ANALYSIS OF BLACK SPRAY PAINTS BY FOURIER TRANSFORM INFRARED SPECTROMETRY, X-RAY FLUORESCENCE AND VISIBLE MICROSCOPY

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ABSTRACT: Black spray paints from different European manufactures were characterised to investigate various types of criminal offences. A total of 40 black spray paints were analysed by three techniques: 1. Fourier transform infrared spectrometry (FTIR) using the attenuated total reflectance technology (ATR), 2. X-ray fluorescence (XRF) and 3. visible microscopy of a coated surface. The results of the qualitative analysis permitted to classify spray paints according to binder type and elemental composition. A searchable spectral library was created. Variations of the paint composition due to can shaking prior to spraying were taken into consideration. A visible microscopic analysis of a coated surface characterised the morphology of the paint layer leading to a further discrimination of spray paints. The results of the latter analysis strongly depend on the structure of the substrate under a questioned paint coating. This can severely hamper a comparative study.

KEYWORDS: Spray paints; Infrared spectroscopy; X-ray fluorescence; Microscopy.

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INTRODUCTION

Spray paints are often used in criminal offences. The most obvious cases are graffiti and vandalism where spray paints are used to blot or destroy various kinds of objects. Secondly, in criminal attempts, offenders leave messages or signs by spraying paint at the place of crime. These marks can sometimes be the only valuable traces of evidence deserving an accurate analysis and discrimination.

At the present time, there is little or no information regarding the chemical characteristics and their variation in a population of black spray paints. The aim of this research was to analyse a range of commercial black spray paints produced in different European countries by: 1. Fourier transform infrared spectrometry (FTIR) using the attenuated total reflectance technology (ATR), 2. X-ray fluorescence (XRF) and 3. visible microscopy of the coated surface in order to differentiate spray paints by brand and by type within a brand and to build up a searchable spectral library of all paints.

Using these three powerful standard techniques for the analysis of paint, a high degree of discrimination of spray paints and a database of information on the black spray paints was obtained.

MATERIAL AND METHODS

All 40 black spray paints were bought in Belgian paint shops and home markets and origin from different European manufactures. This study involves different kinds of black spray paints used for general purposes, special metal or car coatings and in high temperature conditions. For each brand of spray paint all available variations were bought i.e. satin, brilliant and mat, metallic and high temperature paint. The latter variation was always a mat paint. All 40 black spray paints are listed in Table I.

Sampling

Paint was sprayed on microscope glass slides (SuperFrost Color, Menzel-Gläser Germany) for having a uniform coating. On each glass slide a piece of adhesive tape was mounted prior to spraying. Paint, sprayed upon this piece of tape, can be transferred to the sample holder of the XRF-apparatus. Moreover, paint on a glass slide is ideal for microscopic investigation and for infrared analysis with an ATR-objective. A prepared glass slide is depicted in Figure 1.

Two major sets of samples were made. One set concerns samples made with rigorous shaking of the cans, the other one was made without shaking of the cans. Nonshaken cans should stay at least 48 h without moving. Cans were shaken during at least 3 min (on a automatic laboratory shaker), where the bullet inside the could be clearly heard. If a spray can complied with one of these conditions, paint was sprayed on an appropriate glass slide. Spraying was performed from a distance of approx. 0.3 m on the side of the glass slide where the adhesive tape is mounted. Spraying was continued until a clearly visible coating was formed. Finally, the glass slides were allowed to dry horizontally for 72 h.

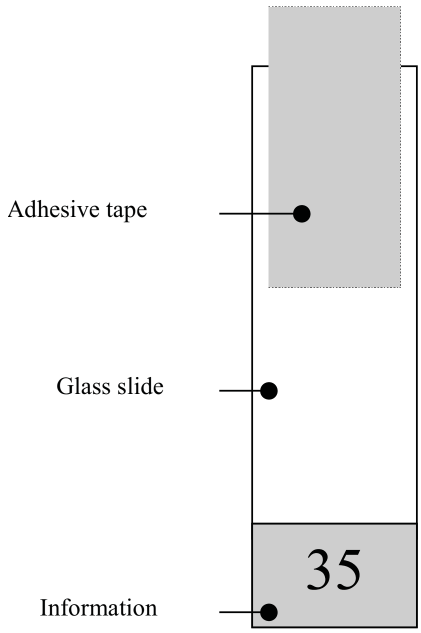
Fourier transform infrared spectrometry (FTIR)

FTIR using a spectrometer (Nicolet 510P, USA) equipped with a CsI beamsplitter, an IR-microscope (NIC-Plan, USA), an ATR objective (Spectra-Tech, USA) and a TGS detector was undertaken to analyse the chemical binders and fillers present in these coatings. 100 spectra were collected with a resolution of 4 cm^{-1} and the intensity (in % reflectance) vs. wavenumber (cm^{-1}) was measured between 650 and 4000 cm^{-1}. The obtained spectra were compared with our commercial and personal spectral libraries of paint materials.

TABLE I. COLLECTION OF BLACK SPRAY PAINTS

No.	Brand	Gloss or type
1	Altona	Satin
2	Altona	Brilliant
3	Altona	Mat
4	THERM	High Temp
5	BRICOBI	Metallic
6	BRICOBI	Mat
7	STOP (Brico)	Brilliant
8	Levis	Brilliant
9	Levis	Satin
10	Hammerite	Brilliant
11	Hammerite	Satin
12	MOTIP	Mat RAL 9005
13	MOTIP	Satin RAL 9005
14	MOTIP	Brilliant RAL 9005
15	MOTIP	Mat
16	MOTIP	Metallic
17	MOTIP	High Temp
18	ITI trimetal	High Temp
19	ITI trimetal	Mat
20	ITI trimetal	Brilliant
21	ITI trimetal	Satin
22	Dupli-Color	Satin RAL 9005
23	Dupli-Color	Brilliant RAL 9005
24	Dupli-Color	Uni A
25	Dupli-Color	Mat
26	Gamma	Satin
27	Gamma	Brilliant
28	Gamma	High Temp
29	ColorWorks	Satin
30	ColorWorks	High Temp
31	Protecton	Mat
32	Protecton	Brilliant
33	Protecton	High Temp
34	Air Crafts	Brilliant RAL9005
35	Air Crafts	Mat 021
36	Spencer	Mat
37	De Keyn	Mat
38	Funny Fashion	Hair spray
39	Aerosol Art	Mat
40	Hammerite	High Temp

Fig. 1. Prepared glass slide.



X-ray fluorescence (XRF)

To analyse the chemical elements present in spray paint coatings, X-ray fluorescence spectroscopy was carried out using a Kevex Omicron (USA) energy-dispersive X-ray fluorescence spectrometer. The operating conditions were as follows: the accelerating voltage was 45 kV; the beam current was 0.2 mA; the live time was 120 s; the energy range/gain was 0 to 40 keV; the resolution was 10 eV/channel; the analysis area diameter was about 2 mm and the measuring atmosphere was helium.

Microscopy

For this last method, but most often giving the first indicative characteristics of a coating, a microscopic investigation of the coated glass slide was done, using a Zeiss Axiotech (Germany) microscope with up to 1000 × magnification and bright- and darkfield observation.

RESULTS AND DISCUSSION

FTIR

The infrared analysis of spray paints revealed some typical characteristics of a paint. Figure 2 lists all possible binders and fillers which were observed by FTIR together with there presence in this paint collection. It is obvious that more than one of these substances can be present in one paint. On the basis of infrared spectra, spray paints were divided into six groups, i.e. nitrocellulose, nitrocellulose + talc, alkyd, alkyd + talc, styrene and silicone containing paints.

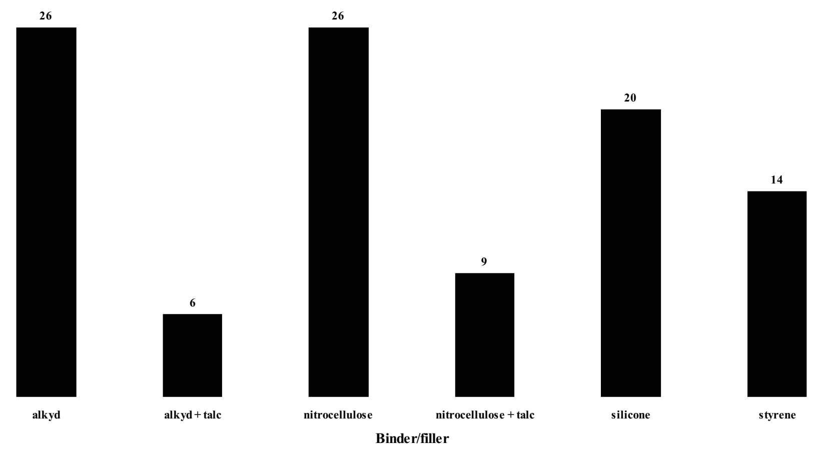


Fig. 2. Typical IR-characteristics and their presence [%] in the paint collection.

XRF

A further discrimination is possible when the elemental composition of the sprayed paint is analysed. All measured chemical elements and their presence (%) in the spray paint collection are depicted in Figure 3. A qualitative analysis does not show considerable differences between shaken and nonshaken cans, although quantitative differences were observed since coatings emanating from nonshaken cans tend to contain higher concentrations of chemical elements.

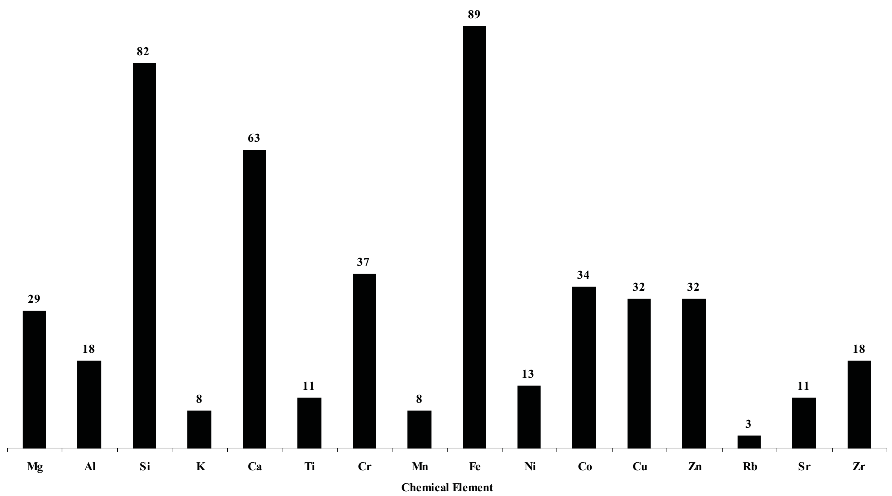


Fig. 3. Presence [%] of chemical elements in black spray paints.

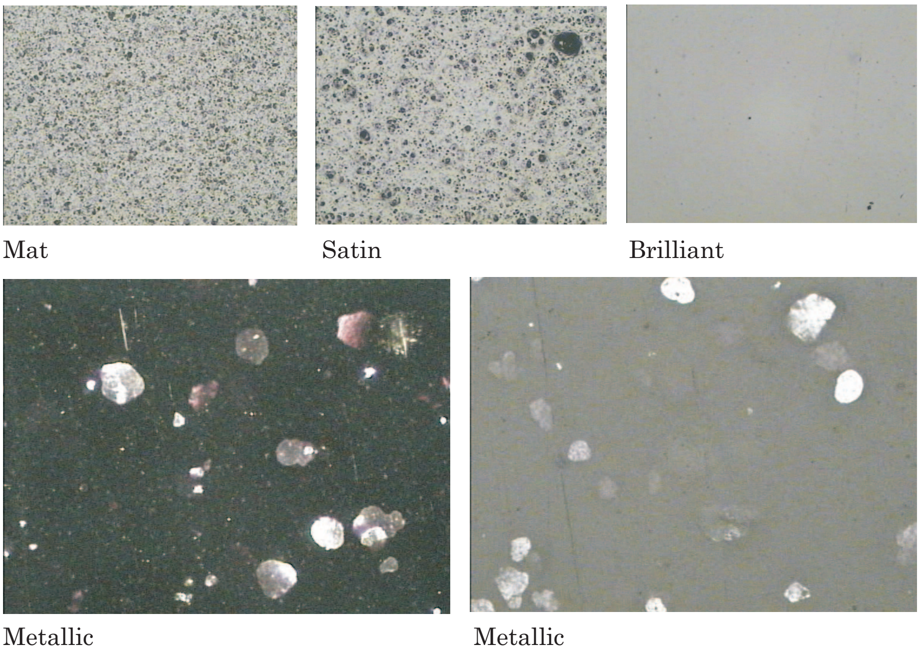


Fig. 4. Different types of spray paints (1000 x magnification).

Microscopy

A reflectance microscopic analysis of the coated surface characterized the morphology of the paint layer. One can differenciate a mat (M), satin (S) and brilliant (B) paint by a decreasing roughness (M > S > B) of the coating. A metallic coating can easily be recognised by the presence of metallic flakes, their distribution and shape. Examples of surfaces are shown in Figure 4. These pictures are made on flat glass slides where differences between paint types are more easily observed than paint sprayed on walls, wooden panels, etc. These supports can be rough or absorb paint leading to the absence of an uniform paint layer. Furthermore, coatings from nonshaken cans tend to be more brittle and get loose of the substrate than those emanating from rigorous shaken cans. All these variations hamper a comparative study.

CONCLUSION

Analysing black spray paints using FTIR and XRF gives valuable results leading to a high degree of discrimination. The reference collection of black spray paints contains 40 different paints building up a searchable

FTIR-spectral library. IR-spectra characterise each spray paint according to binder type and fillers. When information about the elemental composition of each paint is added, a confirmation of the paint characteristics is obtained and even a further discrimination. A visible microscopic analysis can distinguish between mat, satin, brilliant and metallic paints. The results of the latter analysis strongly depend on the structure of the substrate under a questioned paint coating. This can severely hamper a comparative study.