

Application of Infrared Spectroscopy and Pyrolysis-Gas Chromatography–Mass Spectrometry to the Analysis of Automobile Paint Samples

by **Janina Zięba-Palus^{1*}**, **Jakub M. Milczarek^{1,2}** and **Paweł Kościelniak^{1,2}**

*1 Institute of Forensic Research,
ul. Westerplatte 9, 31-033 Kraków, Poland
2 Jagiellonian University, Department of Analytical Chemistry,
ul. R. Ingardena 3, 30-060 Kraków, Poland*

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Two analytical techniques were applied for identification of polymer binder in 60 automobile paint samples. It was found that binders of identical type and similar infrared spectra could be effectively differentiated using Py-GC–MS. When paint samples were indistinguishable on the basis of their IR spectra, application of Py-GC–MS often enabled their differentiation and identification of polymer binder components. Based on the obtained results it was concluded that Py-GC–MS is a valuable and very informative analytical technique complementary to the FT–IR spectroscopy in the investigation of car paint samples for forensic purposes. Only in some exceptional cases of very similar paint samples these methods are unable to detect differences in their chemical composition.

Zastosowano dwie metody analityczne do identyfikacji osnowy polimerowej lakierów samochodowych. Stwierdzono, że metodą pirolitycznej chromatografii gazowej (Py-GC–MS) można efektywnie rozróżnić spoiwa lakierów tego samego typu, których widma w podczerwieni są bardzo podobne. Jeśli próbki lakieru są nierozróżnialne na podstawie ich widm IR zastosowanie Py-GC–MS dostarcza szczegółowych informacji o składnikach osnowy polimerowej umożliwiając rozróżnienie porównywanych próbek. Uzyskane wyniki wykazały, że Py-GC–MS jest cenną techniką analityczną w badaniach lakierów samochodowych do celów sądowych, komplementarną do spektrometrii w podczerwieni. Tylko w wyjątkowych przypadkach metoda ta nie pozwala wykryć różnic w składzie chemicznym dwóch różnych próbek lakieru.

* Corresponding author. E-mail: jzieba@ies.krakow.pl

Paint samples are very often a subject of forensic examinations. Their traces are left often after car accidents directly on the road or on a victim's clothing, as well as after burglary. They occur in the form of micro-fragments of paint coating of the surface area of several mm² or less, or smears of paint visible on clothing or other support. The main task of forensic examinations is to compare the paint trace with a sample from the suspected vehicle or tool in order to find out if they have a common origin. On the other hand, if no comparative material is available, identification of paint components may provide information on the kind of paint and its producer.

The complexity of chemical composition of paints makes their comparative analysis difficult. Application of microscopic and spectrometric methods enables one in many cases to distinguish between the paint samples. Infrared spectroscopy is a very useful method for paint characterization [1–3]. It is a favourable technique for determining the general type of paint and identifying the resins, main pigments, and fillers. However, if the compared paint samples belong to the same class *i.e.* contain similar polymer binders and main pigments/fillers, their further identification requires the application of more sensitive analytical methods.

Pyrolysis chromatography (Py-GC) is the method of choice for examining organic composition of small quantities of macromolecular materials [4, 5]. During pyrolysis thermal fragmentation of a substance in an inert atmosphere is performed. The obtained molecular fragments are usually characteristic for the composition of the original macromolecular material. This technique has been shown to be sensitive to differences in composition of numerous synthetic polymers and has even been employed to successfully demonstrate the differences in crosslinking of the polymers of the same composition [5].

Py-GC has been relatively widely used for quality control and determination of the composition of vehicle paints by the automotive industry [4]. A high degree of discrimination of different samples of forensic interest like paints, motor vehicle rubbers, fibres, adhesives and polyurethane foams has been achieved by this technique [6, 7]. These examinations were extended by McMinn who applied combination of mass spectral data with the „chromatographic fingerprint” in identification of automobile paints [8].

Some authors [9–11] have shown that Py-GC coupled with MS and/or IR enables identification of the pyrolytic decomposition products for paint comparison purposes. Some forensic applications have proven that Py-GC–MS allows further discrimination of solid polymers and can be used as the method for classification of paints [5, 12–14]. Burns *et al.* [9, 10] tried to divide the examined original automobile coatings into several groups on the basis of their pyrograms to make identification of paints more facile. However, the authors took into consideration only high and clearly recognizable peaks omitting the smaller ones. Thus, the obtained pyrograms were simple

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

In this paper an attempt to supplement the results obtained by IR spectroscopy with these obtained by Py-GC-MS was made in order to differentiate between paint samples. All peaks present in the obtained pyrograms were taken into account, including very small ones, as long as they were reproducible. It was found out, that the pyrograms, as containing much more information on the pyrolysis products, provide much more features for sample comparison. Moreover, Py-GC-MS was proven to be useful in differentiation of samples of very similar composition, *i.e.* of those, which are indistinguishable on the basis of their infrared spectra.

EXPERIMENTAL

Two techniques: infrared spectrometry (FT-IR) and pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC-MS) were applied.

Infrared spectra were recorded on a Digilab FTS 40Pro spectrometer equipped with an 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 maxima and peak positions.

The samples were pyrolysed using a CDS Pyroprobe 2000 (Analytix, UK) apparatus and then analysed chromatographically using a TurboMass Gold system (Perkin Elmer Instruments). The GC program was: 40°C for 2 min; ramped at $10^{\circ}\text{C min}^{-1}$ to 300°C , 300°C for 2 min; ramped at $30^{\circ}\text{C min}^{-1}$ to 320°C ; 320°C for 3 min. An RTX-35MS capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) was used. The stationary phase consisted of 35% poly(diphenylsiloxane) and 65% poly(dimethylsiloxane). Carrier gas was helium. Electron ionisation temperature of the transfer line was 240°C and the temperature of the ion source in MS was 180°C . Pyrolysis was performed at 400 and 750°C without derivatisation. The pyrolysis patterns obtained for two or more paint samples were compared visually with respect to the presence or absence of peaks, their retention times, and relative intensities.

Sixty paint samples taken from new and repainted cars (Fiat, Polonez, VW, Opel, Daewoo) were examined. The samples were prepared for analysis by scraping off a top layer of solid and metallic paints under the microscope using a scalpel. For spectrometric measurements the isolated top layers were placed directly onto a KBr plate and inserted into the infrared beam of the microscope. The spectra were measured in the transmission mode. Then, the samples were placed inside a quartz tube held in the platinum coil of the Pyroprobe and inserted into the heated interface of the pyrolyser. Each sample was analysed three times.

RESULTS AND DISCUSSION

On the basis of infrared spectra, the investigated paint samples were classified into three groups. Within each group, IR spectra of the examined paint samples were very similar. The only differences referred to relative intensity of some absorption bands, or their shapes (contours). On the other hand, pyrograms visibly differed with respect to the composition of the samples within the groups. Not always, however,

the observed differences referred to the intensive peaks in the pyrograms; quite often distinction between two different paint samples was made on the basis of low-intensity peaks.

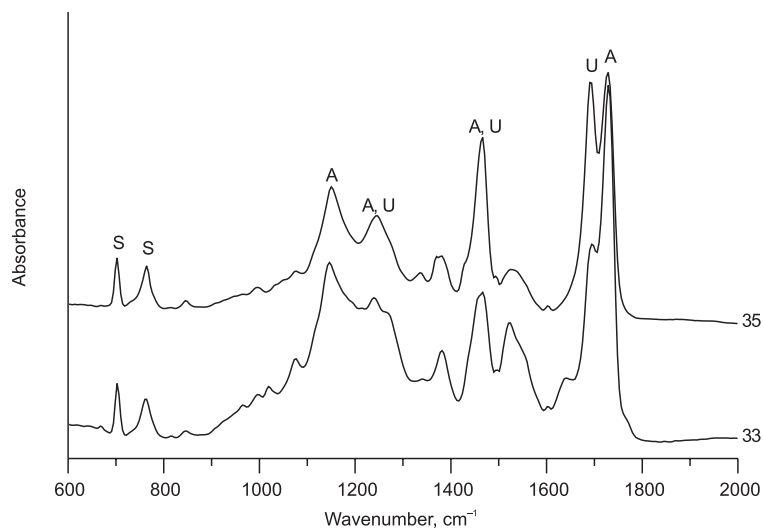


Figure 1. Infrared spectra of paint samples; A – acrylic resin, U – urethane resin, S – styrene

Exemplary IR spectra of acrylic-urethane paints modified with styrene (No. 33 and 35) from two different cars are shown in Figure 1. The main absorption bands belong to the main components of the binder, *i.e.* styrene, acrylic resin, and polyurethane (Tab. 1). The differences between the spectra refer to the intensities of bands at 1690 and 1463 cm⁻¹, originating from urethane. They indicate the difference in contents of this component in each sample. The content of styrene in both cases is comparable. Moreover, the contours of bands of the acrylic component in the range 1050–1300 cm⁻¹ are different suggesting different kinds of acrylic resins used in the studied samples. Unfortunately, the used resins can not be identified from the IR spectra.

Table 1. Absorption bands in IR spectra characteristic for paint binder components

Band	Wavenumber, cm^{-1}	Vibration type	Binder component
S	700	deformation (aromatic ring)	styrene
S	760	out-of-plane deformation of five adjacent H-atom of an aromatic ring	styrene
A	1160	(C-O) stretching in ester	acryl resin
A	1250	(C-O) stretching in ester	acryl resin
A	1450	(C-H) deformation	
A	1735	(C=O) stretching in ester	acryl resin
M	815	out-of-plane deformation of the triazine ring	melamine resin
M	1450, 1550	in-plane deformation of the triazine ring	melamine resin
M	1366	(C-H) deformation	
U	1463	(isocyanurate ring) stretching	urethane resin
U	1690	(C=O) isocyanurate	urethane resin
Al	1075	(C-O) stretching in ester	alkyd resin
Al	1130	(C-O) stretching in ester	alkyd resin
Al	1280	(C-O) stretching in ester	alkyd resin
Al	1730	(C=O) stretching in ester	alkyd resin

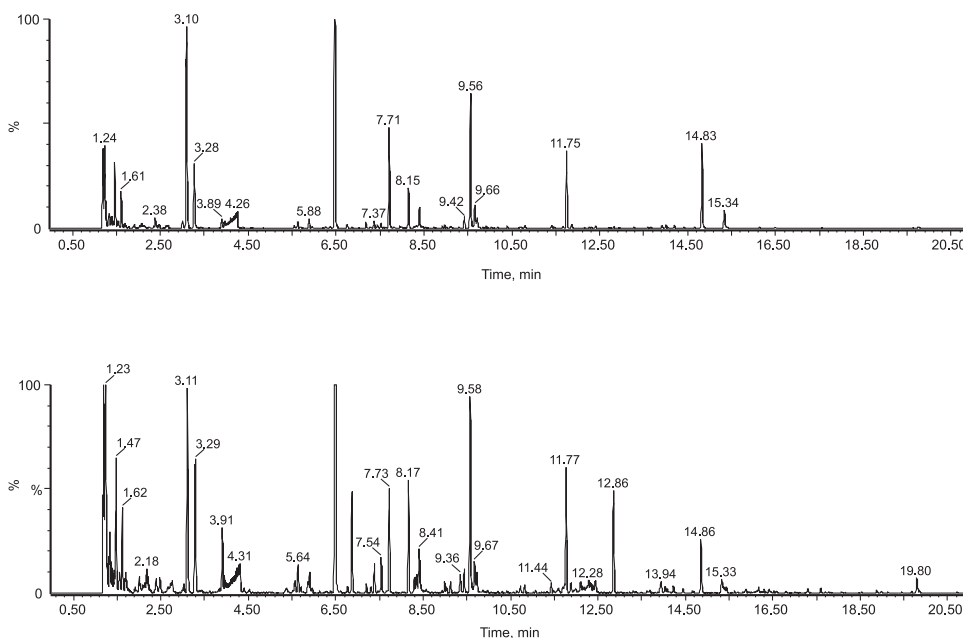


Figure 2. Pyrograms of paint samples No. 33 and 35

Pyrograms (Fig. 2.) obtained for the same investigated samples provide the detailed data on paint components. Intensive peaks at retention times 3.1 min (methyl methacrylate) and 6.5 min (styrene) and weaker peaks recorded after 7.7 min (butyl methacrylate), 9.6 min (2-hydroxypropyl methacrylate), and 14.8 min (1,6-diisocyanatehexane – the product of urethane degradation) were identified. The pyrograms also show poor differentiation between the samples with respect to their polymer composition. Sample no. 35, in contrary to the sample no. 33, contains methylopropylic methacrylate (6.9 min), 2-propenyl methacrylate (5.9 min) and 5-ethyl-1-nonen (12.8 min), (Tab. 2). Therefore, the difference in composition refers to acrylic resins. Urethane appears in all samples at the similar level and the information about its different content in particular samples is obtained only from the IR spectrum. The results obtained by these methods enable one to distinguish between the investigated samples based on the differences in their qualitative (Py-GC-MS) and quantitative (IR) compositions.

Table 2. Main constituents of paint samples No. 33 and 35

Compound	Retention time, min	33	35
Methyl methacrylate	3.1	x	x
3-Methylpentanal	3.3	x	x
Toluene	3.9	x	x
Methacrylic acid	4.3	x	x
Ethylbenzene	5.6	x	x
2-Propenyl methacrylate	5.9		x
Styrene	6.5	x	x
Isobutyl methacrylate	6.9		x
Butyl methacrylate	7.6	x	x
α -Methylstyrene	8.0	x	x
2-Ethylhexanol	8.4	x	
2-Hydroxypropyl methacrylate	9.4	x	x
3-Hydroxypropyl methacrylate	9.5	x	x
2-Ethylhexyl acrylate	11.8	x	x
Octyl methacrylate	12.9		x
1,6-Diisocyanatohexane	14.6	x	x

In Figure 3 the IR spectra of two acrylic-melamine-styrene paints (samples no. 86 and 193) are presented. The spectra differ in the intensity of bands corresponding to styrene (700 and 760 cm^{-1}) suggesting different contents of this compound in the investigated samples. Also the contours of acrylic bands ($1050\text{--}1300\text{ cm}^{-1}$) and melamine bands (1500 and 1366 cm^{-1}) are slightly different, what indicates small differences in the composition of acrylic and melamine resins in these paints.

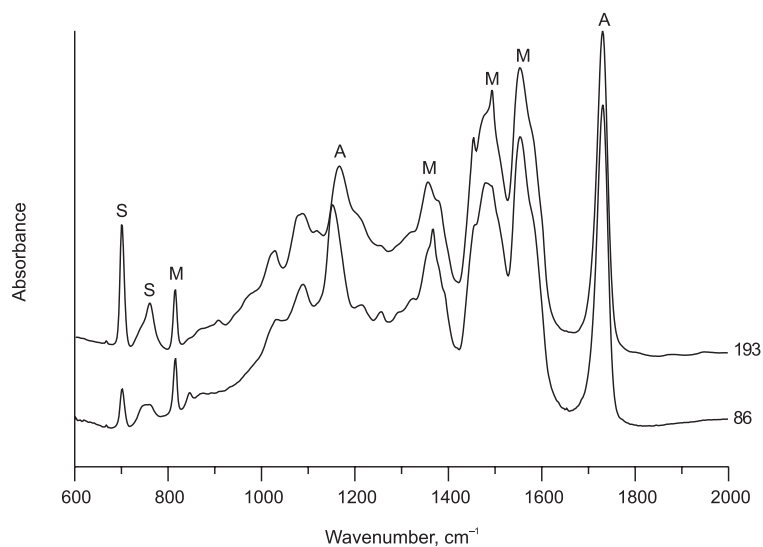


Figure 3. Infrared spectra of paint samples; A – acrylic resin, M – melamine resin, S – styrene

Pyrograms of the examined samples (Fig. 4) confirm the presence of styrene (6.6 min), butyl acrylate (6.4 min), and methacrylic acid (4.4 min) in each of them. The pyrogram of sample no. 86 exhibits, in contrast to the other two, two weak peaks indicating the presence of decyl acrylate (17.5 min) and butyl acetate (4.8 min). In the pyrogram of sample no. 193 there are signals corresponding to 2-ethylhexyl acrylate (11.8 min) and benzyl isocyanate (11.1 min). Thus, the differences in the contours of acrylic bands observed in the IR spectra are justified. Using the pyrolytic method also the traces of styrene in sample no. 86 were detected. Melamine, which is the main crosslinker, was easily identified in the IR spectra, however, any product of its pyrolytic decomposition was identified in the analysed pyrograms.

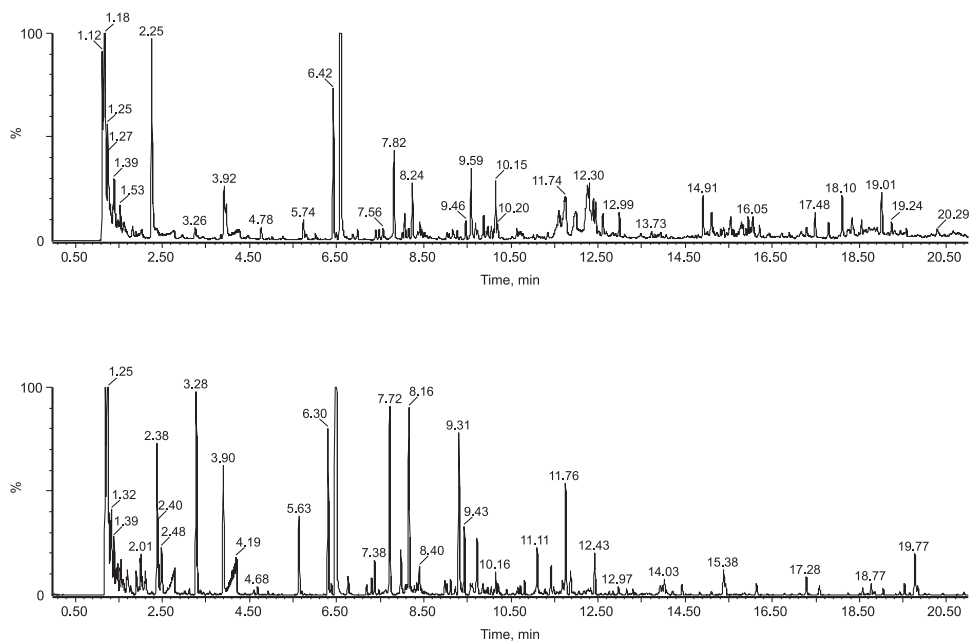


Figure 4. Pyrograms of paint samples No. 86 and 193. (Continuation on the next page)

Figure 5 shows the IR spectra of three alkyl-melamine paints (no. 83, 89 and 95). Distinct absorption bands indicate the presence of melamine, orthophthalic resin, and different quantities of titanium dioxide (Tab. 1). In the pyrograms of these samples (Fig. 6) the main peak originates from phthalic anhydride (15.1 min) corresponding to the phthalic resin. The signals of *o*-cyanobenzoic acid (17.2 min) and benzonitrile (9.3 min) are also visible. The presence of these compounds indicates modification of phthalic resin with melamine. The observed differences refer to the presence of different alcohols: 2-pentene-1-ol (3.7 min, samples no. 83 and 95) and 2-ethyl-2-(hydroxymethyl)-1, 3-propanediol (10.3 min, sample no. 89). The pyrogram of sample no. 95 differs from other pyrograms with respect to the presence of a peak at 16.4 min (2-methyl-1H-isoindole-1,3(2H)-dione), and that of sample no. 89 with respect to the presence of peaks at 10.5 min (3,5,5-trimethyl-hexanoic acid) and 14.0 min (2-ethyl-2-propyl-1-hexanol).

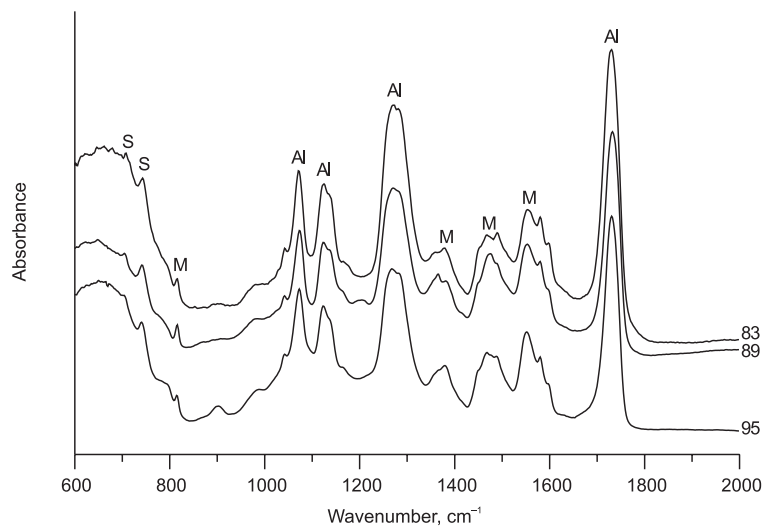


Figure 5. Infrared spectra of paint samples; Al - alkyd resin, M - melamine resin, S - styrene

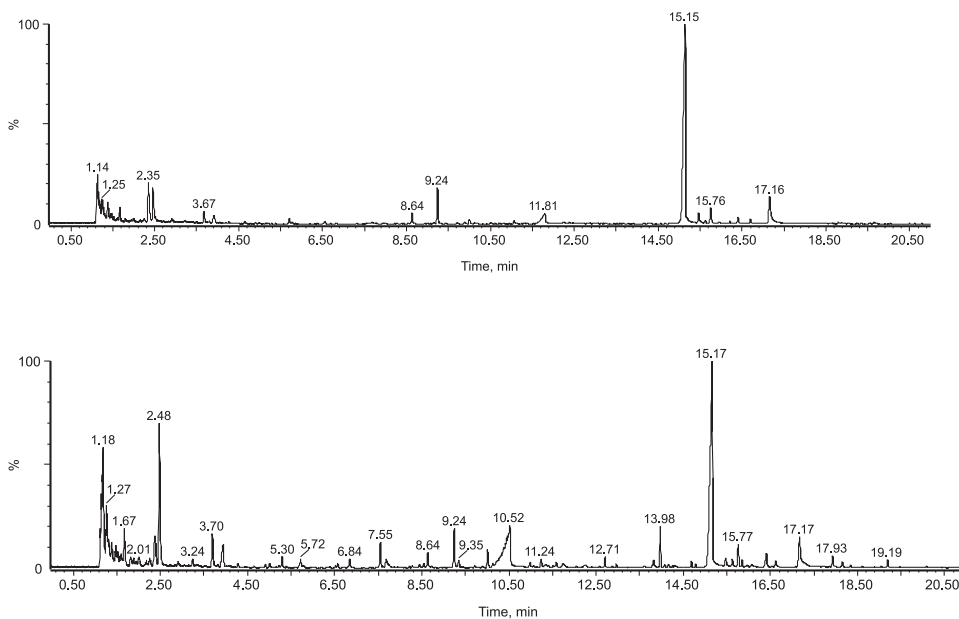


Figure 6. Pyrograms of paint samples No. 83, 89 and 95. (Continuation on the next page)

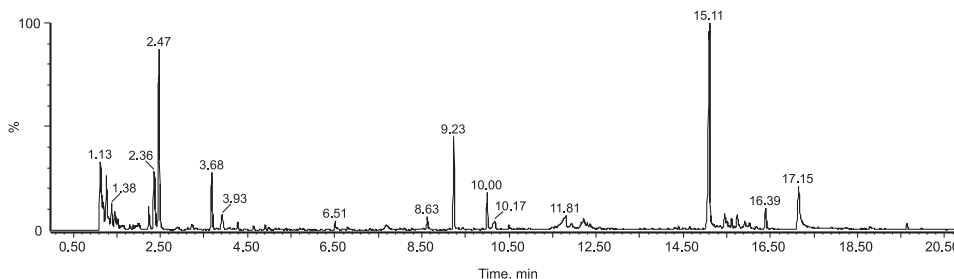


Figure 6. (Continuation)

The presented examples show that IR and Py-GC-MS methods are complementary. The information about the components of the paint sample obtained from a pyrogram are complete and precise in comparison to the information obtained from the IR spectrum – Py-GC-MS is a better method of sample characterisation. It has been observed that in a comparative study on paint samples composition, the presence of peaks originating from low-concentrated components can be essential for differentiation between the samples. These peaks inform about the presence of secondary components of the binder, which can not be detected by the infrared spectrometry. However, the IR spectrometry brightly shows the differences in the quantitative composition of the samples. The differences in the concentrations of the main components of the binder (*e.g.* styrene, urethane) observed in the IR spectra were not confirmed by the pyrolytic method. In the pyrogram, trace quantities of styrene appeared occasionally, and were not observed in the IR spectrum, even as a weak absorption band that can result from poor detection level of the IR spectrometry.

In the group of the analysed samples there were ones that originated from two different vehicles, but were characterised by very similar IR spectra and pyrograms (Figs. 7 and 8). Their qualitative compositions were indistinguishable by both applied methods. Only small differences in peak heights in the compared pyrograms were observed and it was difficult to decide, whether these differences result from the measuring errors or inhomogeneities of the samples, or correspond to the real differences in the composition. Anyway, the obtained results suggested similar chemical composition of different samples.

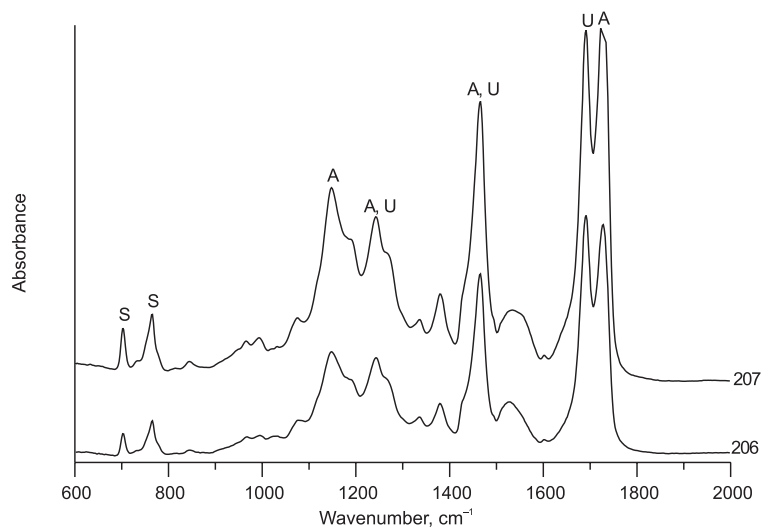


Figure 7. Infrared spectra of paint samples No. 206 and 207; A – acrylic resin, U – urethane resin, S – styrene

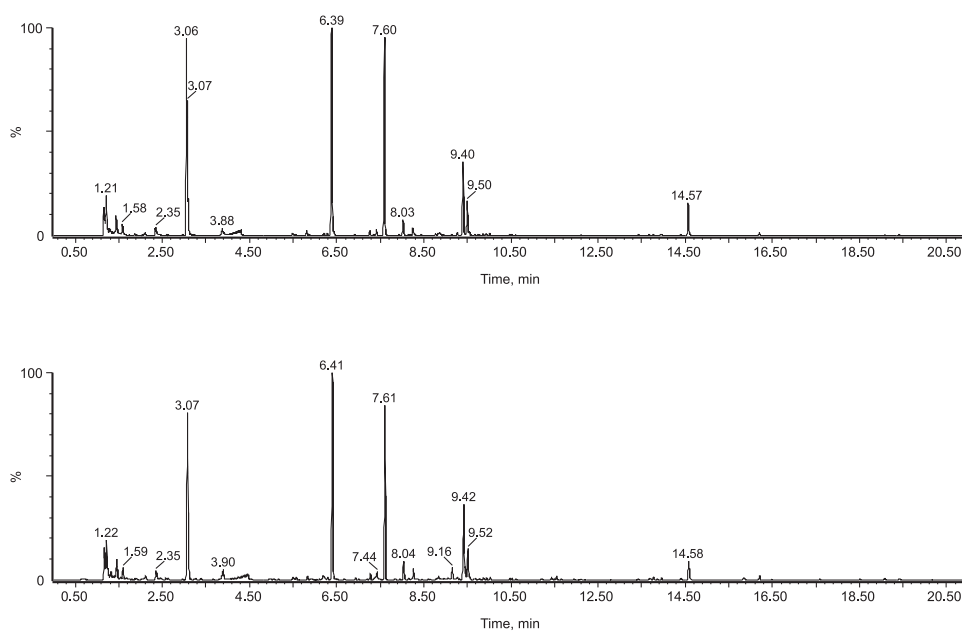


Figure 8. Pyrograms of paint samples No. 206 and 207

CONCLUSIONS

Infrared spectroscopy and Py-GC-MS have proven to be good tools for forensic examination of paints. FT-IR allows easy identification of the type of binders, whereas Py-GC-MS provides additional information helpful in further characterisation of binders as well as either confirms or excludes the presence of traces of other organic compounds like additives, plasticizers, and residual monomers. Since Py-GC-MS provides information on chemical composition, it often enables discrimination between paints having similar IR spectra. In most cases it was possible to differentiate between the paint fragments on the basis of variation in their polymer composition. In the comparative analysis of paint pyrograms also minor peaks should be considered to perform successful differentiation. However, in contrast to the IR spectra, pyrograms do not provide reliable information on the number of sample components.

The presented results have confirmed that the Py-GC-MS method is complementary to the infrared spectroscopy in the domain of paint samples examinations.

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