

Way to Distinguish Car Paint Traces Based on Epoxy Primer Layers Analysis by Pyrolysis-Gas Chromatography–Mass Spectrometry

by Jakub M. Milczarek^{1,2}, Marek Dziadosz¹ and Janina Zięba-Palus²

¹ *Jagiellonian University, Faculty of Chemistry, Department of Analytical Chemistry
ul. R. Ingardena 3, 30-060 Kraków, Poland*

² *Institute of Forensic Research
ul. Westerplatte 9, 30-033 Kraków, Poland*

Keywords: Car paint; Forensic examination; Pyrolysis; Gas chromatography

Fragments of paint coat or paint smears are very often transferred onto the clothing of a hit-and-run accident victim. Identification of paint samples requires examination of their polymer binders by pyrolysis–gas chromatography–mass spectrometry method (Py-GC–MS). Previously, Py-GC–MS has been successfully applied in our laboratory to the analysis of a polymer binder of clear coat layers (top layer of the paint coats). The aim of this research was to analyse the “bottom” side of the paint chip – the epoxy paint layer. Paint samples were analysed at least three times without derivatisation at 750°C, or after derivatisation in two steps at 400°C and 750°C using tetramethylammonium hydroxide (TMAH). It was observed that derivatisation increased the number and the quantity ratios of the pyrolysis products and enabled differentiation between the samples of similar chemical composition. It was found that Py-GC–MS allows for successful comparison of paint samples based on clear coat layer and primer layer analyses.

Odlamki powłoki lakierowej bardzo często przenoszone są na ubranie osoby potrąconej w wypadku samochodowym. W celu identyfikacji takich próbek lakierowych określa się między innymi skład osnowy polimerowej metodą pirolitycznej chromatografii gazowej z detekcją mas (Py-GC–MS). We wcześniejszych badaniach w naszym laboratorium dotyczących analizy osnowy polimerowej warstwy ‘clear coat’ (najbardziej zewnętrznej warstwy w lakierze samochodowym) uzyskano satysfakcjonujące wyniki przy zastosowaniu metody Py-GC–MS. Celem opisywanych badań była analiza warstwy lakierowej leżącej po drugiej stronie odlamka lakierowego – pierwszej warstwy epoksydowej. Próbkę lakierową były analizowane co najmniej trzykrotnie, bez derywatywacji w 750°C lub po derywatywacji

w dwóch etapach przy 400°C i 750°C z zastosowaniem wodorotlenku tetrametyloamoniowego (TMAH) jako odczynnika derywatyzyjnego. Zaobserwowano, iż po procesie derywatywacji zwiększyła się liczba identyfikowanych związków jak również uległy zmianie ich stosunki ilościowe, co pozwoliło na rozróżnienie próbek o bardzo podobnym składzie polimerowym. Wykazano, iż stosując metodę Py-GC-MS można porównywać z dobrymi rezultatami próbki lakierowe nie tylko w oparciu o analizę warstwy 'clear coat' ale również biorąc pod uwagę wyniki analizy warstwy epoksydowej.

Car paint as a physical evidence is commonly examined in forensic laboratories. Chips of paint coat or paint smears on the clothing of a car accident victim or on a car body of damaged vehicles are very often collected from a scene of a hit-and-run accident. As paint samples are often very small and, additionally, it is not usually possible to separate them entirely from the basecoat, non-destructive analytical *in situ* microtechniques are preferred for their examination. Optical microscopic analysis enables recognition of a layered structure of paint sample (the number of paint layers visible in a cross section of the sample, their colour, thickness, and granulation). Microspectrometric analysis (FT-IR, SEM-EDX, or μ -XRF) enables determination of chemical composition of particular layers in the examined paint coat fragments on the basis of the obtained spectra. These two types of methods are routinely applied in paint trace analysis [1–4]. They are frequently supplemented with microspectrophotometry in the UV-VIS range, which allows for objective determination of the colour of particular layers, and with the pyrolysis-GC-MS method used for a detailed analysis of the paint binder composition [5–11].

Typical new automotive finishes consist of at least four layers: the primer, the primer surfacer, the basecoat, and the clear coat. Identification of the polymer binder, which might be different for particular layers, requires application not only of IR spectroscopy but also of pyrolysis-GC-MS. In the second method, small paint samples are decomposed by heating to the gaseous products, later separated on a chromatographic column, and then identified. As a result, the obtained chromatograms may help to distinguish one polymer from another [8–12].

Some authors have shown that Py-GC-MS enables identification of pyrolytic decomposition products for paint comparison purposes [8, 11]. This method could be also used for paint sample classification [12, 13].

The amount of information about the composition of polymers can be increased if *in situ* sample derivatization is performed. Derivatization with tetramethylammonium hydroxide (TMAH) is especially suitable if polar pyrolysis products are present. The use of TMAH has been discussed by Challinor [14, 15]. Alcohols, acids, and amines are methylated yielding derivatives well suitable for gas chromatographic separation. As a result of derivatisation, pyrograms are generally simplified and reflect the composition of the parent material more clearly.

In our laboratory Py-GC-MS has been successfully applied in the analysis of polymer binder of clear coats (top layer of paint coats) [16, 17]. In most cases it was possible to differentiate between paint fragments taking into consideration a variation in polymer composition of clear coats containing acrylic styrene resins modified with urethane or melamine. In the comparative analysis of paint pyrograms it was important to consider minor peaks, because they enabled differentiation between very similar samples that were undistinguishable by means of IR spectrometry.

In this research an attempt has been made to analyze the “bottom” side of the paint chip – the primer. The primer protects the car body against corrosion and contains different epoxy resins and zinc sulfate. It is mostly homogenous. It has been hoped that examination of a polymer binder of a primer layer would help in differentiation of paint samples. To differentiate between the series of examined samples it was necessary to derivatise them prior to the chromatographic examination.

EXPERIMENTAL

Methods

The samples were pyrolysed using a CDS Pyroprobe 2000 (Analytix, UK) and then analysed chromatographically by the use of a TurboMass Gold system (Perkin-Elmer Instruments, USA). An RTX-35MS 35% diphenylpolysiloksan and 65% dimethylpolysiloksan capillary column (30 m × 0.25 mm × 0.25 μm) was used. The GC program was: 40°C for 2.5 min, increase to 320°C at the ramp rate 10.5°C min⁻¹, 320°C for 5 min. The carrier gas was helium, 70 kPa. The parameters of electron ionisation (EI) were: temperature of transfer line 240°C, temperature of ion source in MS 180°C. Each sample was analysed at least three times without derivatisation at 750°C or after derivatisation using TMAH in two steps: at 400°C and 750°C. The pyrolysis patterns obtained from two or more paint samples were compared visually with respect to the presence or absence of peaks, their retention times, and relative intensities.

The IR spectra were recorded on a Digilab FTS 40Pro spectrometer equipped with a UMA 500 microscope. Each spectrum represented a collection of 512 scans at a resolution of 8 cm⁻¹. The spectra were searched automatically by the computer for the peak maxima and positions.

Materials

10 paint fragments taken from new and repainted cars (Lada, VW, Opel, Citroen, Fiat, Mazda, Renault) were examined. The samples were prepared for the analysis by scraping off the bottom layer of solid and metallic paints under a microscope using a scalpel. For the measurements the samples were placed inside a quartz tube held in the platinum coil of the Pyroprobe. Then, derivatisation agent was added and after 30 min the tube was inserted into the heated interface of the pyrolyser. Each paint sample was examined 3 times. The numbers describing paint samples come from the car paint collection of the Institute of Forensic Research, Kraków.

Epoxy-based paints provided by Organika Sarzyna SA (Poland) were analysed and used as reference samples. Several real paint fragments containing epoxy primer layer were analysed as well and the pyrograms were compared to those obtained for the reference set.

Data processing

Identification of compounds was performed with a help of the NIST98 MS library. Retention times given in all tables were averaged from the values obtained in all experiments. In some cases the shift by 0.1–0.3 min was observed.

The previously described procedure was used to differentiate between the paints composed of the same set of major components of very similar pyrolysis patterns [16]. In the first step of the procedure, the baseline of the pyrogram was shifted to the level of 10% of the largest peak height. Then, only the peaks with relative height larger than 10% were visible, analysed, and next marked with A. Similarly, all new peaks, which appeared in the pyrogram when the baseline was downshifted to the level of 5% of the largest peak height, were marked with B. Consequently, C was assigned to the compounds, with produced the signals of relative height in the range from 2 to 5%. The peaks smaller than 2% were insufficiently reproducible and in most cases were not considered.

RESULTS AND DISCUSSION

IR spectra of the examined epoxy primer layers were very similar. All spectra contained absorption bands at 830, 1180, 1240, 1510, 1610 cm^{-1} originating from the presence of epoxy resin (bisphenol-A type). The only differences between the spectra referred to the relative intensity of some absorption bands or their shape (contour).

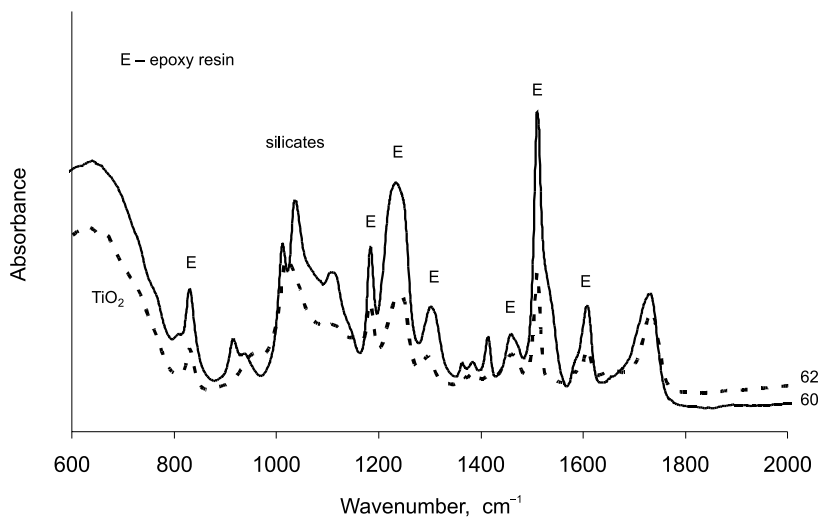


Figure 1. Infrared spectra of two different paint samples

In Figure 1 exemplary IR spectra of the primer layers from 2 different cars are shown. Based on these spectra it was neither possible to identify the kind of the epoxy resin nor to differentiate between the polymer binders. Much more information about the

epoxy resin was obtained from the Py-GC-MS analysis. The pyrograms of the exemplary epoxy resins (from the reference set) analysed without and with derivatisation are shown in Figures 2 and 3, respectively.

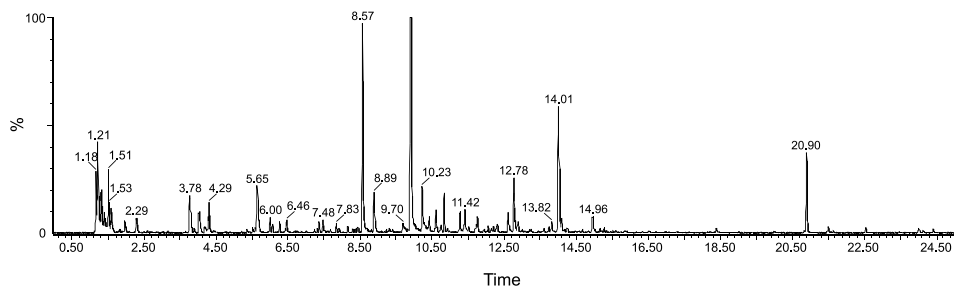


Figure 2. A pyrogram of exemplary epoxy resin (epidian 61_et) without derivatisation

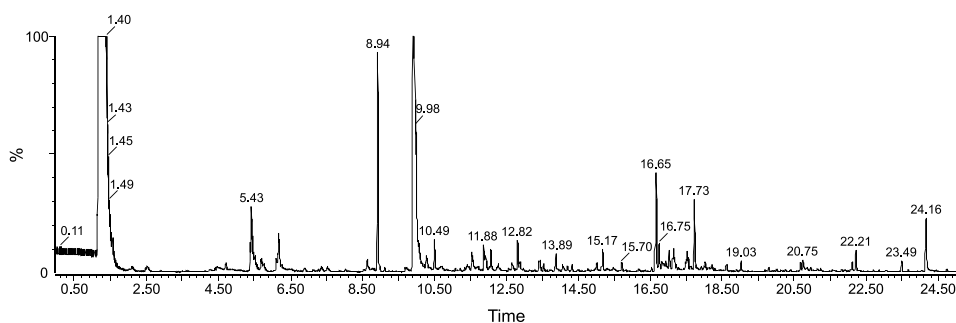


Figure 3. A pyrogram of example epoxy resin (epidian 61_et) after derivatisation step at 400°C

These pyrograms offer rich information about the structure of the analysed resin. Their reproducibility was satisfactory – very good for retention time and fair for peak heights. Possible structure of epoxy resin based on bisphenol A and epichlorhydrine, cured with triethylenetetramine, is given in Figure 4.

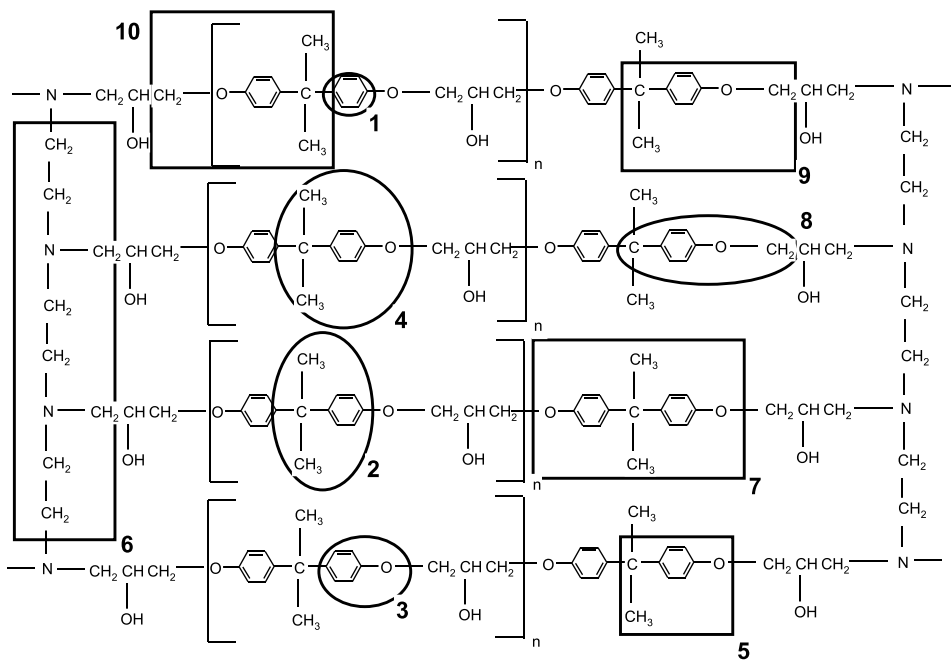


Figure 4. Exemplary structure of the epoxy resin based on bisphenol A and epichlorohydrine cured with triethylenetetramine

The main compounds identified in the pyrogram of non-derivatised sample (Fig. 2) are (numbers in parentheses refer to retention times, numbers in braces refer to the numbers of polymer fragments marked in Figure 4): benzene (2.3 min) {1}, isopropylbenzene (7.5 min) {2}, p-isopropylphenol (12.6 min) {4}, 4-ethylphenol (11.3 min) {5}. The compounds detected in the pyrogram for derivatised samples (Fig. 3) and correlated to the suggested structure are: phenol (8.6 min) {3}, methyl- and ethyl-1,2-ethandiamine (5.5, 8.9 min) {6}, bisphenol A and methylated bisphenol A (23.5–25.0 min) {7}, 1-methoxy-4-methylbenzene (8.9 min) {8}, 1-methoxy-4-ethylbenzene (14.1 min) {9}, 1-methoxy-4-(1-methylethyl)benzene (12.9 min) {10}.

After the experiments with the set of standard epoxy resins, a set of real paint fragments with the first epoxy layer was analysed without prior derivatisation. For a comparison, the pyrograms of 3 exemplary paint samples (No. 60, 62, 82) are presented in Figure 5. The compounds identified in these pyrograms and specified in the way described previously [17] are listed in Table 1.

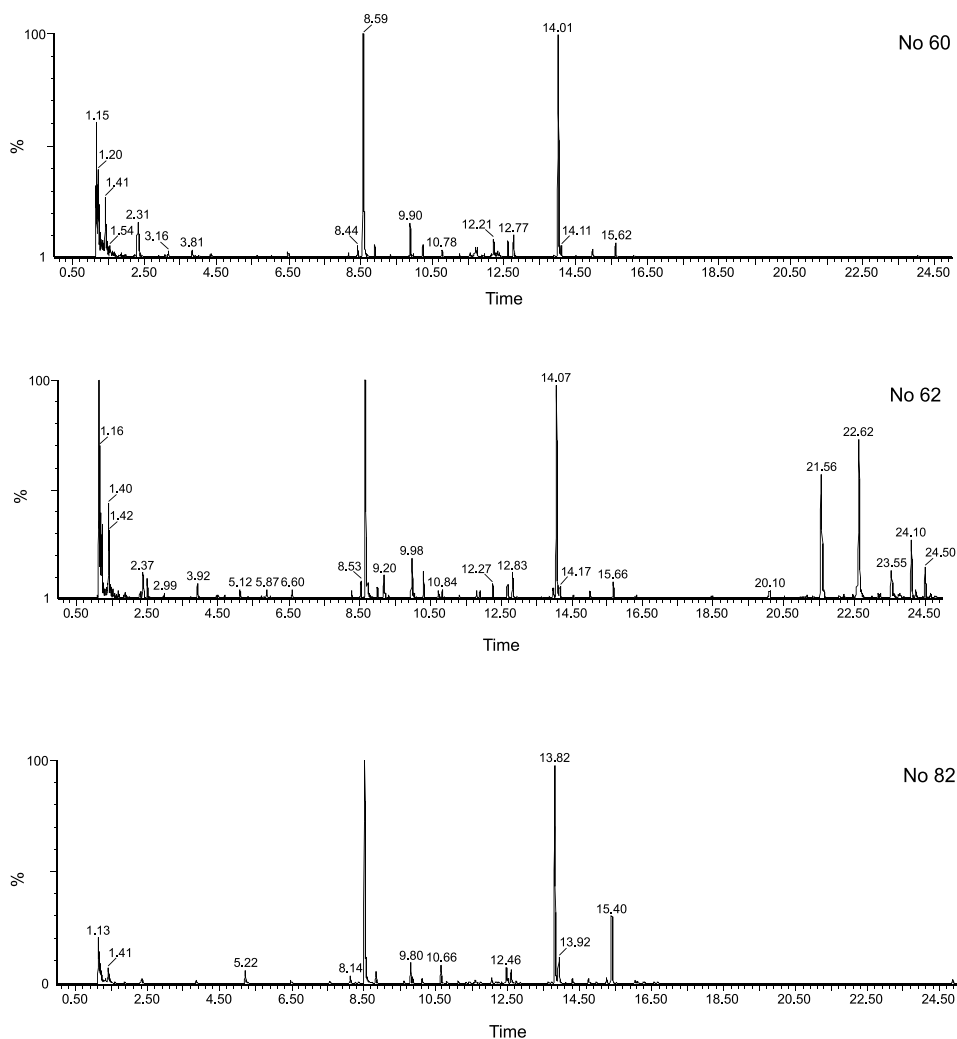


Figure 5. Pyrograms of paint samples No. 60, 62 and 82 without derivatisation

The major peaks, present in all three pyrograms (marked with A or B) correspond to phenol, 2-methylphenol, 4-(methylethyl) phenol, 2,3-dihydro-2(3)-methyl-benzofuran, and 3-methyl-2-(1-methylethyl) benzofuran. Other compounds appear only in one or two out of three pyrograms (Tab. 1). The pyrograms of samples No. 60 and 82 are very similar to each other but different from that of sample No. 62. To differentiate successfully between the samples No. 60 and No. 82, derivatisation step with TMAH should be performed.

Table 1. Compounds identified in the pyrograms of sample No. 60, 62 and 82

Compound name	Retention time, min	60	62	82
Benzene	2.3	A	B	–
2-Methyl-2-butanal	2.4	–	B	–
Toluene	3.7	C	B	–
Styrene	6.5	C	C	-
α -Methylstyrene	8.2	C	C	–
2-Ethyl-1-hexanol	8.4	B	C	–
Phenol	8.6	A	A	A
Benzofuran	8.9, 9.1	C	B	C
2-Methylphenol	9.8	A	A	B
4-Methylphenol	10.2	C	B	–
4-Methylbenzenamine	10.6	–	C	–
2-Methylbenzofuran	10.7	–	C	B
4-Ethylphenol	11.7	C	C	–
1,2-Dihydro-6-methyl-naphthalene	12.2	B	B	–
4-(Methylethyl)phenol	12.5	B	B	B
2,3-Dihydrobenzofuran	12.7	B	A	C
2,3-Dihydro-2-methyl-benzofuran	13.9	–	–	A
2,3-Dihydro-3-methyl-benzofuran	14.0	A	A	B
2-Methyl-3-phenylpropanal	15.0	C	C	–
3-Methyl-2-(1-methylethenyl)benzofuran	15.5	B	B	A
1,2-Dimethyl-4-(phenylmethyl)benzene	21.6	–	A	–

(Continuation on the next page)

Table 1. (Continuation)

Compound name	Retention time, min	60	62	82
3,4-Diethyl-1,1'-biphenyl	22.6	–	A	–
Phenylmethyl ester propanoic acid	24.1	–	B	–

The pyrograms obtained after derivatisation are shown in Figure 6. The differences between them are obvious. All identified peaks are given in Table 2. Few weak peaks were neglected because of the problems with correlating their MS spectra to the spectra from the MS database.

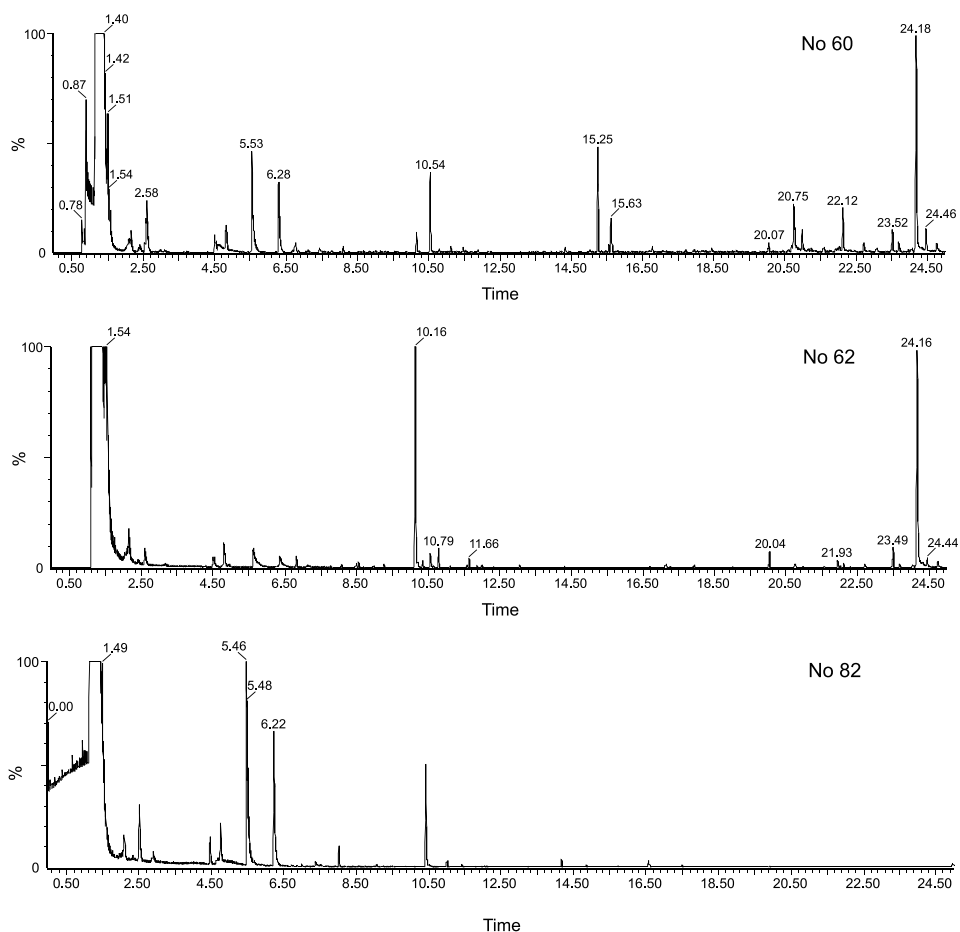
**Figure 6.** Pyrograms of paint samples No. 60, 62 and 82 after derivatisation step at 400°C

Table 2. Compounds identified in the pyrograms of sample No. 60, 62 and 82 after derivatisation

Compound name	Retention time, min	60	62	82
1,5-Hexadien-3-yne	2.3	–	–	C
2-Methylpropanoic acid methyl ester	2.5	A	B	A
Methoxyacetic acid methyl ester	4.5	B	C	A
2-Methoxypropanoic acid methyl ester	4.8	A	B	A
N,N'-Diethyl-1,2-ethandiamine	5.5	A	B	A
N,N'-Diethyl-N,N'-dimethyl-1,2-ethandiamine	6.2	A	C	A
1,2,3-Trimethoxy-propane	6.8	C	C	–
N,N,N'-Triethyl-1,2-ethanediamine	7.4	C	–	–
2-Hydroxycyclohexanone	8.0	–	–	A
1-Methoxy-2-methyl-benzene	8.9	C	–	–
Tributylamine	10.2	B	A	–
N,N,N',N'-Tetramethyl-1,2-ethandiamine	10.5	A	C	A
Methylene-butanedioic acid dimethyl ester	11.0	C	–	C
Pentanedioic acid dimethyl ester	11.5	C	–	–
Nonanoic acid methyl ester	11.6	–	C	–
N-Ethyl-2-methoxy-N-(2-methoxyethyl)ethanamine	14.1	C	–	–
4-Cyclohexene-1,2-dicarboxylic acid dimethyl ester	15.1	A	–	–
3-Cyclohexene-1,2-dicarboxylic acid dimethyl ester	15.5	A	–	–
2,4-Bis(1-methylethyl)phenol acetate	15.7	–	–	B
Dimethyl phthalate	16.6	–	–	A
N,N,N',N'-Tetramethyl-1,2-benzenediamine	17.4	–	–	B

(Continuation on the next page)

Table 2. (Continuation)

Compound name	Retention time, min	60	62	82
8-Methyldecanoic acid methyl ester	17.7	–	–	C
Methyl tetradecanoate	19.8	–	–	C
2-Methylaminoctan-3,5-dione	20.8	B	–	–
N,N',N''-Trimethyldipropylenetriamine	21.0	C	–	–
1,2,4-Benzenetricarboxylic acid trimethyl ester	21.3	C	–	–
n-Ethyl trimethylene diamine	21.6	C	–	–
1-(3-Aminopropyl)-4-methylpiperazine	22.1	B	–	–
1-Piperazineethanamine	22.7	C	–	–
Methylated bisphenol A	23.5	B	C	–
Diethylhydrazone-2-propanone	24.2	A	A	–
p-Cresyl glycidyl ether	24.5	B	C	–
Bisfenol A	25.0	–	–	B

In all three pyrograms, 2-methylpropanoic acid methyl ester, methoxyacetic acid methyl ester, 2-methoxypropanoic acid methyl ester, N,N'-diethyl-1,2-ethandiamine, N,N'-diethyl-N,N'-dimethyl-1,2-ethandiamine, N,N,N',N'-tetramethyl-1,2-ethandiamine were detected and marked with A, B, or C (in a few cases). All other components detected in the pyrograms and given in Table 2 allowed for easy differentiation between three paint samples.

CONCLUSIONS

Application of Py-GC-MS has shown that this method is potentially appropriate tool for forensic examination of paints. Py-GC-MS provides additional information to that obtained from IR. This information is helpful in characterization of binders and detection of traces of other organic compounds, such as additives, plasticizers, and residual monomers. Py-GC-MS gives information about the chemical composi-

tion and thus enables discrimination between the paints producing similar IR spectra. In most cases it was possible to differentiate between the car paint samples not only based on the analysis of their clear coat but also of their primer layer.

It has been shown that epoxy paints should be always analysed before and after derivatisation step with TMAH. In some cases the samples can be differentiated without prior derivatisation. However, derivatisation process increases the number and the amount of the pyrolysis products, hence more peaks are formed in the pyrogram and the corresponding data spectrum becomes significantly broader. Consequently, if epoxy paint samples are very similar with respect to their chemical composition, their differentiation after derivatisation is less problematic.

The described research can be regarded as a preliminary work. Good and promising results concerning differentiation have been obtained for a set of 10 epoxy layers in paint coats. In the future, the same methodology will be applied to the larger number of samples.

Acknowledgments

The research was financially supported by the Ministry of Science and Higher Education, Poland, project No. O N204 003034 and by the Institute of Forensic Research, project II/K.

The authors are grateful to Organika Sarzyna S.A. for providing them with standard epoxy resin samples.

REFERENCES

1. Beveridge A., Fung T. and MacDougall D., *Use of infrared spectroscopy for characterisation of paint fragments*, in: *Forensic examination of glass and paints*, [B. Caddy, Ed.], Taylor and Francis, London and New York 2001.
2. Allen T.J., *Forensic Sci. Int.*, **57**, 5 (1992).
3. Zięba-Palus J., *J. Mol. Struct.*, **511–512**, 327 (1999).
4. Roland S.G., Jergovich T.A. and Kirkbride K.P., *Forensic Science Review*, **18**, 98 (2006).
5. Zięba-Palus J. and Borusiewicz R., *J. Mol. Struct.*, **792–793C**, 286 (2006).
6. Cassista A.R. and Sandercock P.M.L., *J. Can. Forensic Sci.*, **27**, 209 (1994).
7. *Gas Chromatography*, in: *Forensic Science*, [I. Tebbett, Ed.], Ellis Horwood Limited, New York, London, Toronto, Sydney 1992.
8. Burns D.T. and Doolan K.P., *Anal. Chim. Acta*, **422**, 217 (2000).
9. Burns D.T. and Doolan K.P., *Anal. Chim. Acta*, **571**, 25 (2006).
10. Burns D.T. and Doolan K.P., *Anal. Chim. Acta*, **539**, 145 (2005).
11. Burns D.T. and Doolan K.P., *Anal. Chim. Acta*, **539**, 157 (2005).
12. Wampler T.P., *J. Anal. Applied Pyrolysis*, **71**, 1 (2004).
13. Wampler T.P., Bishea G.A. and Simonsick W.J., *J. Anal. Applied Pyrolysis*, **40–41**, 79 (1997).
14. Challinor J.M., *J. Anal. Applied Pyrolysis*, **20**, 15 (1991).
15. Challinor J.M., *J. Anal. Applied Pyrolysis*, **16**, 323 (1993).

16. Zięba-Palus J., Milczarek J.M. and Kościelniak P., *Chem. Anal. (Warsaw)*, **53**, 109 (2008).
17. Zięba-Palus J., Zadora G., Milczarek J.M. and Kościelniak P., *J. Chrom. A*, **1179**, 41 (2008).

Received October 2008

Revised December 2008

Accepted march 2009