The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

SMR/1843-2

X-Ray Emission Techniques for Forensic Applications

28 May - 1 June, 2007

X-ray spectrometry in examination of criminalistic traces in practice of Institute of Forensic Research

Janina Zieba-Palus
Institute of Forensic Research, Cracow, Poland

X-ray spectrometry in examination of criminalistic traces in practice of Institute of Forensic Research

Janina Zięba-Palus

Institute of Forensic Research, Cracow, Poland

So-called contact traces like paint chips, glass fragments, oil stains, fibres, metal attrition, soils, building materials, loose powdered materials, appear in the traditional areas of forensic science. Their identification and comparison can help to establish if the suspected person was involved in a crime. Currently, the most suitable method for trace evidence analysis in most forensic laboratories is SEM equipped with an energy dispersive X-ray spectrometer. In the paper the application of X-ray analysis in the examination of selected contact traces in Institute of Forensic Research (IFR) in Cracow.

Paint traces

Particles of paint coats are revealed most often in connection with events such as car accidents, robberies or burglaries. They occur as micro-fragments of paint coat or visible smears of paint in the form of coloured streaks on the clothing of persons being involved in these events or on other substrates. The aim of paint examining is to establish the degree of similarity between the sample forming the paint trace and the sample originating from the suspect (from his vehicle, tools used in the act etc.). Identification analysis is also carried out, which leads to the determination of the type of paint product, its use, the producer and the year of production. Routine examination of the paint includes also of its chemical composition.

Most often fragments of paint have a multilayer structure while paint smears contain one or two layers of painting material mixed with together and sunk into the base (e.g. among the fibres of the fabric). Each layer is a mixture of many chemical compounds i.e. polymer binder, several organic and inorganic pigments and extenders. Samples of paint coats can have the same binder but different pigments. This is especially true for car paints (one type of car paint is offered in various colours and shades). Paints of the same colour can also contain a different set of pigments and extenders, which depend on the type of paint and on its producer. Thus, when comparing paint samples it is necessary to identify pigments and extenders on the basis of the elemental composition of the paint sample, making use of IR spectra and data on possible pigment sets used in the paint industry.

The method of scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM/EDX) has been applied in the analysis. It enables imaging of the sample and determination of elemental content. The results of elemental analysis can be registered in the form of X-ray spectra as well as the elemental map of the sample, which shows the kinds of detected elements and their distribution in the sample. However, elemental maps are generally not quantitative and may lack the sensitivity to demonstrate minor sample differences.

Because of the small size of fragments of paint coat and their layer structure, a number of sample preparation techniques have to be applied, making possible interaction of the beam with every layer, and thus ensuring registration of the X-ray signal for each of them. The fragment of paint coat can be embedded in the resin and then cut into slices perpendicular to the surface of the coat fragment, using a microtome to obtain a cross-section of the examined sample. In many cases cutting of paint sample with a scalpel in order to expose all paint layers is preferred. Determination of the elemental composition of paint forming smears requires the isolation of a paint particle from the substrate.

In comparative analysis of paint samples identification of pigments and extenders enables in many cases differentiation between the car paint fragments of the same colour of the external layer [1]. It is also helpful in revealing the paint traces in smears on tools used in crime, clothing of victim or on the bullet which penetrates the painted surface, e.g. car body [2].

Oils

Oil traces are revealed on the clothing of car accident victims as greasy stains, arising as a result of contact between the victim and the chassis of a vehicle. In the course of a criminalistic examination, an oil sample extracted from the fabric is compared with oil taken from the suspected car in order to establish their similarity. Chromatography, IR spectrometry and various methods of the elemental analysis are routinely applied in the examination of oils. Elemental analysis of oil helps both, in its identification and in an assessment of its degree of use.

Oil contains additives suspended in the hydrocarbon base i.e. organic compounds like alkylosulphonates, alkylonaphtenates, alkylophenolates or alkylodithiophosphates of zinc, barium, magnesium and calcium, which are added to the oil in order to improve its usage properties. Particular types of oils differ amongst themselves both, in the hydrocarbon base and in the kind and concentration of additives. When the engine is working during use of the vehicle, the composition of the oil changes. Small bits of metal originating from the wearing away of, e.g. cylinders, pans, valves and other parts of the oiled engine transfer to the oil. Their quantity depends on usage conditions and on technical state of the vehicle.

Formerly, atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES) were commonly used in examination of oils. Nowadays, a convenient method of elemental analysis of oil is X-ray fluorescence (XRF). Less sensitive in comparison to AAS, it does, however, have one big advantage. This method makes it possible to analyse an oil sample directly in the unchanged state or possibly after dilution with an organic solvent. However, the XRF method for the quantitative determination of elements requires complicated calibration with standard samples. So, comparison of the composition of oil samples is often performed by a non-quantitative method such as peak ratioing.

Examinations on differentiation among fresh and used oils were performed at the IFR. Comparing fresh oils the presence of Zn, Ca, P and S could be detected by means of XRF method. Although the spectra obtained manifested to be generally similar, the peak intensities differed slightly in fact. The calculated sets of peak integral ratios: S/Zn, Ca/Zn, P/Zn were in general systematically different for the studied oil samples. It was found that the elemental analysis providing information on the additives is complementary to IR spectroscopy in differentiating among oil samples [3].

A model experiment was performed in order to establish the possibility of discriminating between used oil samples on the basis of their elemental composition. Oil samples were withdrawn from the sumps of two cars after various time of exploitation. Elements originating both from the additives and from the wearing away parts of the engine were determined in an oil sample. The semiquantitative method was applied, comparing characteristic signals for particular elements with the signal of a chosen element in the sample. It was observed that as the oil in the car was used up, the concentrations of, amongst other things, iron, cadmium, lead and copper increased. The concentration of these metals in oil is related to its degree of use, whereas the concentration of calcium, barium, magnesium, zinc and phosphorus is stable. Providing information on the kind and quantities of refining additives can be helpful in differentiating between types of oil. A schema of criminalistic inference on the basis of comparison of metal contents was proposed as well [4].

Glass

Glass fragments are known to transfer to the clothing of a person breaking a window. They are revealed in cases of traffic accidents, fights or robberies. They have various sizes.

Those found at the scene of the event are larger fragments, whereas those revealed on the clothing, hair or body of persons are small - with linear dimension less than 1 mm. Routine examination of glass fragments includes establishing their elemental composition and determining the refractive index. These data can be used by a forensic scientist for comparison of glass samples, and also for ascertaining the kind of object they could have originated.

The main elements such as Na, Ca, Si and Al are present in all glass categories at nearly the same level. The differences concern other elements originating from various additives, which are added to improve the usage properties of the glass or in connection with its later application or else originate from impurities in raw materials used in the production process. Their concentration is significantly lower (at trace level).

The chemical composition of glass can be determined by many methods. Non-destructive methods are preferred, allowing the sample to be examined using two or more analytical methods. Another desirable feature is the possibility of simultaneous determination of several elements (analytes), using the smallest possible amount of studied material. In the case of analysis of glass microfragments, these requirements are fulfilled by SEM/EDX and XRF methods. However, they permit identification of elements occurring in glass in large quantities.

Currently, SEM/EDX is applied in the routine examination and evaluation of glass evidence in our institute. For qualitative determination, a glass fragment is placed on a stub and, after sputtering with carbon, assuring its conductivity, the elemental composition is determined. In the case of quantitative analysis, sample preparation is required, involving embedding the glass fragment in a plastic resin and then polishing the surface until it is flat, using grinding methods. The surface is usually coated with a carbon layer and the fragment is sampled at different locations.

In the interpretation of analytical data obtained during examinations of glass fragments by elemental analysis statistical and chemometric methods are usually applied. Car window glass, car headlamps, external glass of car light bulbs, internal glass of car light bulbs, internal glass of ordinary light bulbs, and sheet glass were investigated by SEM/EDX and a scheme of glass classification based on results of quantitative analysis was elaborated. Concentrations of aluminium, barium, calcium, iron, lead, magnesium, potassium, sodium and zinc were determined. A non-statistical method and the use of cluster analysis led to correct classification of most of the studied glass samples [5].

The administration of justice raises new challenges for forensic examiners, i.e. an evaluation of the probability that the suspect committed the crime. It requires taking into account the objective data, i.e. analytical data obtained from the analysis of the evidence material such as glass fragments, data obtained from population studies (e.g. on the recovery of traces from clothing), as well as subjective data, i.e. an information on the course of the crime. A study was performed at IFR to obtain an information on the persistence of glass fragments resulting from the primary transfer from broken multiply glazed window sets as well as on glass found by chance and the secondary transfer. The obtained results in the form of multivariate data became a starting point for developing a statistical approach to evaluation of the evidential value of glass microtraces in terms of likelihood ratio approach [6].

GSR

Gunshot residue (GSR) examination plays an important role in establishing some circumstances of a crime with the use of a firearm. The most characteristic gunshot residues are metallic particles arising from components of the primer, demonstrating characteristic morphology (size of the order of micrometers, approximately spherical shape) and also specific chemical composition (lead, antimony and barium in the case of lead ammunition). Found around the gunshot hole and on the clothing and body of the shooter, they provide information on which to base about the shooting distance and the kind of ammunition used (and thus the weapon) and, most importantly, they enable to link the suspect to the shooting.

The most successful technique to date for the analysis of GSR particles is scanning electron microscopy with an energy dispersive X-ray analyser (SEM/EDX). With most of the other techniques that have been used for GSR analysis, the sample is destroyed during examination.

Mostly, half-inch diameter aluminium stubs with an adhesive layer of double-sided tape are used for sampling. When the sample has been secured on the stub, one then searches through it for spherical metallic particles of defined diameter and chemical composition. Suitable software for automatically searching through the secured material on the stub (in order to detect particles with specific features) helps in receiving results in a quite short time.

An attempt was made to identify used ammunition on the basis of qualitative assessment of differences in the chemical composition of GSR [6]. Evaluation of the obtained analytical results was carried out by, amongst other things, chemometric methods. These studies showed significant differences between gunshot residues originating from different ammunition types, and thus it was possible to achieve at least group identification of ammunition (and hence the type of firearm used) from information on GSR alone. The idea was later developed in collaboration with other European forensic institutes within a project founded by EU. The aim of the project was differentiation among GSR originating from various brands of Luger 9mm taking into account X-ray spectra and morphology of particles as well as collection of a database and elaboration of a program for comparison of an unknown sample with the database [7,8].

Miscellaneous

XRF spectrometry is applied in screening analysis of complex materials, such as sediments from waters , the soil, body fluids, hair or stomach contentsas well as unknown materials, with the aim of quickly establishing the qualitative elemental composition (especially heavy metals being components of inorganic poisons) of the examined material. Although, quantitative analysis is usually performed by means of AAS or ICP/MS methods, XRF being able to analyse the material *in situ* allows us to obtain information on all elements in the sample, and then to select those that are interesting for further examinations.

Combined methods

In routine examination of criminalistic traces both elemental composition and molecular structure are very useful for identification process. So, the efforts have been made within the European project to combine two methods i.e. X-ray and Raman spectrometry in the form of a single apparatus (named PRAXIS). The aim of work of IFR was to assess the usefulness of this apparatus in forensic analysis of pigmented materials.

Measurements were performed using a PRAXIS prototype – a combined μ-XRF and μ-Raman spectrometer which enables the determination of all elements heavier than Mg (Z=12) with the help of X-ray fluorescence and additionally the analysis of complex molecules by Raman spectroscopy. The apparatus consists of two parts, i.e. a Raman spectrometer (Jobin Yvon, France) with 633 nm laser excitation and a fibre optic connection of the measuring head to the spectrometer, resolution approximately 3 cm^{-1} and also an energy dispersive micro-beam X-ray fluorescence spectrometer (IFG, Germany) with a fine focus X-ray tube (max. 50kV, 30W), a polycapillary optics with spot size of approx. 30 μm and a drift chamber detector with a sensitive area of $5mm^2$ with energy resolution of <140 eV. It enables analysis by means of two techniques which are normally used in identification of the kind of pigments and dyes in different materials creating traces on the scene of crime. In order to evaluate its usefulness for criminalistic purposes multilayer paint chips and modern inks were chosen for examinations.

Ten fragments of multilayer automobile paint coats were examined. Examination of the elemental composition was possible after dividing the paint sample into single layers.

Examinations were also performed for blue, red and black inks originating from ballpoint pens and gel pens of various brands and made by various manufacturers, commonly available in Poland. For each of the investigated inks, lines were drawn or a short text was written on smooth white paper (IBM Laser Paper 90 g/m^3). The ink samples were examined by Raman spectrometry in the visible range and XRF spectrometry directly on the paper. Additionally, the ink samples were analysed by XRF after drying on glass plates.

The conducted studies confirmed the usefulness of the Praxis apparatus in the examination of criminalistic traces [9]:

- PRAXIS allows forensic experts to examine paint samples in normal case work and enables them to perform a non-destructive analysis of very small paint samples as well as ink lines on documents.
- The measurements could be performed without prior sample preparation. However, the relatively large spot size of the X-ray beam makes it impossible to measure the XRF spectrum of a thin paint layer. So, the particular thin paint layer should be isolated from the base before measurements. Similarly, for ink samples the influence of paper on XRF spectra obtained has to be taken into account.
- In the analysed samples, light elements such as Al, Si and Mg – present in typical paint extenders - were not usually detected, whereas an application of commercial XRF spectrometers enables identification of elements beginning with boron.

Conclusions

X-ray spectrometry, either alone or in conjunction with scanning electron microscopy, has a well-established position in the forensic analysis of elemental composition. Great expectations are currently linked to the µ-XRF technique. The small diameter of the X-ray beam focused on the sample allows analysis of single microfragments of glass objects or individual paint layers. It does not involve complicated sample preparation prior to the examinations. It is possible that further development of this technique will enable forensic experts to examine evidential traces directly on the substrate on which they occur.

References

[1] Zięba-Palus J.: The Use of Micro-Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy with X-Ray Micro Analysis for the Identification of Automobile Paint Chips, „Microchimica Acta", suplement 14, 1997, 14, s. 357-359.

[2] Brożek-Mucha Z., Matching projectiles to gunshot holes in the case of multiple shooting to a passenger car by a number of shooters, ENFSI Firearms and GSR Working Group 2005 Meeting, 31August - 2 September 2005, Oslo, Norway.

[3] Zięba-Palus J., Kościelniak P.: Differentiation of Motor Oils by Infrared Spectroscopy and Elemental Analysis for Criminalistic Purposes, „J. Molecular Structure", 1999, Vol. 482–483, s. 531–536.

[4 Zięba-Palus J., Kościelniak P.: An analysis of the similarity of motor oils on the basis of their elemental composition, „Forensic Science International", 2000 112 (2-3) 81-89

[5] Brożek-Mucha Z., Zadora G., Differentiating between various types of glass using SEM-EDX elemental analysis. A preliminary study, Problems of Forensic Sciences, 1998,vol. XXXVII, 68 – 89.

[6] Z. Brożek-Mucha, G. Zadora, Breaking of multiply glazed windows – research on the persistence of glass microtraces on clothing, Problems of Forensic Sciences, 2006 (in press).

[7] Steffen S., Niewoehner L., Barth M., Otto M., Brożek-Mucha Z., Biegstraaten J., Horvath R., Differentiation of Gunshot Residue of Various Ammunition Brands Investigated by SEM/EDX, (in:) Chemometrics – Methods and Applications, Zuba D., Parczewski A. (ed.), Institute of Forensic Research Publishers, Krakow 2006, pp. 235 – 245.

[8] Brożek-Mucha Z., Steffen S., Niewoehner L., Barth M., Otto M., Biegstraaten J., Horvath R., A Study of the Element Contents and Morphology of GSR Originating from Chosen Brands of 9 mm Luger Ammunition, (in:) Chemometrics – Methods and Applications, Zuba D., Parczewski A. (ed.), Institute of Forensic Research Publishers, Krakow 2006, pp. 247 – 258.

[9] PRAXIS – combined μ-XRF and μ-Raman spectrometers in the examination of forensic samples, Forensic Sci. Int.(in press)