GUIDELINE for the forensic examination of paint by Pyrolysis Gas Chromatography – Mass Spectrometry			
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2 **GENERAL REMARK**

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

7

8 **CONTENTS**

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

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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. DEFINITIONS AND TERMS

For the purposes of this guideline, the relevant terms and definitions are given in ENFSI documents, in ILAC G19 [1], in ISO/IEC 9000 [2], ISO/IEC 17020 [3] and ISO/IEC 17025 [4] standards, and in ASTM E1610-18 [5] 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.

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37
38
39 ## 4.   BACKGROUND
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41 4.1 Introduction

42 Pyrolysis is the breaking apart of chemical bonds by use of thermal energy. Analytical pyrolysis
43 is the technique of studying molecules either by observing their behaviour during pyrolysis or
44 by studying the resulting molecular fragments. The analysis of these processes and fragments
45 tells us much about the nature and identity of the original larger molecule. The production of
46 a variety of smaller molecules from a larger original molecule has fostered the use of pyrolysis
47 as a sample preparation technique, extending the applicability of instrumentation designed for
48 the analysis of gaseous species to solids, and especially polymeric materials. As a result,
49 GC/MS may be used routinely for the analysis of samples such as synthetic polymers, paints,
50 biopolymers, composites and complex industrial material.
51
52 The fragmentation, which occurs during pyrolysis, is analogous to the processes that occur
53 during the production of a mass spectrum. Energy is put into the system, and as a result, the
54 molecules break apart into stable fragments. If the energy parameters (temperature, heating
55 rate, and time) and the sample amount are controlled in a reproducible way, the fragmentation
56 is characteristic of the original molecule, based on the relative strengths of the bonds between
57 its atoms. The same distribution of smaller molecules will be produced each time an identical
58 sample is heated in the same manner, and the resulting fragments carry with them much
59 information concerning the arrangement of the original macromolecule.
60
61 The application of pyrolysis techniques to the study of complex molecular systems covers a
62 wide and diversified field.

63 4.2 Basic principles

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

67

68 ### 4.2.1 Random scission
69 Polyolefins generally degrade by this mechanism, and polyethylene is a good example.
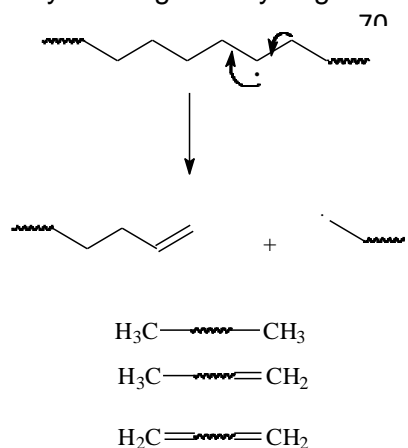
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Figure 1: Random scission

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.

H_3C——CH_3
H_3C——$=CH_2$
$H_2C=$——$=CH_2$

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86 ### 4.2.2 Monomer reversion
87 Several polymers degrade by this mechanism, including polystyrene and poly (meth)acrylates.
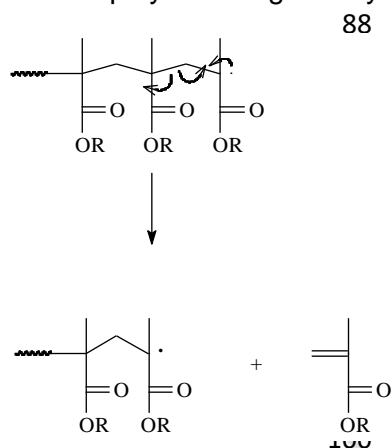
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Figure 2: Monomer reversion

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.

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101

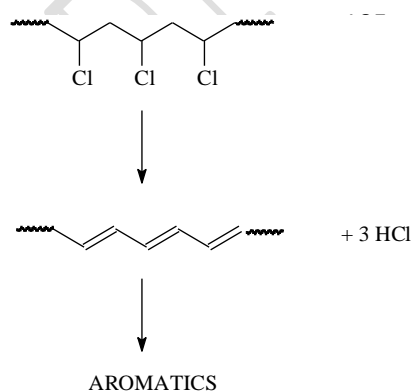102

103 ### 4.2.3 Side group elimination
104

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.

+ 3 HCl

AROMATICS

116

117

118 4.3 <u>Other factors</u>
119
120 The most significant parameter is the pyrolysis temperature. Low pyrolysis temperatures lead
121 to selective bond cleavage and result in a small number of relatively large degradation
122 products. At medium pyrolysis temperatures the number of reaction pathways increases
123 resulting in a larger number of pyrolysis products. At high pyrolysis temperature, however, low
124 molecular weight fragments of low diagnostic significance are formed.
125
126 The heating rate also plays an important role in pyrolysis. Samples heated slowly will degrade
127 considerably before the set pyrolysis temperature is reached. Consequently, reproducibility
128 will depend heavily on the ability of the instrument to heat the sample rapidly, reproducibly and
129 uniformly.
130
131

132 **5.   SAMPLE HANDLING AND PREPARATION**
133
134 5.1 <u>Sample amount</u>
135
136 As a rule of thumb a minimal sample amount corresponding to 10 - 50 µg of polymer material
137 should be suitable for binder and polymer discrimination.
138 Thorough analysis of additives for discriminating homogeneous samples (plastic materials,
139 clear coats) demands 4 to 5 times this amount of sample.
140
141 5.2 <u>Sample preparation</u>
142
143 Analysis should consider individual layers, either single layer paint or sectioned multilayer
144 systems.
145
146 In multilayer systems it is mandatory to analyze and compare the corresponding layers.
147 Sample preparation should be performed according to one of the following methods:
148 - Scraping or cutting the layer to be sampled using a scalpel blade (if necessary after
149   having removed the upper layers of no interest). This method should only be used, if
150   the successive layers present a sufficient colour difference.

151 - Sectioning of cross sections: 3-10 µm thin cross sections obtained by using a
152   microtome can be sectioned using a low power microscope and a razor blade.
153
154 Samples should be cleaned in order to avoid contamination. Two methods are available for
155 samples of at least 1 mm size:
156 - In case of sufficient sample thickness the surface of the top layer is scraped off using
157   a scalpel blade.

158 - The surface is cleaned using a cotton swab moistened with alcohol or water, and
159   thoroughly dried before analysis.
160
161
162 5.3 <u>General sample considerations</u>

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

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

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

168 Good thermal contact between sample and the pyrolysis device is important.
169

170 5.4 <u>Sample application</u>

171

172 5.4.1 Application as a thin film

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

176

177 5.4.2 Sample fixation by mechanical means
178 As in Curie point pyrolysis metal foils are used for heating, the sample can be squeezed
179 between parts of the metal foil, a metal wire or a metallic tube.

180

181 5.4.3 Sample fixation by thermal means
182 If the sample has thermoplastic properties the sampling device can be heated up to 250°C, in
183 order to melt the surface of the sample onto the surface of the pyrolysis device.
184 It should be demonstrated there is no negative influence on the pyrograms due to sample
185 breakdown.

186

187 5.4.4 Sample fixation by using sticking compounds
188 Compounds used for inline derivatization (TMAH, TBAH) as well as low boiling solvents
189 partially dissolving the sample are appropriate means to fix the sample on/in the pyrolysis
190 device.

191

192

193 **6.   METHODOLOGY**

194

195 6.1 <u>General</u>

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

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

202

203 6.2 <u>Low temperature pyrolysis</u>

204 In order to detect small amounts of additives and solvents in the polymer matrix it is mandatory
205 to evaporate the target analytes without pyrolysing the bulk material.

206 The useful pyrolysis temperature range will be 300°C to 400°C, depending on the thermal
207 contact within the pyrolysis unit.

208

209 6.3 <u>High temperature pyrolysis</u>

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

211

212 6.4 Step pyrolysis

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

215

216 6.5 Replicate analysis

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

220

221

222 **7.   INSTRUMENTATION**

223 The standard parameters used for the pyrolysis of paint samples are:

224 7.1 Pyrolyzer conditions

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

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

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

233 -   The pyrolysis time should be optimized on the actual instrument.

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

236

237 7.2 Gas chromatography conditions

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

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

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

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

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

254　　- The recommended transfer line temperature is 280°C – 320°C in order to avoid cold
255　　　　spots.
256

257　7.3 Mass spectrometer settings

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

260　　- Scan mode and range:
261　　　　- Electron impact 70 eV
262　　　　- Scan range 29 – 550 amu
263　　　　- At least 2 scans per second

264　　- In order to increase sensitivity, the mass spectrometer range could be configured by
265　　　　segments, i.e. 29 – 250 amu for 15 min, 29 – 550 amu for the remainder of the time of
266　　　　the PyGC/MS analysis.
267
268
269 **8.　　QUALITY ASSURANCE**
270 As continuous operation is better for performance and stability. It is recommended to leave
271 the PyGC/MS system on or in the stand-by mode 24 hours a day.
272
273　8.1 Control sample

274 The control sample should be a material easily available, that can be pyrolyzed reproducibly.
275 We recommend a molecular thermometer such as Shell Kraton 1107 (styrene isoprene block
276 copolymer) whose pyrolysis products ratio depends on the pyrolysis temperature.
277
278　8.2 Reproducibility

279 The reproducibility of any PyGC/MS system should be thoroughly tested and documented.
280 This is really part of the validation of the system to show that it is fit for purpose. In general,
281 the reproducibility of non-polar pyrolysis products is much better than that of polar pyrolysis
282 products.
283
284　8.2.1 Mounting resin
285 Upon opening new bottle of resin, it is mandatory to prepare a blank mount, to make and
286 pyrolyze cross-sections of the mounting resin itself in the same way as with actual samples.
287 This control pyrogram should be used to document if the resin is free of contamination.
288 Moreover, each sample pyrogram should be tested for the presence of the main mounting
289 resin components using this control pyrogram.
290
291　8.2.2 Problematic samples
292 In the case of problematic samples (smears, mixtures or small samples) or if small peaks are
293 decisive for interpretation or comparison, it is highly recommended to re-analyse a sample
294 several times to check the reproducibility - if sufficient sample is provided.
295
296　8.2.3 Data processing
297 An original pyrogram without any data manipulation has to be stored.
298 All aspects of data collection, processing and storage should be computer controlled. There
299 should be a provision for long term data storage.
300

301 8.2.4 Environmental requirements
302 Recommendations of the manufacturer concerning temperature limits, temperature variations,
303 humidity, vibrations, electrical or magnetic interferences should be considered.
304
305 8.2.5 Check of the parameter set
306 Before starting a measurement, the set of parameters has to be checked to make sure that
307 no unintended changes of parameters were made.
308
309

310 9. INTERPRETATION

311

312 9.1 Comparison

313

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

316

317 The comparison of a sample pyrogram to a reference is based on these main steps:

318 - Experimental acquisition of the pyrograms; the amount of reference material should be
319   adjusted in order to obtain comparable intensities of the main resin components.

320 - Visual inspection of the TIC and mass chromatograms in order to ensure that the
321   reference pyrogram is a subset of the sample: the resins are not identical if not all
322   components of the reference are present in the sample.

323 - The intensity ratios of corresponding component peaks should not differ by more than
324   20% unless these differences can be explained.

325 - Low temperature 'pyrolysis' (actually evaporation) for the analysis of additives can be
326   performed as an additional support to this process.

327

328 9.2 Identification

329

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

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

337

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360 **11.   AMENDMENTS AGAINST PREVIOUS VERSION**
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362 New document
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364   ###
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