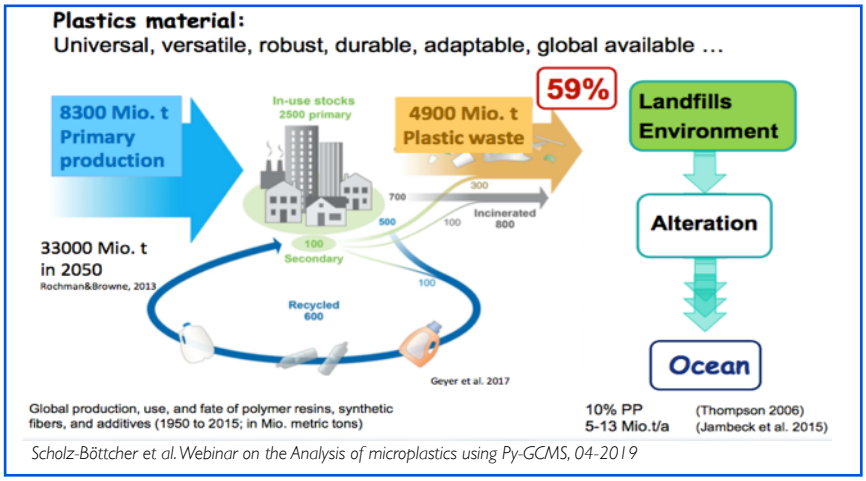
SRA INSTRUMENTS
ANALYTICAL SOLUTIONS

SRA Pyrolysis GC/MS Solutions for determination of microplastics

Introduction

Many analytical laboratories and scientists around the world are seeking new technologies and developments that can analyze these microplastics qualitatively and quantitatively. The analysis of microplastics is critical in many industries, such as food safety, drinking water, and consumer products. In addition, analyzing microplastics in seas and their effects on aquatic life and people who are endogenous to the islands enables scientists to create a social awareness on the pollution.



Scholz-Böttcher et al. Webinar on the Analysis of microplastics using Py-GCMS, 04-2019

One of the primary analytical techniques used for analyzing these microplastics is Pyrolysis-GC/MS.
Today, analytical pyrolysis encompasses much more than simple flash pyrolysis of polymeric materials. Multi-mode pyrolysis system can characterize virtually any material (liquid or solid) in microplastics: volatiles, additives, oligomers, polymeric, and heavier components.

Pyrolysis-GC/MS main advantages:

- **No Need for Solvent Extraction or Sample Pretreatment**

Many analytical techniques require multi-step sample preparation prior to chromatographic analysis. These procedures often include solvent extraction, filtration, and concentration. These traditional techniques are cumbersome, time-consuming, and suffer from analyst-to-analyst variability while producing data of limited value. Using the Pyrolysis GC/MS technique, samples are analyzed "as is". In fact, sample preparation using PY-GC/MS technique is very simple and straightforward; no solvent and no sample pretreatment needed. In other words, the solid and liquid samples can be injected into the Pyrolyzer without any solvent and sample pretreatment like solvent extraction. Eliminating the solvent extraction process enhances the precision of quantitative analysis while virtually prevent sample contamination and improves analytical efficiency.

- **Green and Thermal Extraction of Additives/Impurities**

This technique thermally extracts additives, volatiles, and lighter compounds from the polymeric mixture in the microplastics. The volatile compounds are thermally extracted by dropping the sample into the furnace (EGA provides the appropriate temperature to program the furnace). The volatiles collect at the head of the analytical column and are chromatographically separated. During the GC analysis of the additives/volatiles, the sample is lifted out of the furnace and rests at near ambient. Upon completion of the GC analysis, the GC oven is reset, and the pyrolyzer furnace temperature is raised (the EGA provides the appropriate temperature for the second analysis). The sample is dropped a second time into the furnace for pyrolysis. The Pyrolzates are trapped at the head of the column and subsequently separated. As a result, two sets of analysis can be performed on a single sample for thermally extracting the additives/volatiles from the polymeric and heavier components present in microplastics.
Think about the amount of money a laboratory can save over time with Pyrolysis-GC/MS capability. In addition to enhancing efficiency, saving a user's time and eliminating solvent costs, laboratories are protecting their scientists from solvent exposure while operating in an environmentally-friendly way.

- **Only Small Amount of Sample is Needed**

Traditional techniques performed by solvent extraction and sample pretreatment prior to the analysis require a significant amount of sample (usually several grams). In contrast, the Pyrolysis-GC/MS technique enables scientists to perform multiple analyses on a single sample using a few micrograms of samples. These sample sizes are particularly suited for microplastics samples. The sample can be easily placed in the Frontier Eco-Cup, then introduced into the GC/MS by the Frontier pyrolyzer for material characterization.

FRONTIERLAB PY-GC/MS SOLUTION for analyzing microplastics:

The Frontier EGA/PY-3030D is a versatile multi-shot pyrolyzer that offers temperature programmability from ambient (+10°C) to 1050°C with precise temperature control (+/- 0.1°C) of the ceramic micro furnace. This allows the user to analyze materials using a variety of techniques for greater flexibility. This system is capable of full automation of up to 48 samples with the AS-1020E Auto-Shot Sampler. Elegantly designed for qualitative and quantitative analysis with excellent accuracy and precision—guaranteed!

Features:

Frontier Pyrolyzer can analyze any organic materials using some or all of these techniques:

– **Evolved Gas Analysis (EGA)**
– **Thermal Desorption (TD)**
– **Heart-Cutting (HC)**
– **Pyrolysis (PY)**
– **Reactive Pyrolysis (RxPy)**
– **Single, Double or Multi-Shot Analysis**

F-Search software and four MS libraries provide essential tools for polymer and additive interpretation when using GC with MS detection.

Accessories add even more capability
– UV Irradiator (UV-1047E)
– Micro Thermal Desorption Sampler (PY-1060)
– Micro Reaction Sampler (PY-1050)
– MicroJet Cryo-Trap (MJT-1035E)

FRONTIER LAB

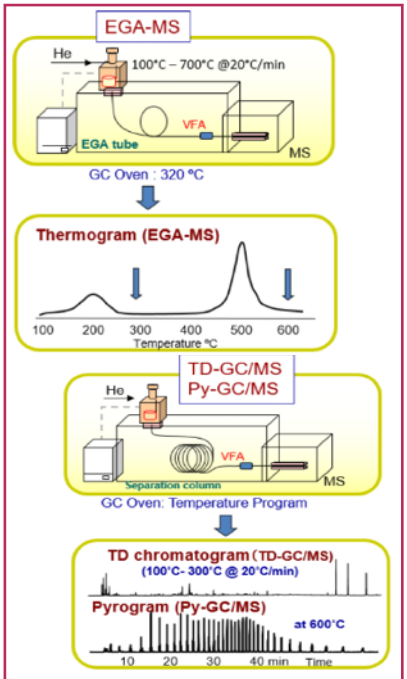
The Frontierlab Multi-Mode Pyrolyzer directly interfaced to a GC/MS system provides a **simple two-step method map for determining the composition of any unknown samples**.

Step 1 the first step in analyzing the unknown sample is Evolved Gas Analysis (EGA) technique. EGA provides a "picture" of the sample's complexity. In this technique, the sample is dropped into the furnace which is at a relatively low temperature. The furnace is then programmed to reach a much higher temperature. Compounds "evolve" from the sample as the temperature increases and then a plot of detector response vs. furnace temperature is obtained.

Step 2, is to analyze the thermal zones of interest obtained from EGA thermogram. Frontier Selective Sampler slices a thermal zone out of the sample and separates the components chromatographically using a Mass Spectrometer (MS). This technique is called Heart Cutting (HC) and provides up to 8 programmable temperature zones for analyzing the unknown sample. Volatile compounds can be reliably chromatographed using a Frontier MicroJet Cyro-trap that Cyro-focus the components at the head of the analytical column prior to starting the chromatographic run. Or a Thermal desorption chromatogram (referred to as TD-GC/MS) can be obtained by a customized temperature programming of the micro-furnace of pyrolyzer. After TD-GC/MS, the sample can be subjected to a pyrolysis temperature. The obtained pyrogram is then referred to as PY-GC/MS.

The F-Search Engine Library

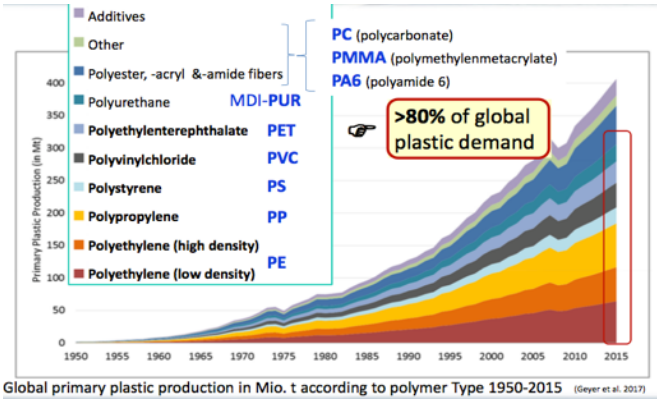
Microplastic materials often contain a variety of polymers and additives These compounds might be identified using commercial mass spectral (MS) libraries; however, these general-purpose MS libraries contain very few entries for pyrolyzates and additives. This severely limits their utility for polymer characterization.



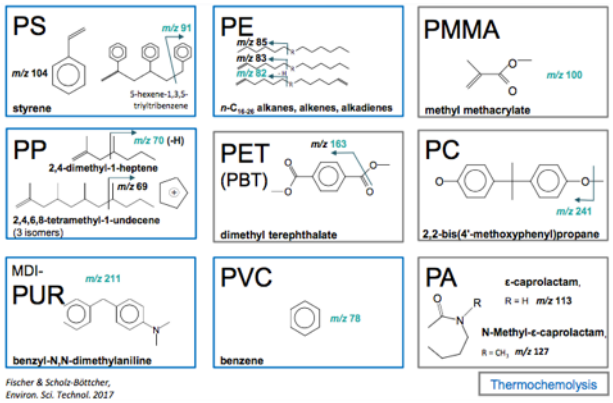
Double-Shot method using the obtained EGA thermogram from the Frontier Multi-Shot Pyrolyzer is developed. One can learn about the volatiles and/or additives in the sample by simply programming the Frontier Pyrolyzer furnace temperature from 100 to 300 °C. This stage of analysis identifies only the compounds between the set temperature range (100 – 300 °C) by transporting the evolved compounds to the head of the analytical column. To study the second peak in EGA, the furnace temperature can be set to 600 °C to obtain a pyrogram for any polymeric and/or heavier compounds identification. EGA uses a Frontier uncoated and inert stainless-steel tube (2.5m x 0.15mm i.d.) to connect the GC inlet to MS. Subsequence analyses (TD-GC/MS and PY-GC/MS referred to as Double-Shot) are performed using a Frontier analytical column (30m x 0.25mm x 0.25µm). Switching from the metal tube to the analytical column takes only minutes using Frontier Vent-free GCMS Adaptor (VFA).

To improve and simplify data interpretation, F-Search libraries are being used for analyzing the microplastics. The libraries include both chromatographic and mass spectral data. There are four unique libraries which allow users to select among them for specific purposes. The ability to create in-house specialty libraries is incorporated into the standard software. The custom user library enables scientists to perform contamination and comparative analyses on their microplastic

Py-GCMS Indicator ions of 9 polymers



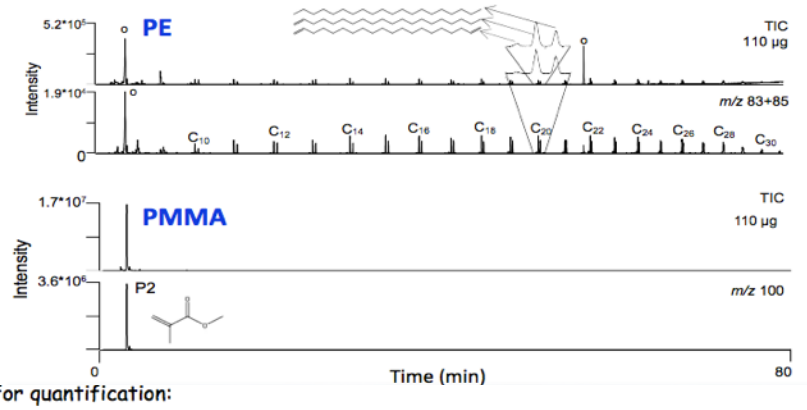
Global primary plastic production in Mio. t according to polymer Type 1950-2015 (Geyer et al. 2017)



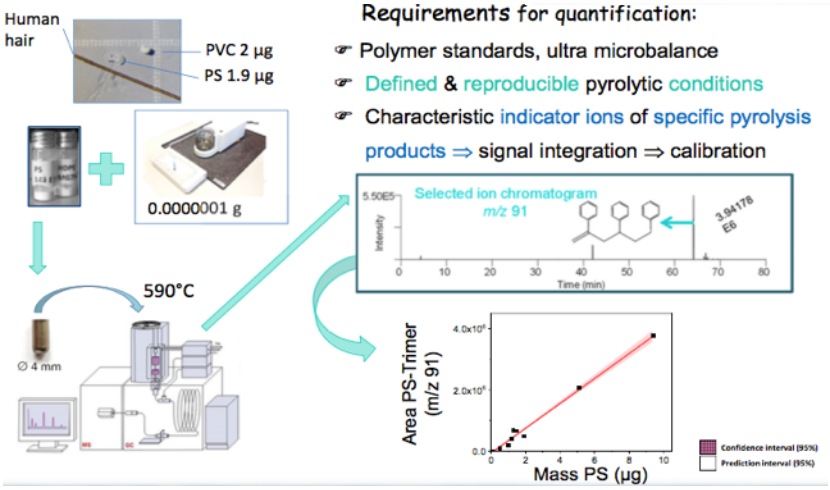
Fischer & Scholz-Böttcher, Environ. Sci. Technol. 2017

Thermochemolysis

Different pyrolytic behavior of polymers



Py-GCMS MP quantification



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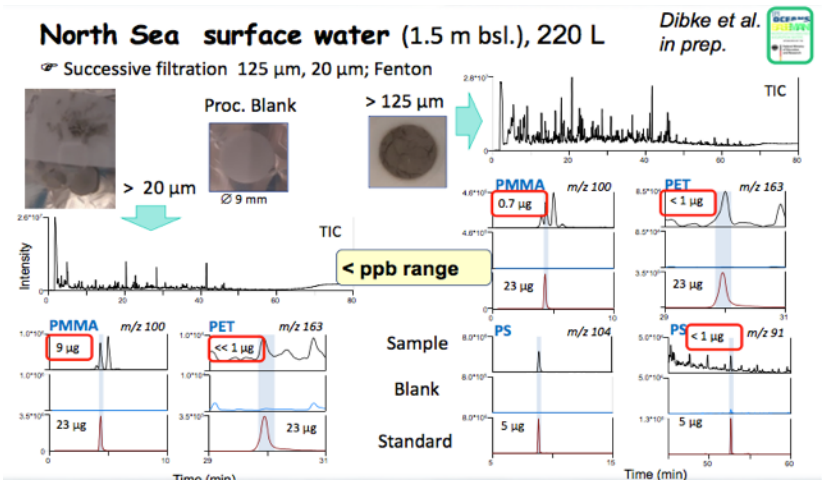
Py-GCMS – Environmental samples



Automated Pyrolysis GERSTEL PYRO

The GERSTEL PYRO enables highly flexible and efficient automated pyrolysis of solids and liquids at up to 1000 °C combined with determination in a GC/MS system of the thermal decomposition products. If required, thermal desorption and pyrolysis of the same sample can be performed in sequence, enabling the analyst to obtain the cleanest possible pyrogram and the maximum amount of information in the shortest possible time. When combined with GERSTEL MultiPurpose Sampler MPS, up to 196 samples can be pyrolyzed automatically in one batch.

The Pyrolyzer is very easy to operate:
The sample is placed in a sample holder, which is mounted onto the TDU pyrolysis transport adapter and placed in the MultiPurpose Sampler PYRO tray. The sample is then automatically inserted into the TDU Pyrolyzer. Pyrolysis break-down products are transferred directly to the GC column in split mode or refocused in the GERSTEL Cooled Injection System CIS before being introduced as a narrow band onto the GC column for separation.

PYRO features and benefits:
- Wide pyrolysis temperature range
- Programmed heating at rates ranging from 0.02 to 100°C/s.
- Split- or splitless operation
- Selectable cryo trapping
- Efficient and reliable automation
- Dedicated optimized sample holders for liquid and solid samples
- Flexible and proven resistance heating using Pt filament provides selectable pyrolysis temperature from 350-1000°C
- Liner in liner system / No valve in sample flow path
- Flexible modular system
- Integrated MAESTRO software control

Multiple pyrolysis technique available
PYRO performs:
- standard pulsed pyrolysis at temperatures from 350°C to 1000°C
- sequential pyrolysis on multiple identical samples in series
- fractionated pyrolysis on a single sample for more indepth information
- thermal desorption with solvent venting and pyrolysis of the same sample.

MPS autosampler with Pyrolysis Option mounted on an Agilent 8890/7010B GC/MS system

Thermal Desorption Unit TDU

The Thermal Desorption Unit (TDU 2) is a flexible automated solution for thermal desorption and thermal extraction.
The TDU 2 incorporates the latest advances in thermal desorption technology. Intelligently designed and based on a "Liner-in-Liner" concept it has no valves or transfer lines. The TDU 2 is connected directly to the GERSTEL Cooled Injection System (CIS), which serves both as a cryo-focusing trap and as a temperature programmable GC inlet. Active sites are eliminated, reducing the risk of analyte loss, discrimination and memory effects to an absolute minimum. The TDU 2 can be operated in split or true splitless mode enabling it to cover the widest range of concentrations, to protect the column from water and contamination and to achieve the lowest possible detection limits.

Several techniques are supported by the TDU:
- Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister
- Dynamic Headspace (DHS) based on standard headspace vials
- DHS Large based on sample containers up to 1 L volume
- Thermal desorption of adsorbent tubes used for air sampling
- Thermal extraction of solid samples placed in fritted TDU tubes
- Thermal extraction of liquid placed in µ-vials inside the TDU 2
- Direct introduction and thermal extraction of liquids such as standards
- Automated Pyrolysis of liquid and solid samples using the PYRO module
- When configured with the GERSTEL MultiPurpose Sampler (MPS), all technique are automatized
- Samples can be analyzed in one automated sequence using one or more methods.

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