https://doi.org/10.34836/pk.2025.324.3

Microtraces in forensic examinations in the past and today as demonstrated by the example of metal, metal alloy and glass traces

Major Anita Czerwińska
Central Forensic Laboratory of the Police
ORCID: 0009-0005-2434-8313
e-mail: clkpw6@policja.gov.pl

Abstract

The article presents the evolution of methods for examining microtraces of metals, their alloys and glass in Polish forensics over the last few decades. It describes the transition from classical, destructive analytical techniques to modern instrumental analysis such as X-ray fluorescence. Modern physicochemical methods enable fast, precise and non-destructive examinations with high sensitivity, as illustrated by examples from expert practice in assessing the authenticity of jewelry products and detecting forgeries.

Keywords: microtaces, metal and their alloys, glass, jewelry products, analysis of elemental composition

When comparing analyses of interesting cases from the 1970s and 1980s presented by experts from the Forensic Department of the then National Police Headquarters (KG MO), with current papers published in “Problemy Kryminalistyki”, one can clearly see differences in the descriptions of the evidence submitted for examination. In the past, those descriptions were very detailed and employed specialist parlance specific to the field to which the subject belonged. This was often due to the fact that those commissioning an expert opinion required comprehensive examinations and requested that the method/technique used for manufacturing a given piece of jewellery or a coin be determined, or that the type of moulds, dyes and tools used be identified. Those opinions could be issued in collaboration with the Assay Offices and experts from the National Museum and the Issue Vault of the National Bank of Poland. Nowadays, these descriptions are more concise, often supplemented by extensive photographic documentation, with a significant portion of the opinion devoted to the description of the specialised instrument methods used for analysing a given trace. The number of methods available now is far greater, and they are more sensitive and accurate, while examinations are non-destructive.

Previously, in addition to a thorough preliminary examination of a coin, its specific gravity and the colour of the metal from which it was made were determined, along with its weight, diameter and thickness. These were then compared with tabulated weights and hallmarks of the most common original gold and silver coins. In many cases, the data enabled preliminary identification of type of metal or alloy from which a counterfeit coin was made. However, if the counterfeit was more complex, the PGS-2 emission spectrograph was usually employed (Fig. 1 and 2) to establish the elemental composition. It was a non-computerised

and time-consuming technique, involving destructive tests, and the sample size required for analysis was in the order of milligrams. It offered an advantage of determining trace elements [1].

Fig. 1. A spectrograph stand with electrodes mounted on it (a UBI-1 generator can be seen in the background)

Fig. 2. A Zeiss PGS-2 spectrograph

The samples were placed in graphite electrodes and burned in a direct current arc. When excited, the atoms of the elements in the substance under examination emitted radiation which, after passing through the cleaving system, produced a spectrum that was recorded on a glass plate coated with photographic emulsion and placed in a special cassette, which was then subjected to photographic processing. This involved removing the plate from the cassette and immersing it first in a tray with developer and next in a tray with fixer, followed by rinsing and drying in a room with no light access, known as a 'darkroom'. The exposed spectral plate was placed in a spectroprojector, where the enlarged image of the plate, projected onto the table, was compared with an atlas of spectral lines [2].

Fig. 3. Zeiss SP 2 spectroprojector (without the outer casing and curtains)

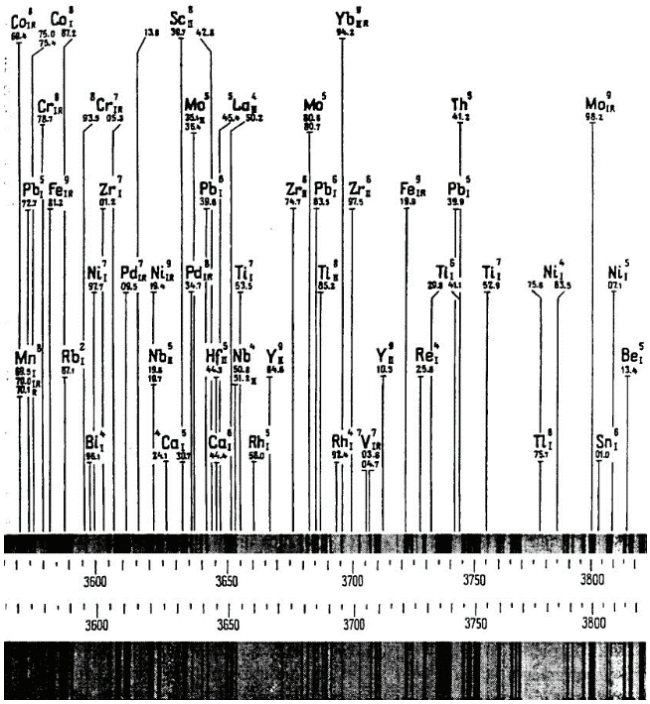

Fig. 4 A section of the spectrum from the spectral line atlas (above the scales) compared with a section of the sample's spectrum (below the scales)

At present, cases are reported that involve bars that resemble investment gold bars produced by various mints around the world, including ARGOR-HERAEUS S.A., PAMP, The Perth Mint Australia, among others. The very accurate finishing of those bars, combined with the requirement to place them in plastic packaging, means that buyers do not suspect them of being counterfeit.

Fig. 5. A bar resembling a PAMP-minted investment gold bar, complete with a certificate

Fig. 6. A bar resembling a PAMP-minted investment gold bar, complete with a certificate

Following a detailed description of the macro- and microscopic examinations of this type of traces (weight, dimensions, description of defects or surface abrasions on the bars found in the previously opened packages with certificates), instrumental examinations of the elemental composition are carried out using the micro-X--ray fluorescence (μXRF ED) method. This is a quick and non-destructive method.

Fig. 7. An EAGLE II μ-X-ray fluorescence spectrometer

Upon examination, the bars are often found to be made of a copper-nickel alloy coated with a thin layer of gold. In other words, their elemental composition does not match the specifications stated on their surfaces and in their certificates, according to which they should be made of fine gold.

Currently, the Chemical Examination Department's latest instrument for elemental composition analysis is the SPECTRO XEPOS XRF spectrometer, which is characterised by high sensitivity, resulting in a threefold improvement in measurement precision. This provides the basis for ensuring accuracy of analyses across a range of element concentrations, from trace levels to high concentrations.

This method is currently used for examining jewellery items secured in connection with fraud cases. Fraud is an offence that involves causing disadvantageous disposal of property to obtain a financial advantage by misleading the other party as to the material from which the jewellery offered for exchange was made.

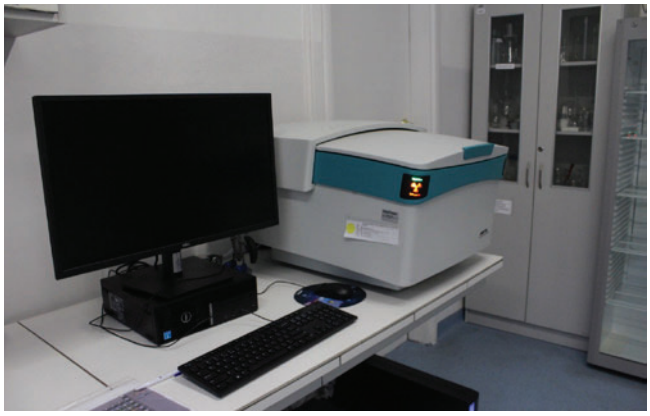

Fig. 8. A XEPOS X-ray fluorescence spectrometer

Based on quantitative examination of the elemental composition of a piece of jewellery, it is possible to estimate its fineness. Previously, this purpose was achieved by means of touchstone testing, which relied on the relationship between the colour of the alloy and its qualitative and quantitative composition.

Fig. 9. A test kit for determining fineness of precious metal products

The examinations involve comparing the intensity of the chemical reactions that occurred when test liquids are applied to the streaks. The analysis was carried out on a touchstone using the test specimen and a reference test needle with the closest matching alloy colour. "Streaks" were made on the clean surface of the touchstone using the object under examination and needles with matching colours with finenesses higher and lower than that suspected for the object under examination. Next, a drop of the test liquid appropriate for the suspected fineness (e.g. for 3-carat gold, this is a solution of gold(III) chloride, 18 g of 0.999 fine gold in the form of gold(III) chloride, water to the volume of 1000 cm^3) was applied to the streaks on the touchstone with a glass rod, and the course of the reaction was observed for 20 seconds. Next, the excess liquid had to be removed and the intensity, colour and quantity of the resulting precipitate compared. If the effect of the liquid on the "streaks" was the same, it indicated that the alloy contained the same proportion of precious metal. If not, the procedure had to be repeated with further needles until the matching effect of the liquid on the "streaks" was obtained [3].

Microscopic examination of such traces plays an important role, particularly in the observation of hallmarks and other symbols stamped on products. These marks are unique to individual manufacturers. There is no doubt that the ongoing development of microscopy and its advanced techniques have an impact on the quality of examinations. Furthermore, the availability of specialist literature online makes it easier to familiarise oneself with the subject of a particular field. In the case in question, the products were found to be made of a copper-zinc alloy, i.e. brass, coated with a thin layer of gold, while according to the hallmarks "585", which had most likely not been applied by the Assay Office, said items should primarily consist of gold, as the "585" hallmark indicates 58% gold content. In addition, the jewellery submitted for testing was found to bear the

stamped symbols “XP”. According to online sources, the XP symbol is the logo of Xuping, a Chinese manufacturer of gold-plated jewellery made from copper and electroplated with a layer of gold.

In examinations of glass traces, it is now possible to examine increasingly smaller glass particles by means of routine use of an electron microscope for qualitative and quantitative analysis of elemental composition using the energy-dispersive X-ray microanalysis (SEM/EDX) method.

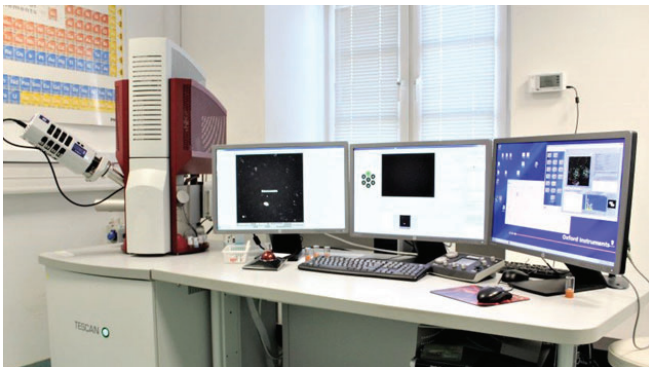

Fig. 10. A scanning electron microscope

The Chemical Examination Department at the Central Forensic Laboratory of the Police (CLKP) currently carries out examinations using an integrated analytical system: a *Tescan Mira 3* LMU scanning electron microscope coupled with an Oxford Instruments SSD-type X-Max^N energy-dispersive X-ray spectrometer with the Aztec EDS detector software package ver. 2.4. This method can be used for examining glass microfragments with a surface area of less than 0.2 mm ^{2}. It is a quick, non-destructive technique that does not require any complicated preparation of the test material. Traces with a similar elemental composition are passed to the next stage of testing, which involves measuring their refractive index. The refractive index (RI) of glass is measured with the thermo-immersion method and the GRIM III system from Foster & Freeman in monochromatic light (590 nm), employing B-series glass standards and type B immersion oil from Locke Scientific. This latest system offers measurements that are accurate to five decimal places, with a standard deviation of 0.00002 over a five-hour period and 0.00003 over a five-day period. The system can analyse up to four edges of a single fragment simultaneously, which significantly improves the speed of measurement and ensures greater statistical accuracy. The test results are archived and password protected along with such details as the case number and the operator’s identity. In addition, basic statistical data on the results is generated, including the mean, range and standard deviation. The software contains two clustering algorithms and two match-test options, offering the examiner the flexibility to choose the approach that is best suited to their laboratory’s quality requirements. The results can be displayed as charts and formatted for export to Microsoft Office for further analysis.

Fig. 11. A refractive index measurement kit GRIM III

In the 1970s, the absolute thermo-immersion method, which had been developed at the Forensic Department of the then National Police Headquarters, was also used for comparative glass analysis. The examinations were carried out using a Boetius microscope fitted with a heating table. The refractive index results were given with the accuracy to four decimal places [4].

A relative thermo-immersion method was also employed with the use of the aforementioned microscope, in which an immersion fluid with the refractive index of $n_D^{25} = 1.5241$ was applied. The temperatures (in degrees Celsius) at which the refractive indices of the immersion fluid and the test samples were equalised were recorded. The test results indicated that the temperatures at which the refractive indices of the reference samples and the test samples became equal differed by less than 2^{o}C (which was the margin of error) or showed no difference at all. The similarity between the traces was confirmed through X-ray fluorescence analysis on a Finnigan QM-905 spectrometer [5].

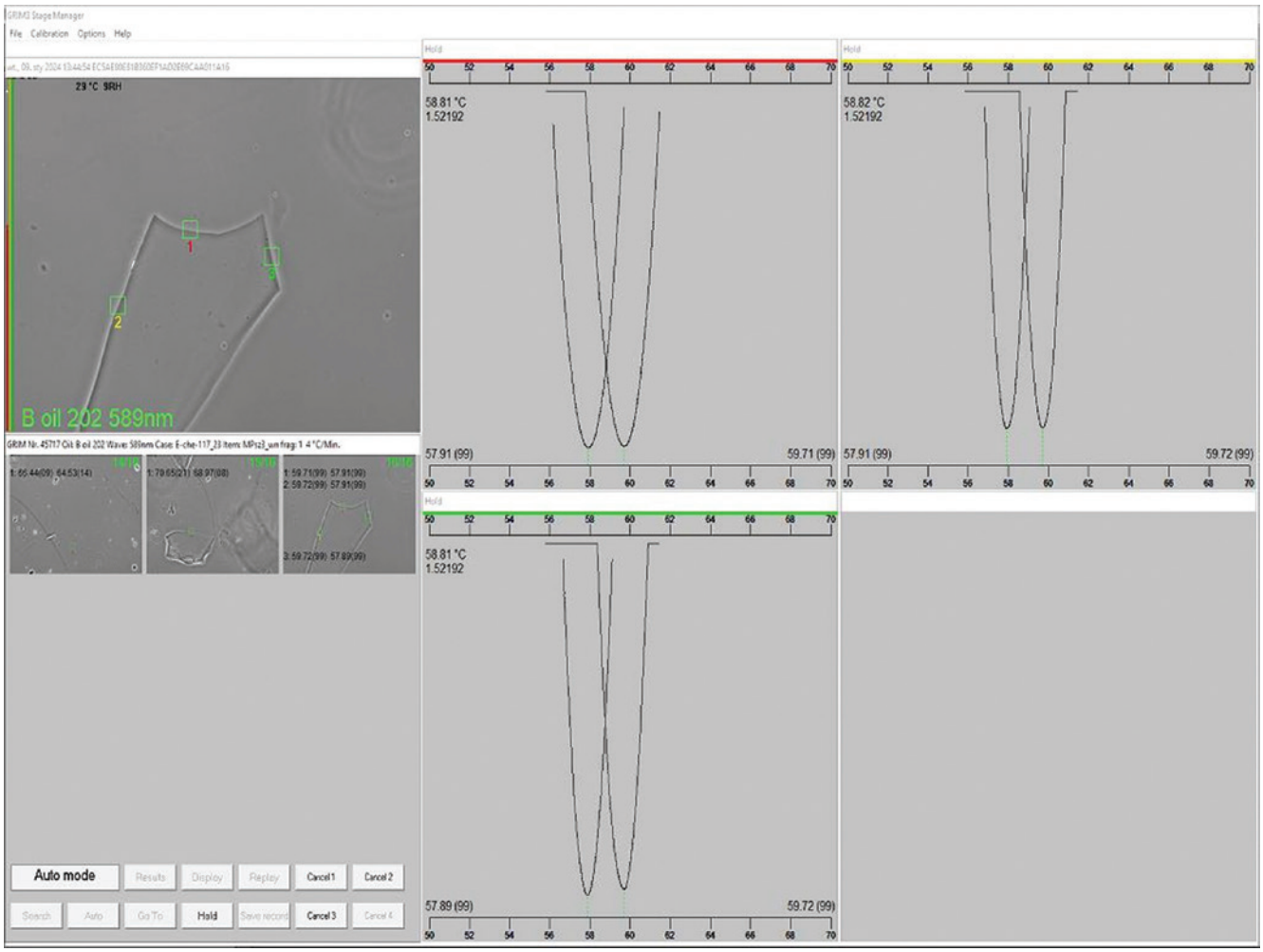

Fig. 12, 13, 14. Results of refractive index measurements carried out using the system GRIM III

Used for comparative examination of glass traces was also the spectral emission analysis method mentioned above, in which a glass sample had to be ground into a powder (approx. 30 mg), mixed in a 1:3 ratio with graphite, and then placed between graphite electrodes. The subsequent course of action was identical to the procedure described earlier. However, it was rare to have enough evidence material to apply that method. Examinations were often abandoned due to an insufficient amount of material.

Given as an example of a highly specialised and comprehensive forensic evidence involving dactyloscopic, physicochemical and mechanoscopic examinations in the 1980s can be the case of the burglary of the Primatial Cathedral Basilica in Gniezno which took place on the night of 19–20 March 1986. In the incident, the coffin of St. Adalbert and the saint's body were destroyed. The reference material was preserved from the fragments remaining on the destroyed coffin. The silver ingots found during the subsequent investigation were also secured. Physicochemical examinations were also carried out on metal filings and particles found in a bag belonging to the perpetrators, as well as on a screw and filings recovered from the coffin, metal particles sampled from the tools, and metal particles found in the suspects' clothing pockets. The elemental composition examination was carried out using X-ray fluorescence and emission spectroscopy. The Assay Office in Warsaw determined the silver content using the touchstone assay method and conventional quantitative analysis. Based on the results, it was established that the elemental composition of the evidence was similar to that of the reference material. Forensic examination of the physical evidence secured in connection with the burglary of the Primatial Cathedral Basilica in Gniezno contributed to the drafting of the indictment and finding the suspects guilty by the court [6].

In summary, it can be said that the methods and instruments used in the forensic examination of microtraces of metals, metal alloys and glass in the past by Polish forensic experts were advanced and modern compared to the methods and instruments in use around the world at that time. The Forensics Department was well-equipped and staffed by the best experts.

Nowadays, thanks to advances in science, instruments offer greater levels of sensitivity, precision and automation, making it possible to examine larger numbers of objects and leading to greater efficiency.

What links the two eras is the human factor. In theory, human involvement is now reduced due to the automation of many processes. In practice, however, the input of an expert who demonstrates perceptiveness, patience and composure was, and still is, essential in forensic examination of traces such as microtraces.

Bibliography:

1. Szymborska, K., (1987). *Badania monet i innych dzieł sztuki w praktyce Zakładu Kryminalistyki KG MO*. Problemy Kryminalistyki, nr 175(1), s. 52-72.
2. Wachowicz M., (2001). Analiza nieorganiczna w praktyce kryminalistycznej. Rozdział I - Spektralna analiza emisyjna, s. 12-17. *Zeszyt Metodyczny nr 10*. Wydawnictwo Centralnego Laboratorium Kryminalistycznego Komendy Głównej Policji.
3. Wachowicz, M., (2001). Analiza nieorganiczna w praktyce kryminalistycznej, Rozdział VI - Kamień probierczy, s. 47-59. *Zeszyt Metodyczny nr 10*. Wydawnictwo Centralnego Laboratorium Kryminalistycznego Komendy Głównej Policji.
4. Filochowski, E., Musiał A., (1974). Zidentyfikowanie pojazdu na podstawie odłamków szkła i lakieru. *Problemy Kryminalistyki*, nr 107(1), s. 106-109.
5. Marcinkowski, T., Pogodzińska P., (1983). Zastosowanie fluorescencyjnej analizy rentgenowskiej do zbadania odłamków szkła wyjętych z uszkodzonej gałki ocznej. *Problemy Kryminalistyki*, nr 160(3), s. 262-265.
6. Szulc, Cz., (1986). Kompleksowa ekspertyza kryminalistyczna w sprawie kradzieży z włamaniem do Bazyliki Archikatedralnej w Gnieźnie. *Problemy Kryminalistyki*, nr 174(4), s. 531-546.