GUIDELINE FOR THE FORENSIC EXAMINATION OF PAINT BY PYROLYSIS GAS CHROMATOGRAPHY – MASS SPECTROMETRY			
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GENERAL REMARK

This guideline assumes prior knowledge in the forensic discipline. It is based on consensus among the relevant forensic experts and reflects the accepted practices at the time of writing. The requirements of the judicial systems are addressed in general terms only.

TABLE OF CONTENTS

1.   AIMS

This guideline is intended to assist individuals and laboratories in the utilization of Pyrolysis Gas Chromatography - Mass Spectrometry (abbreviated to PGC-MS or PyGC/MS) in the forensic examination of coatings and polymeric materials. It will also address the fields of application, the different modes of pyrolysis and evaluation of PyGC/MS methods for the characterisation and comparison of paint resin systems and polymers. It is designed to be used in conjunction to the Best Practice Manual for the Forensic Examination of Paint EPG-BPM-001 [1].

2.   SCOPE

This guideline is intended to provide understanding of the possibilities, advantages, limitations and the proper use of PyGC-MS. Users of the PyGC/MS method should at least be able to discriminate paints, binders and polymers. Further discrimination by detection of additives is an asset and can extend the value of conclusion.

3.   TERMS AND DEFINITIONS

For the purposes of this guideline, the relevant terms and definitions are given in ENFSI documents, in ILAC G19 [2], in ISO/IEC 9000 [3], ISO/IEC 17020 [4] and ISO/IEC 17025 [5] standards, and in ASTM E1610-18 [6] apply. Specific technical terms used in this guideline include:

Terms	Definition
Furnace pyrolyzer	Pyrolyzer having a pyrolysis chamber of several ml size. Normally low heating rate.
Filament pyrolyzer	Pyrolysis is obtained by contacting the sample to a filament that is heated by an electric current. The light emitted by the filament provides a means to control the pyrolysis temperature (see Optical temperature control).
Curie point	Pyrolysis takes place on a ferromagnetic piece of metal which is heated by a high frequency electromagnetic field. At the Curie point temperature, the material loses its ferromagnetic properties and heating stops. Material with Curie point temperatures between 300 °C and 750 °C are available.
Split flow	Part of the gas-flow through the pyrolyser which is vented instead of being applied to the chromatographic column.
Purge flow	Gas flow through the pyrolyser before starting the pyrolysis which is vented.
Low temperature pyrolysis	Heating the sample to max. 300 °C. There is hardly any real pyrolysis. Useful to determine high boiling compounds in polymer blends such as e.g. plasticizers and stabilisers in paint films.
Transfer line	Heated inert tubing connecting pyrolyser and GC injector.
Pyrolysis temperature	Nominal temperature, selected on the pyrolyzer controller.
Volume of the pyrolysis chamber	Volume in the pyrolyzer heated to high temperature during the pyrolysis.
Automated pyrolyzer	Apparatus which introduces samples sequentially and automatically.
Coil pyrolyzer	The sample is placed in a small quartz tube which is heated by a surrounding metal coil.
Sample mass	Weight of the sample to be pyrolyzed. Depending on the sample 10 to 50 µg.
Heating rate	Nominal heating rate set on the pyrolyser controller.
Transfer line temperature	Temperature of the transfer line. Very critical as temperatures > 300°C may promote secondary degradation of the pyrolysis products, temperatures < 200°C will significantly discriminate high boiling pyrolysis products.

Terms	Definition
Temperature of the pyrolysis chamber	Temperature of the pyrolysis chamber when no heating for pyrolysis takes place. Usually 280°C.
On-column cryofocussing	Method to improve the band-width of early eluting peaks by trapping the low boiling pyrolysis products on a temporarily cooled section at the beginning of the chromatographic column.
Effective pyrolysis temperature	Pyrolysis temperature depending on the experimental conditions producing the same as the "standard pyrogram" at that temperature.
Optical temperature control	The temperature of the pyrolysis device is controlled by measuring its optical emission.
Temperature control by resistivity	The temperature of the pyrolysis device is controlled by measuring the resistivity of the heating coil or foil.
Ballistic heating	Heating at maximum rate depending only on the output of the power supply used for heating.

4.   BACKGROUND

4.1 Introduction

Pyrolysis is the breaking apart of chemical bonds by use of thermal energy. Analytical pyrolysis is the technique of studying molecules either by observing their behaviour during pyrolysis or by studying the resulting molecular fragments. The analysis of these processes and fragments tells us much about the nature and identity of the original larger molecule. The production of a variety of smaller molecules from a larger original molecule has fostered the use of pyrolysis as a sample preparation technique, extending the applicability of instrumentation designed for the analysis of gaseous species to solids, and especially polymeric materials. As a result, GC/MS may be used routinely for the analysis of samples such as synthetic polymers, paints, biopolymers, composites and complex industrial material.

The fragmentation, which occurs during pyrolysis, is analogous to the processes that occur during the production of a mass spectrum. Energy is put into the system, and as a result, the molecules break apart into stable fragments. If the energy parameters (temperature, heating rate, and time) and the sample amount are controlled in a reproducible way, the fragmentation is characteristic of the original molecule, based on the relative strengths of the bonds between its atoms. The same distribution of smaller molecules will be produced each time an identical sample is heated in the same manner, and the resulting fragments carry with them much information concerning the arrangement of the original macromolecule.

The application of pyrolysis techniques to the study of complex molecular systems covers a wide and diversified field.

4.2 Basic principles

During pyrolysis, polymeric materials may degrade via a number of mechanisms, which are generally grouped into three classes, namely: random scission, monomer reversion and side group elimination.

4.2.1 Random scission

Polyolefins generally degrade by this mechanism, and polyethylene is a good example.
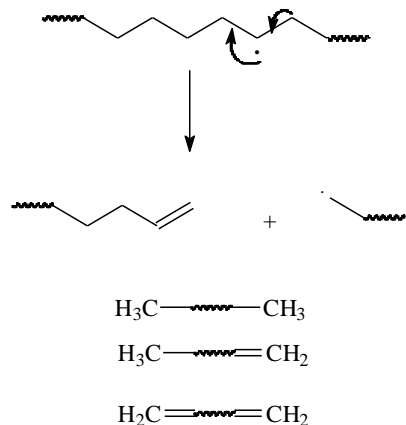
Figure 1: Random scission

When a free radical is formed along its chain, scission occurs producing a molecule with an unsaturated end and another one with a terminal free radical. This free radical may take hydrogen from a neighbouring carbon, producing a saturated end and a new radical, or combine with another free radical to form an alkane. Multiple cleavage produces molecules small enough to be volatile, with double bonds at both ends, one end, or neither. Since scission occurs randomly, molecules are produced with a wide variety of chain lengths. These appear in the pyrogram as a series of triple peaks: an alkane, an alkene and a diene.

4.2.2 Monomer reversion

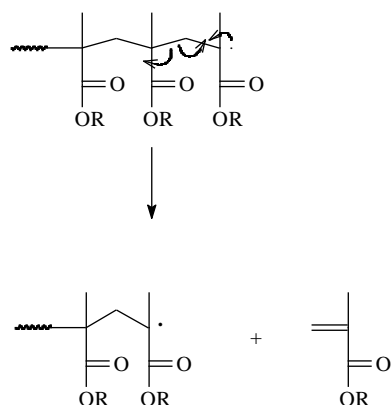Several polymers degrade by this mechanism, including polystyrene and poly (meth)acrylates.

Figure 2: Monomer reversion

When a free radical is produced in the backbone of polyethyl methacrylate for example, the molecule undergoes scission to produce an unsaturated small molecule (ethyl methacrylate) and another terminal free radical. This radical will also cleave to form ethyl methacrylate and propagate the free radical.

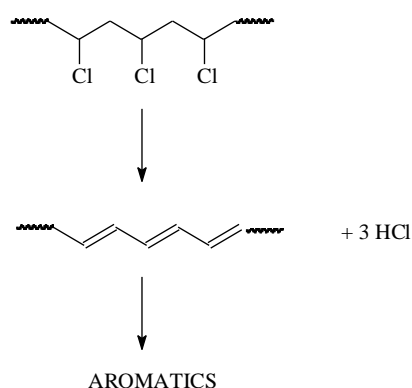## 4.2.3 Side group elimination

Figure 3: Side group elimination

A good example is polyvinylchloride (PVC). PVC first undergoes a loss of HCl to form a conjugated polyene backbone. This unsaturated chain further degrades forming aromatic as well as some smaller unsaturated hydrocarbon fragments. The main pyrolysis products (in addition to HCl) are benzene, toluene and naphthalene. Small amounts of chlorinated aromatics may also be produced, which indicates that some chlorine is still attached to the polymer chain during aromatisation.

4.3 Other factors

The most significant parameter is the pyrolysis temperature. Low pyrolysis temperatures lead to selective bond cleavage and result in a small number of relatively large degradation products. At medium pyrolysis temperatures the number of reaction pathways increases resulting in a larger number of pyrolysis products. At high pyrolysis temperature, however, low molecular weight fragments of low diagnostic significance are formed.

The heating rate also plays an important role in pyrolysis. Samples heated slowly will degrade considerably before the set pyrolysis temperature is reached. Consequently, reproducibility will depend heavily on the ability of the instrument to heat the sample rapidly, reproducibly and uniformly.

5. SAMPLE HANDLING AND PREPARATION

5.1 Sample amount

As a rule of thumb a minimal sample amount corresponding to 10 – 50 µg of polymer material should be suitable for binder and polymer discrimination. Thorough analysis of additives for discriminating homogeneous samples (plastic materials, clear coats) demands 4 to 5 times this amount of sample.

5.2 Sample preparation

Analysis should consider individual layers, either single layer paint or sectioned multilayer systems.

In multilayer systems it is mandatory to analyze and compare the corresponding layers. Sample preparation should be performed according to one of the following methods:
- Scraping or cutting the layer to be sampled using a scalpel blade (if necessary after having removed the upper layers of no interest). This method should only be used, if the successive layers present a sufficient colour difference.
- Sectioning of cross sections: 3 – 10 µm thin cross sections obtained by using a microtome can be sectioned using a low power microscope and a razor blade.

Samples should be cleaned in order to avoid contamination. Two methods are available for samples of at least 1 mm size:
- In case of sufficient sample thickness the surface of the top layer is scraped off using a scalpel blade.
- The surface is cleaned using a cotton swab moistened with alcohol or water, and thoroughly dried before analysis.

5.3 General sample considerations

The masses of samples to be compared must not differ by more than ± 20 % w/w. Otherwise it has to be demonstrated that the sample mass does not influence the pyrograms significantly.

The surface to volume ratio of samples to be compared should be as equal as possible.

The position of the samples in/on the device used for the actual pyrolysis should be kept constant.

Good thermal contact between sample and the pyrolysis device is important.

5.4 Sample application

5.4.1 Application as a thin film

If a sufficient amount of sample is available, a highly concentrated solution of the sample in an appropriate solvent can sometimes be prepared. Application of this solution to the device, creates very favourable conditions with respect to a reproducible pyrolysis.

5.4.2 Sample fixation by mechanical means

As in Curie point pyrolysis metal foils are used for heating, the sample can be squeezed between parts of the metal foil, a metal wire or a metallic tube.

5.4.3 Sample fixation by thermal means

If the sample has thermoplastic properties the sampling device can be heated up to 250°C, in order to melt the surface of the sample onto the surface of the pyrolysis device.

It should be demonstrated there is no negative influence on the pyrograms due to sample breakdown.

5.4.4 Sample fixation by using sticking compounds

Compounds used for inline derivatization (TMAH, TBAH) as well as low boiling solvents partially dissolving the sample are appropriate means to fix the sample on/in the pyrolysis device.

6.   METHODOLOGY

6.1 General

The pyrolysis method selected depends very much on the compounds considered indicative of a certain material. Pyrolysis products of paint very often contain melamine, fatty acids or polyols. These polar compounds have to be derivatized for optimum detection. The reagent of choice is tetramethyl ammonium hydroxide (TMAH).

For optimum gas chromatographic separation of the non-polar and polar compounds more polar stationary phases like polysiloxane with 35% phenyl are recommended.

6.2 Low temperature pyrolysis

In order to detect small amounts of additives and solvents in the polymer matrix it is mandatory to evaporate the target analytes without pyrolysing the bulk material. The useful pyrolysis temperature range will be 300°C to 400°C, depending on the thermal contact within the pyrolysis unit.

6.3 High temperature pyrolysis

The optimum pyrolysis temperature for organic polymers is between 550°C and 700°C.

6.4 Step pyrolysis

High and low temperature pyrolysis are combined within one single analysis. This is not possible in a Curie-Point pyrolysis unit.

6.5 Replicate analysis

Every pyrolysis should be performed at least in duplicate provided enough sample is available. If the larger peaks surface area ratios of replicate pyrograms do not match within 20%, a third analysis should be performed.

7. INSTRUMENTATION

The standard parameters used for the pyrolysis of paint samples and recommendations are described further in this section.

7.1 Pyrolyzer conditions

The pyrolyzer chamber temperature should be high enough to prevent condensing of the pyrolysis products inside the chamber. Actual settings depend on the instrument used and should be set according to the manufacturer's recommendations.

Heating rate: a fast heating rate avoids secondary reactions between pyrolysis products. It should be reproducible in order to yield significant results.

The final pyrolysis temperature depends on the sample: for bulk products in most cases pyrolysis temperatures between 550°C and 700°C are chosen; for evaporation of additives temperatures should be between 300°C and 400°C.

The pyrolysis time should be optimized on the actual instrument.

The amount of sample depends on the sample and the chromatographic conditions used.

7.2 Gas chromatography conditions

The analytical column should be suitable to separate the common pyrolysis fragments. Capillary columns (30 metre length, 0.25 – 0.32 mm internal diameter, 0.25 – 1.0 µm film thickness) with an apolar to slightly polar stationary phase (dimethyl siloxane with max. 35% phenyl groups) are suitable.

The carrier gas is helium, its flow adjusted to optimal chromatographic separation efficiency on the column used.

The injector should be set to a temperature high enough to prevent condensation of pyrolysis fragments. 280°C is recommended.

The split ratio should be set high enough to obtain good peak shapes for early eluting peaks, depending on the instrument a ratio of 1:10 to 1:20 should be chosen. For small samples in casework using splitless injection is an option.

The oven temperature program recommended settings are:
- start temperature 40°C, hold for 3 min;
- ramp 10°C/min rate to 320°C depending on the column and manufacturer recommendations;
- hold at final temperature for 10 min.

The recommended transfer line temperature is 280°C – 320°C in order to avoid cold spots.

7.3 Mass spectrometer settings

The source temperature should be chosen as high as possible according to the manufacturer's recommendations.

Scan mode and range:
- electron impact 70 eV;
- scan range 29 – 550 amu;
- at least 2 scans per second.

In order to increase sensitivity, the mass spectrometer range could be configured by segments, i.e. 29 – 250 amu for 15 min, 29 – 550 amu for the remainder of the time of the PyGC/MS analysis.

8. QUALITY ASSURANCE

As continuous operation is better for performance and stability. It is recommended to leave the PyGC/MS system on or in the stand-by mode 24 hours a day.

8.1 Control sample

The control sample should be a material easily available, that can be pyrolyzed reproducibly. We recommend a molecular thermometer such as Shell Kraton 1107 (styrene isoprene block copolymer) whose pyrolysis products ratio depends on the pyrolysis temperature.

8.2 Reproducibility

The reproducibility of any PyGC/MS system should be thoroughly tested and documented. This is really part of the validation of the system to show that it is fit for purpose. In general, the reproducibility of non-polar pyrolysis products is much better than that of polar pyrolysis products.

8.2.1 Mounting resin

Upon opening new bottle of resin, it is mandatory to prepare a blank mount, to make and pyrolyze cross-sections of the mounting resin itself in the same way as with actual samples.

This control pyrogram should be used to document if the resin is free of contamination.

Moreover, each sample pyrogram should be tested for the presence of the main mounting resin components using this control pyrogram.

8.2.2 Problematic samples

In the case of problematic samples (smears, mixtures or small samples) or if small peaks are decisive for interpretation or comparison, it is highly recommended to re-analyse a sample several times to check the reproducibility – if sufficient sample is provided.

8.2.3 Data processing

An original pyrogram without any data manipulation has to be stored.

All aspects of data collection, processing and storage should be computer controlled. There should be a provision for long term data storage.

8.2.4 Environmental requirements

Recommendations of the manufacturer concerning temperature limits, temperature variations, humidity, vibrations, electrical or magnetic interferences should be considered.

8.2.5 Check of the parameter set

Before starting a measurement, the set of parameters has to be checked to make sure that no unintended changes of parameters were made.

9.   INTERPRETATION

9.1 Comparison

PyGC/MS is mainly a comparative technique and therefore the consistency of the experimental parameters for the samples being compared is of the uttermost importance.

The comparison of a sample pyrogram to a reference is based on these main steps:
- Experimental acquisition of the pyrograms; the amount of reference material should be adjusted in order to obtain comparable intensities of the main resin components.
- Visual inspection of the TIC and mass chromatograms in order to ensure that the reference pyrogram is a subset of the sample: the resins are not identical if not all components of the reference are present in the sample.
- The intensity ratios of corresponding component peaks should not differ by more than 20% unless these differences can be explained.
- Low temperature 'pyrolysis' (actually evaporation) for the analysis of additives can be performed as an additional support to this process.

9.2 Identification

The major pyrolysis products should be identified by mass spectrometry and relative retention times. The identification of pyrolysis products may be accomplished through the use of pyrolysis gas chromatography-mass spectrometry (PyGC/MS) and subsequent library search.

For some compounds no library match can be found because of the lack of pyrolysis products in spectral libraries. The libraries mostly contain commercially available substances, hence, pyrolysis products like dimers or oligomers are mostly missing. It is necessary to build up one's own pyrolysis product library.

10. REFERENCES

[1]   EPG-BPM-001, Best Practice Manual for the Forensic Examination of Paint, issue 2, 2022.

[2]   ILAC G19:06/2022, Modules in a Forensic Science Process.

[3]   ISO/IEC 9000:2015, Quality management systems – Fundamentals and vocabulary.

[4]   ISO/IEC 17020:2012, Conformity assessment – Requirements for the operation of various types of bodies performing inspection.

[5]   ISO/IEC 17025:2017, General requirements for the competence of testing and calibration laboratories.

[6]   ASTM E1610-18 (2018), Standard Practice for forensic paint analysis and comparison.

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11. AMENDMENTS TO PREVIOUS VERSION

Not applicable.

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