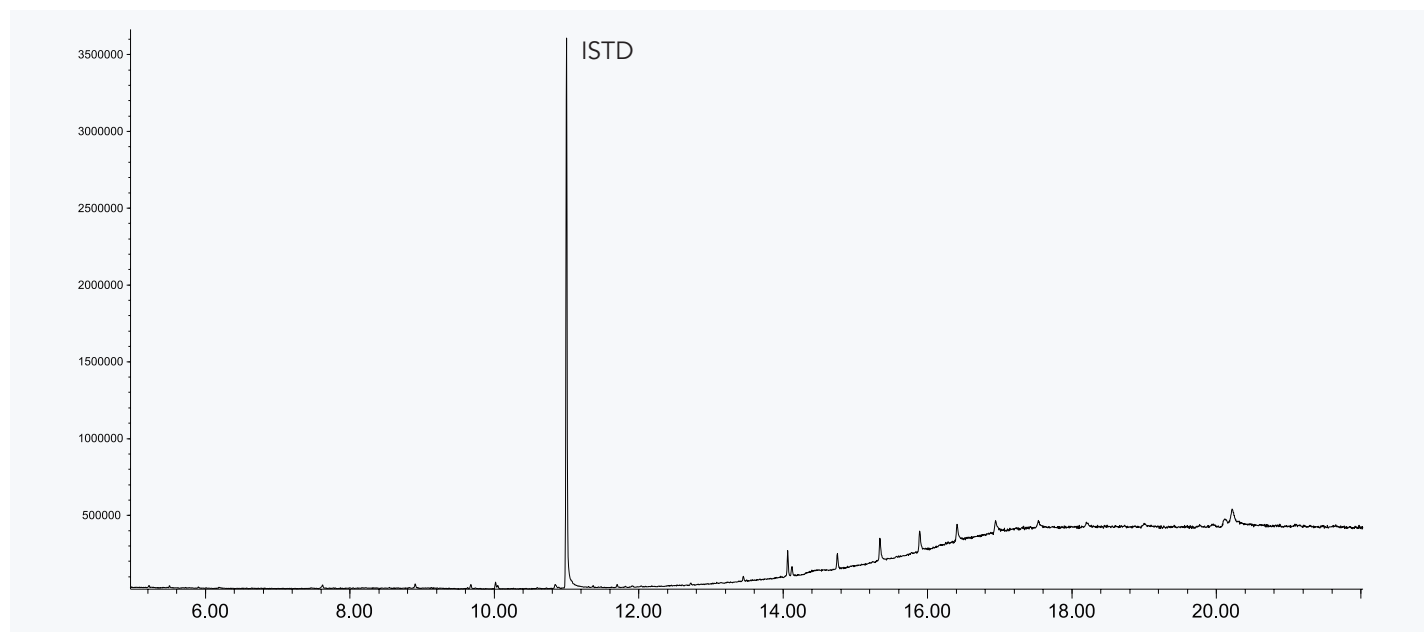


Figure 15: Extractables from polymer film-based packaging used for sausage cold cuts.

A comparison between materials from a polypropylene lunch box and from a polypropylene SPE cartridge showed that the polymer of the lunch box emits significantly more compounds. The chro-

matogram resulting from extraction of the SPE cartridge material shows that it is possible to produce clean polypropylene with good characteristics at a reasonable price (figure 16).

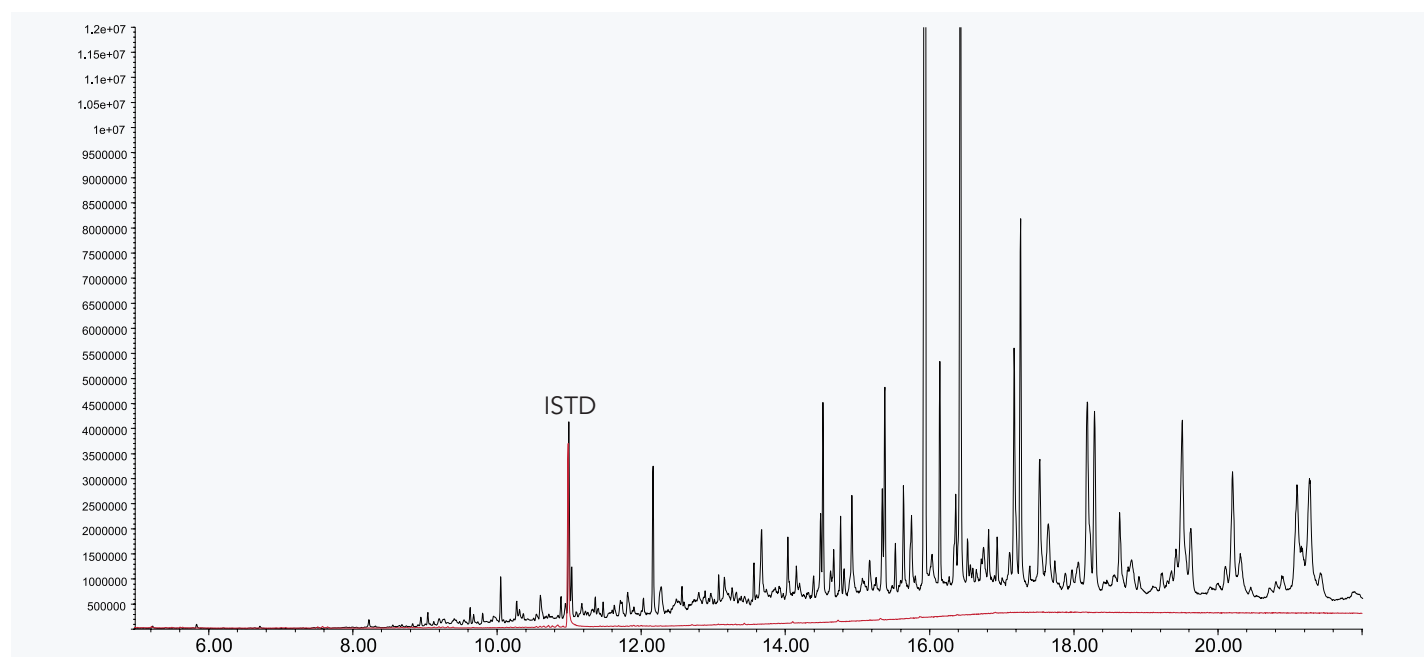


Figure 16: Extractable profiles for material from a polypropylene lunch box (black trace) and from a polypropylene SPE cartridge (red trace).

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The quality of materials for medical or laboratory devices is generally high. On the other hand, the extractables profile of an examined children's drinking bottle was found to be similar to, or even significantly worse than, that of a garbage bag we examined, emitting far more than the clean material used for medical devices (figure 17). This is astonishing and alarming since children are especially susceptible to contaminants and since most consumers use food packaging materials on a daily basis while they are rarely

exposed to medical devices. It must be kept in mind that this study deals with extractables and not with leachables, which means it is a worst case simulation. Also, most of the extracted compounds are regarded as non-toxic but exposure to some of these may still result in chronic health effects. Moreover, fat containing foodstuffs can be expected to extract organic compounds from packaging material quite efficiently.

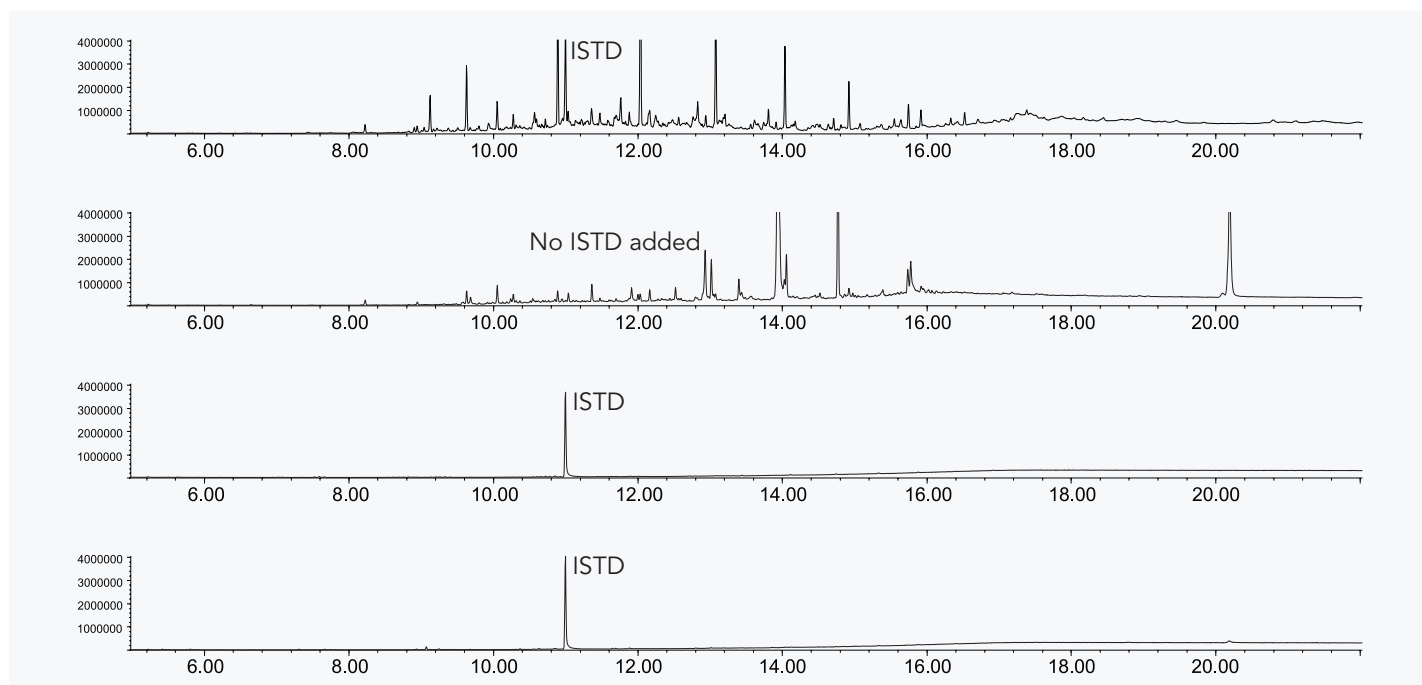


Figure 17: Extractables profiles of from top: 1) Children's drinking bottle, 2) Garbage bag, 3) SPE cartridge and 4) Plastic part of a disposable syringe needle. The profile of the children's drinking bottle is more similar to the profile of the garbage bag than to those of the SPE cartridge or disposable syringe.

Currently, aliphatic and aromatic hydrocarbons from mineral oil (MOSH/MOAH) contained in recycled cardboard and transferred to foodstuff through packaging are widely discussed [6]. Obviously this discussion needs to be expanded to address the quality of

food packaging material in general. It is fair to say that packaging materials should be monitored more and just maybe new legislation is needed.

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Conclusions

Two alternative methods for the qualitative determination of extractable compounds in materials were developed. The following was achieved:

- Two automated, rapid and easy methods for screening of extractables in packaging materials were developed.
- Comparable extractables profiles were obtained using the developed methods.
- The thermal desorption method was shown to be far more sensitive, but it could be adjusted to give similar intensities as the liquid extraction for better comparability.
- Liquid extraction was shown to be more sensitive for high boiling compounds.
- The quality of solvents and the emission potential of the extraction container were shown to be key factors that must always be checked carefully prior to the determination of extractables in a material.

Regarding the analytical results of the extractables screening the following statements can safely be made:

- Most of the examined food packaging materials showed a medium to high extractables profile.
- Hydrocarbons, organic acid esters, organic acid amides, phenolic compounds and long chain organic acids were the most widely found extractables.
- In some packaging materials, very critical compounds like isocyanates, phthalates, dichlorobenzene and bisphenol A were found.
- Examined materials for use in medical or laboratory devices were found to be clean. It is, in other words, possible to produce clean, high quality polymers at a reasonable price.
- Fat-containing foodstuffs are quite likely to be contaminated by compounds that are leached from the packaging material.

References

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