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# Pyrolysis-gas chromatography/mass spectrometry analysis as a useful tool in forensic examination of automotive paint traces

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## Abstract

Pyrolysis (Py)-GC/MS was applied in comparative analysis of polymer binder of 150 automobile clearcoat samples. It was found that binders of identical type and similar infrared spectra can be, in most cases, effectively differentiated, sometimes based only on the presence of peaks of very low intensity originating from minor paint components. The qualitative procedure of pyrograms comparison was developed. The results obtained, enable one to draw the conclusion that Py-GC/MS appears as valuable, very informative analytical technique of car paint samples examination. Providing identification of paint pyrolysis products, it enables discrimination of samples on the basis of their composition. However, in some cases, paint samples were still indistinguishable on the basis of their pyrograms.

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**Keywords:** Pyrolysis-GC/MS; Forensic analysis; Car paints; Clearcoats; Discrimination

## 1. Introduction

Paint chips are commonly found at the scene of car accidents. They can be collected from the road or the victim's clothing and compared with the paint from suspected car in order to state if they could have originated from the same paint coat. The criminalistic examination of car paint samples includes the comparison of their chemical content. The complex chemical composition of paints as well as their small amount available for examination makes their analysis difficult. Usually, applied microscopic and spectrometric methods (especially FT-IR technique) enable, in many cases, to distinguish between the paints [1]. However, if the paint samples belong to the same class and contain similar polymer binder and main pigments/fillers, the further individualisation required the application of more sensitive and discriminating analytical methods, e.g. pyrolysis (Py)-GC/MS [1,2].

During pyrolysis, polymeric binder may degrade via a number of mechanisms like random scission, monomer reversion or the side group elimination and as a result, smaller (simpler) compounds which can be easily identified are formed. Additionally, minor components of paint samples could be visible as

separate peaks in the pyrograms obtained. Py-GC is used primarily for the comparative analysis of the organic components of paint. The pyrolysis patterns obtained from two or more samples are compared visually noting the presence or absence of peaks, their retention times and relative intensities. Coupled with MS and subsequent library search, the technique is used to identify pyrolysis products [3–5].

Py-GC/MS can be applied to classify, characterise and compare coating materials and polymers by determination of chemical components such as binders, additives, solvents, plasticizers and residual monomers. It is also possible to find subtle structural or compositional variations within a similar matrix. Challinor reported its application for examination of different samples of forensic interest like paints, motor vehicle rubbers, fibres, adhesives and polyurethane foams [6,7]. Some examiners tried to use the method for automobile paint classification and identification [8–11]. Automotive paint binder type can be identified on microgram-sized samples of topcoat. Information about the binder composition of some samples can be extended if paints are derivatised during pyrolysis [2,14]. Burns and Doolan [12,13] have recently applied the method to split the examined paints samples into several groups characterised by different break down products obtained by pyrolysis suggesting that it might be useful for criminalistic identification of paints. However, the authors took into consideration only high and clearly recognisable peaks in pyrograms, omitting smaller ones. So,

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the pyrograms obtained were simple and easy for interpretation, but without information about some minor components of paints.

As noted by some authors, this method of analysis may offer improved discrimination of chemically similar paints [8,12]. Py-GC/MS, however, is a destructive technique and its applicability depends on the paint type and amount of sample. It is best applied to individual paint layers.

The aim of the study was evaluation of the Py-GC/MS application in discrimination between paint samples of very similar composition for forensic purposes. Three groups of car paints of indistinguishable infrared spectra within each group were analysed and components of polymer binder were identified. The procedure of comparison of similar pyrogram patterns was proposed. The obtained results became a starting point for developing a statistical approach to discrimination of the samples examined.

## 2. Materials and methods

Samples were pyrolysed by means of CDS Pyroprobe 2000 (Analytix, UK) and then transferred to the RTx-35MS chromatographic capillary column (30 m × 0.25 mm, 0.25 μm), where compounds were separated [15]. As a GC/MS system, TurboMass Gold (Perkin-Elmer Instruments) was used. The GC pyrogram was: 40 °C held for 2.5 min; ramped 10.5 °C min<sup>-1</sup> to 320 °C; 320 °C maintained for 5 min. The stationary phase of GC column consisted of 35% diphenylpolysiloxane and 65% dimethylpolysiloxane. Carrier gas was helium, pressure 70 kPa. Electron ionisation (EI) temperature of transfer line 240 °C, temperature of ion source in MS 180 °C was applied.

Three groups of paint samples found at Polish market, characterised by different type of binder (acrylic styrene, acrylic styrene urethane and acrylic styrene melamine), were chosen for examination. There were top layers of solid and metallic paints (clearcoats) taken from new and repainted cars (Fiat, Polonez, Opel, Ford and VW). The samples were prepared for analysis

by scraping off top layer under the microscope using a scalpel. Then, the samples (50–100 μg) were placed inside a quartz tube held in the platinum coil of the Pyroprobe and then inserted into the heated interface of the pyrolyser. Pyrolysis was performed at 750 °C for 10 s without derivatisation process. Each sample was analysed at least three times.

## 3. Results

Collection of 150 acrylic clearcoat samples taken from different cars were analysed by means of Py-GC/MS. In most cases, differences in obtained pyrograms were significant and clearly visible. However, there were several samples which differ only slightly, and evaluation of the significance of the observed differences was difficult. So, the procedure was elaborated to face the problem of differentiation of paints characterised by the same set of major components where Py-GC/MS analysis gave very similar pyrolysis patterns. The main goal was to subtract and identify small peaks correlated to important compound from the background noise. The procedure is briefly described below.

In first step of the procedure, the baseline of the pyrogram is shifted to the level of 10% of largest peak height—in most cases styrene (6.6 min). In this situation, only peaks with relative height larger than 10% are visible, analysed and next marked with 'A'. Similarly, all new peaks, which appear on the pyrogram when the baseline is downshifted to the level of 5% of largest peak height, are marked with 'B'. Consequently, 'C' is given for the compounds with signals of relative height in range from 2 to 5%. Peaks smaller than 2% in most cases are skipped because their reproducibility was unsatisfactory.

From the collection of analysed paints, four pairs of samples were chosen as an example of the newly worked out procedure for comparative qualitative analysis of results obtained from Py-GC/MS experiments.

The first example of discrimination is presented to show the situation where differences between analysed paint samples are

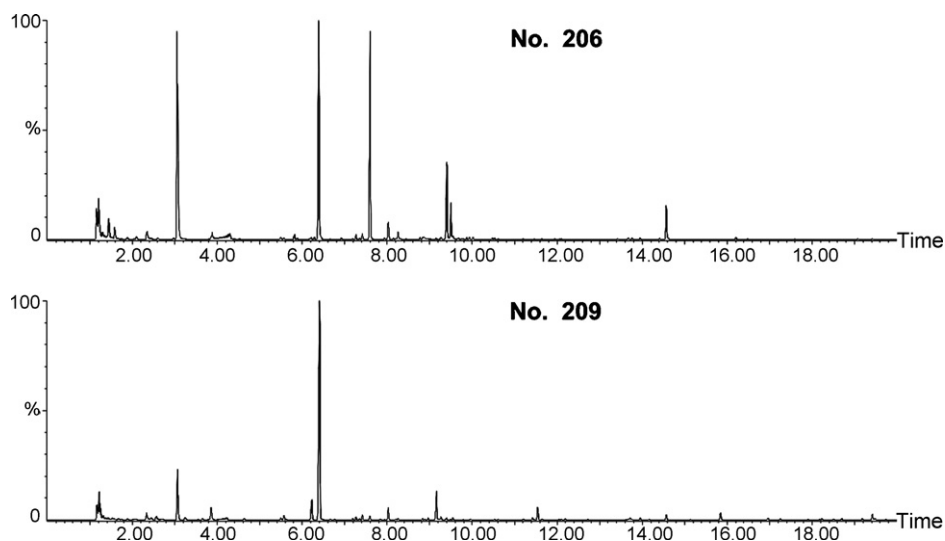


Fig. 1. Pyrograms of paint sample nos. 206 and 209.

Table 1  
Compounds identified in pyrograms of sample nos. 206 and 209

Compound name	Retention time (min)	206	209
3-Methylpentanal	2.4	C	C
Methyl methacrylate	3.1	A	A
Toluene	3.9	C	C
Methacrylic acid	4.6–5.0	C	–
4-Heptenal	5.7	C	–
Ethylbenzene	5.8	–	C
2-Propenyl methacrylate	6.0	C	–
Butyl acrylate	6.5	–	B
Styrene	6.6	A	A
<i>o</i> -Methylstyrene	7.5	C	–
Isocyanatocyclohexane	7.6	C	C
Butyl methacrylate	7.8	A	–
$\alpha$ -Methylstyrene	8.2	B	B
2-Ethylhexanol	8.5	C	–
2-Hydroxyethyl methacrylate	9.3	–	A
2-Hydroxypropyl methacrylate	9.6	A	–
3-Hydroxypropyl methacrylate	9.7	A	–
2-Ethylhexyl acrylate	11.5	–	C
1,6-Diisocyanatohexane	14.6	A	C
Cyclohexene	15.8	–	C

obvious and clearly visible. Obtained pyrograms of two samples (nos. 206 and 209) originating from different automobile manufacturers are shown in Fig. 1.

Compounds identified in the pyrograms are given in Table 1. The major peaks (marked A) present in both samples are methyl methacrylate and styrene. Also, other products of polystyrene degradation were detected, e.g.  $\alpha$ -methylstyrene (B), toluene (C), ethylbenzene (C) and *o*-methylstyrene (C). 1,6-diisocyanatohexane (A,C) and traces of isocyanatocyclohexane (C) pointing urethane modification also occurred in both pyrograms. Only in sample no. 206, butyl methacrylate (A), 2-propenyl methacrylate (C), 2-hydroxypropyl methacrylate (A) and 3-hydroxypropyl methacrylate (A) were detected. In sample no. 209, other acrylic compounds, e.g. 2-hydroxyethyl methacrylate (A), butyl acrylate (B) and 2-ethylhexyl acrylate (C) were observed.

Table 2  
Compounds identified in pyrograms of sample nos. 193 and 86

Compound name	Retention time (min)	193	86
<i>n</i> -Butanol	2.3	B	A
3-Methyleneheptane	3.3	B	C
Toluene	3.9	B	A
Ethylbenzene	5.7	C	C
Butyl acrylate	6.4	B	A
Styrene	6.6	A	A
Methylpropyl methacrylate	7.0	–	C
<i>o</i> -Methylstyrene	7.5	–	C
1-Ethyl-3-methylbenzene	7.6	–	C
Butyl methacrylate	7.8	B	A
2-Hydroxyethyl acrylate	8.0	–	B
$\alpha$ -Methylstyrene	8.2	B	B
2-Propylenbenzene	8.4	–	C
2-Hydroxyethyl methacrylate	9.3	B	–
(1-Methylenpropyl)-benzene	9.5	C	C
2-Hydroxypropyl methacrylate	9.6	–	A
3-Hydroxypropyl methacrylate	9.7	–	C
Indene	9.8	C	–
1-Methyl-4-(1-methylethyl)benzene	9.9	–	C
4-Ethenyl-1,2-dimethylbenzene	10.0	–	C
1-Undecanol/nonylcyclopropane	10.2	–	B
Neodecanoic acid	11.8, 12.3	–	B
2-Ethylhexyl acrylate	11.8	C	–
2-Ethylhexanoic acid methyl ester	12.0	–	C
7-Tetradeken	13.0	–	C
1-Dodecanol	14.9	–	B
Dodecyl acrylate	17.5	–	B
Phenylpentanol	18.1	–	B
1-Ethyl-1,2,3,4-Tetrahydronaphthalene	19.0	–	B

In this case, the discrimination between samples is easy. Differences between pyrograms are obvious, concerning peaks detected at levels A and B. So, it can be stated that differences originate mostly from main acrylic components of polymer binder.

As a second example, a comparison of two acrylic styrene melamine paint samples (nos. 86 and 193) was shown. All constituents in each pyrogram are given in Table 2 and obtained pyrograms are shown in Fig. 2. Samples were differentiated

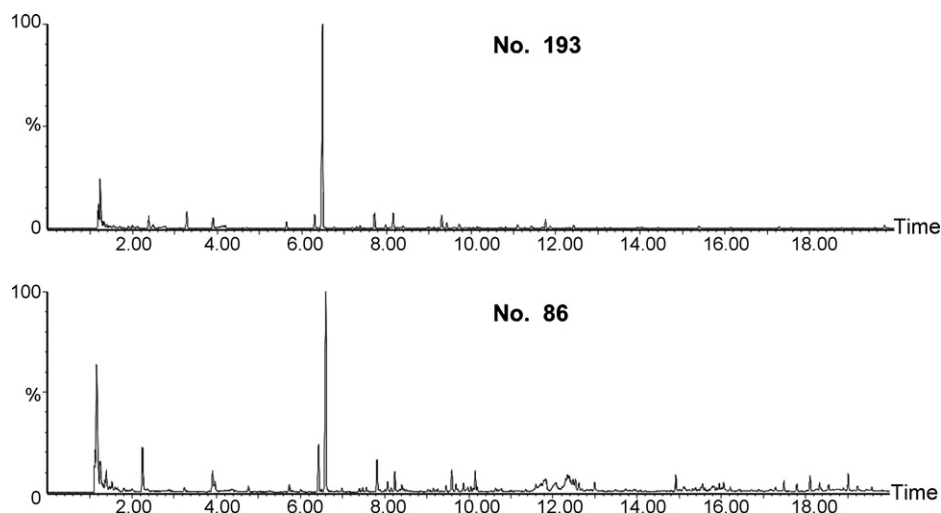


Fig. 2. Pyrograms of paint sample nos. 193 and 86.

on the basis of the presence of different acrylic compounds, despite no melamine compounds detected in the pyrograms. Melamine resins and their degradation products need a pre-column derivatisation with tetramethylammonium hydroxide (TMAH) or tetrabutylammonium hydroxide (TBAH) to be detected [14].

Styrene (A) and other polystyrene degradation product, e.g. toluene (A, B),  $\alpha$ -methylstyrene (B) and ethylbenzene (C) were found in both samples. Differences between paints were only in the occurrence of various acrylic compounds. In both samples appeared butyl acrylate (A, B) and butyl methacrylate (A, B). In sample no. 86, 2-hydroxyethyl acrylate (B), 2-hydroxypropyl methacrylate (A), 3-hydroxypropyl methacrylate (C) and dodecyl acrylate (B) were detected. Only in sample no. 193, 2-hydroxyethyl methacrylate (B) and 2-ethylhexyl acrylate (C) were found. In analysed pyrograms, differences in content of other additional substances (probably products of degradation of main components) were also visible, e.g. in sample no. 86, 1-undecanol (B), neodecanoic acid (B), 2-propenylbenzene (C), phenylpentanol (B) and in sample no. 193, indene (C). So, it was found that compared samples are different, taking into account both major and minor components of binder.

Two acrylic styrene urethane paint samples (nos. 290 and 291) were the example of samples taken from the cars of the same model, originating from the same manufacturer but produced in different years. Obtained pyrograms are shown in Fig. 3 and the identified peaks are given in the Table 3.

As seen, these pyrograms are very similar. In both of them, styrene (A) and other products of polystyrene degradation, e.g. toluene (C),  $\alpha$ -methylstyrene (B) were detected. Compounds pointing urethane modifications were not observed in this case; probably, relative height of peaks correlated to urethane were much below 2% (level C). Both samples can be characterised as acrylic paints by presence of methyl methacrylate (A), butyl acrylate (B) and 2-ethylhexyl acrylate (B). In sample no. 291, addition of plasticizer phthalate anhydride (C) and other additive or degradation product 1,4-diethylcyclohexane (C) were

Table 3

Compounds identified in pyrograms of sample nos. 290 and 291

Compound name	Retention time (min)	290	291
3-Methylpentanal	2.3	B	C
Methyl methacrylate	3.1	A	A
3-Methylenheptan	3.3	C	C
Toluene	4.0	C	C
Ethylbenzene	5.8	C	–
Butyl acrylate	6.5	B	B
Styrene	6.6	A	A
$\alpha$ -Methylstyrene	8.3	B	B
(1-Methylenpropyl)-benzene	9.5	C	–
2-Ethylhexyl acrylate	11.7	B	B
Neodecanoic acid	11.7–12.6	C	C
Phthalate anhydride	15.2	–	C
1,4-Diethylcyclohexane	19.0	–	C

detected, whereas in sample no. 290, these compounds are absent. These two minor compounds (at level C) allowed the paint samples analysed to be differentiated.

Finally, two acrylic styrene urethane paints (nos. 152 and 155) were analysed as an example of two samples originating from the same manufacturer and from the same year of production, but from different car models. Obtained pyrograms are shown in Fig. 4 and all identified peaks are given in Table 4. Samples were identified as acrylic styrene urethane paints.

In both pyrograms, styrene (A) and other products of degradation of polystyrene, e.g. toluene (B),  $\alpha$ -methylstyrene (A), ethylbenzene (C) were detected. Acrylic compounds present in both pyrograms are methacrylic acid (C), 2-propenyl methacrylate (C), butyl acrylate (C), butyl methacrylate (A), 2-hydroxypropyl acrylate (B), 2-hydroxypropyl methacrylate (A) and 3-hydroxypropyl methacrylate (A). Urethane content was confirmed with occurrence of 1,6-diisocyanatohexane (B) and isocyanatocyclohexane (B) in both pyrograms. Also, some other compounds were detected in both pyrograms at the same levels, e.g. n-butanol (A), 4-heptenal (C) and 2-ethyl-1-hexene (C).

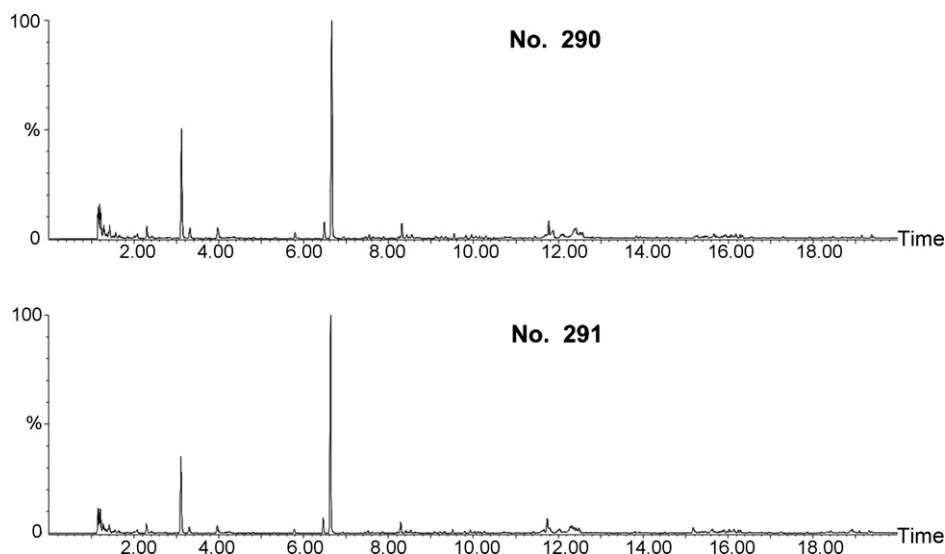


Fig. 3. Pyrograms of paint sample nos. 290 and 291.

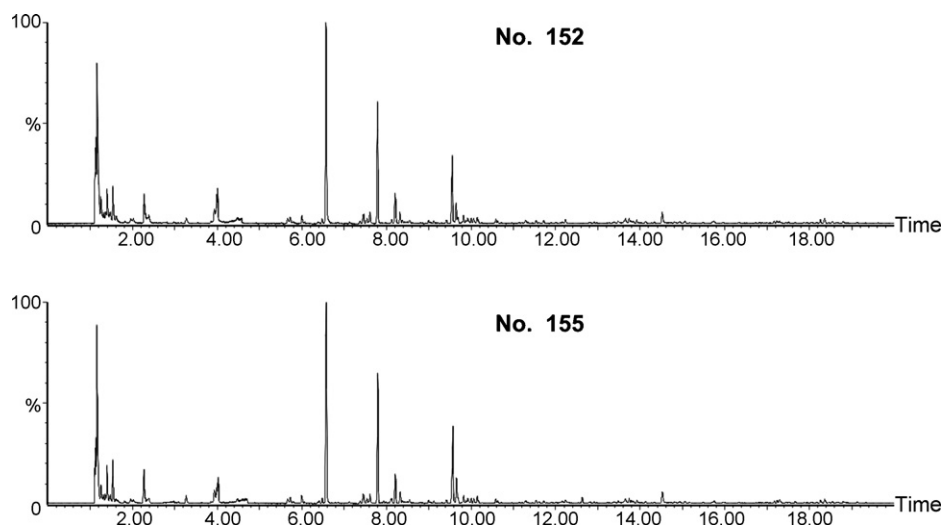


Fig. 4. Pyrograms of paint sample nos. 152 and 155.

In case of polystyrene degradation products and acrylic compounds in both pyrograms, their levels were the same. The only observed difference correspond to presence of the minor peak of octyl methacrylate (C) in sample no. 155 and peak of naphthalene (C) in pyrogram of sample no. 152. The first compound is acrylic binder component and the second is a degradation product of polystyrene. Both samples produce the similar amount of styrene, but only one makes naphthalene. This effect is observed probably due to the differences between polymer internal structures (e.g. crosslinking). So, it was found that compared samples are different.

Table 4  
Compounds identified in pyrograms of sample nos. 152 and 155

Compound name	Retention time (min)	152	155
<i>n</i> -Butanol	2.3	A	A
Benzene	2.4	C	C
2-Ethyl-1-hexene	3.3	C	C
Toluene	3.9	B	B
1,2-Propanediol	4.0	A	A
Methacrylic acid	4.5–4.7	C	C
4-Heptenal	5.7	C	C
Ethylbenzene	5.7	C	C
2-Propenyl methacrylate	6.0	C	C
Butyl acrylate	6.5	C	C
Styrene	6.6	A	A
<i>o</i> -Methylstyrene	7.5	C	C
<i>o</i> -Methyltoluene	7.5	C	C
Isocyanatocyclohexane	7.6	B	B
Butyl methacrylate	7.8	A	A
1,2,4-Trimethylbenzene	8.1	C	C
$\alpha$ -Methylstyrene	8.2	A	A
2-Hydroxypropyl acrylate	8.3	B	B
2-Hydroxypropyl methacrylate	9.6	A	A
3-Hydroxypropyl methacrylate	9.7	A	A
1-Methyl-2-isopropenylbenzene	9.8, 9.9, 10.0, 10.1	C	C
2,5-Dimethylstyrene	10.2, 10.6	C	C
Naphthalene	12.3	C	–
Octyl methacrylate	12.6	–	C
1,2-Dimethylcyclopentane	13.7	C	C
1,6-Diisocyanatoheptane	14.5	B	B

In the group of over 150 clearcoats analysed in presented research, many samples were indistinguishable, based on the observation of presence or absence of main peaks even when procedure described in this paper was applied. In these cases, for almost identical pyrograms containing the same set of compounds, other analytical methods should be applied (e.g. Py-GC $\times$ GC/MS, SEM-EDX, XRF, Raman).

#### 4. Conclusions

The results obtained, draw to the conclusion that Py-GC/MS appears as valuable, very informative analytical technique, being complementary to the FT-IR technique in the field of investigation of car paint samples for forensic purposes. In the case when paint samples belong to the same group characterised by the same polymer binder (i.e. when they are indistinguishable on the basis of their IR spectra), the application of Py-GC/MS can lead to their complete differentiation. Firstly, samples of car paints can be split into subclasses, based on major peaks. If this assignment is not sufficient, peaks of small relative intensity (i.e. less than 5% of largest peak height) correlated to minor polymer components are analysed. Based on such approach, even very similar paint coatings can be differentiated.

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