

X-RAY DIFFRACTION ANALYSIS IN THE FORENSIC SCIENCE: THE LAST RESORT IN MANY CRIMINAL CASES

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ABSTRACT

X-ray diffraction methods are especially significant for the analysis of solid materials in the forensic science. They are often the only methods that allow a further differentiation of materials under laboratory conditions. Smears, minute contact traces, small sample quantities, or tiny sample areas can be successfully analyzed as well as large quantities of materials. Investigations with our GADDS microdiffractometer system with devices for fixed, scanning, oscillating and rotating specimens, the used strategies of measurement, and the applied sample preparation technique are discussed at examples from the daily case work.

INTRODUCTION

The Forensic Science Laboratory of Stuttgart currently employs 130 staff members. This includes 40 scientists and 50 assistants, and it covers the four natural sciences: physics, chemistry, biology / medicine and psychology as well as both the classical fields of ballistics / weapons and fingerprints.

The task of the Forensic Science Laboratory is to examine and to evaluate suspected specimens within the bounds of the material evidence. With their evaluations the expert witness assists police departments, the prosecuting attorney's office and courts in criminal and infringement proceedings. Our tasks include analytical studies, comparative investigations, and reconstructed examinations. They involve work at the scene of the crime, and the education of police officers and crime scene technicians.

In the case of a criminal offense, a connection between the perpetrator and either the crime scene or the victim may be made by a witness's testimony, or by other evidence such as fingerprints or footprints.

In cases where material traces are available, they can be evaluated by forensic investigation methods. The selected method is determined by the quality and the quantity of the material, as well as the question raised by the crime at hand.

The applied techniques must achieve reliable, definite and accurate results, and provide additional information about the chemical and physical properties of the suspected material. If possible, methods such as XRD and XRF are used, whose results overlap. These overlapping results confirm each other and give a secure result to the examination.

This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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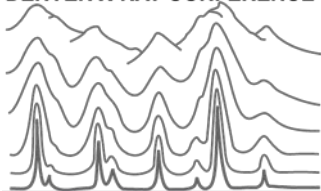
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In the Physics Department of the Forensic Science Laboratory the following techniques are at our disposal for material analysis: a scanning electron microscope with an energy-dispersive analysis system, a classical wavelength-dispersive X-ray fluorescence spectrometer, an energy-dispersive micro X-ray fluorescence spectrometer with capillary optics, a Bragg-Brentano diffractometer, and a General Area Detector Diffraction System.

We analyze all kinds of inorganic materials, because in a criminal case any type of specimen may turn out to be of forensic interest. These materials include paints from automobiles, buildings and tools, building materials, minerals, ceramics, asbestos, metals, alloys, explosives, gemstones, soils, abrasives, and drug impurities and extenders.

The decisive advantage of X-ray diffraction methods in forensic science is based on the unique character of the diffraction patterns of crystalline substances, the ability to distinguish between elements and their oxides, and the possibility to identify chemical compounds, polymorphic forms, and mixed crystals by a non-destructive examination.

This particular quality of X-ray diffraction examinations in the forensic science is verified here in the comparison of the diffraction patterns from iron, from iron oxides and from iron oxide hydroxide. These substances are used as pigments in paints.

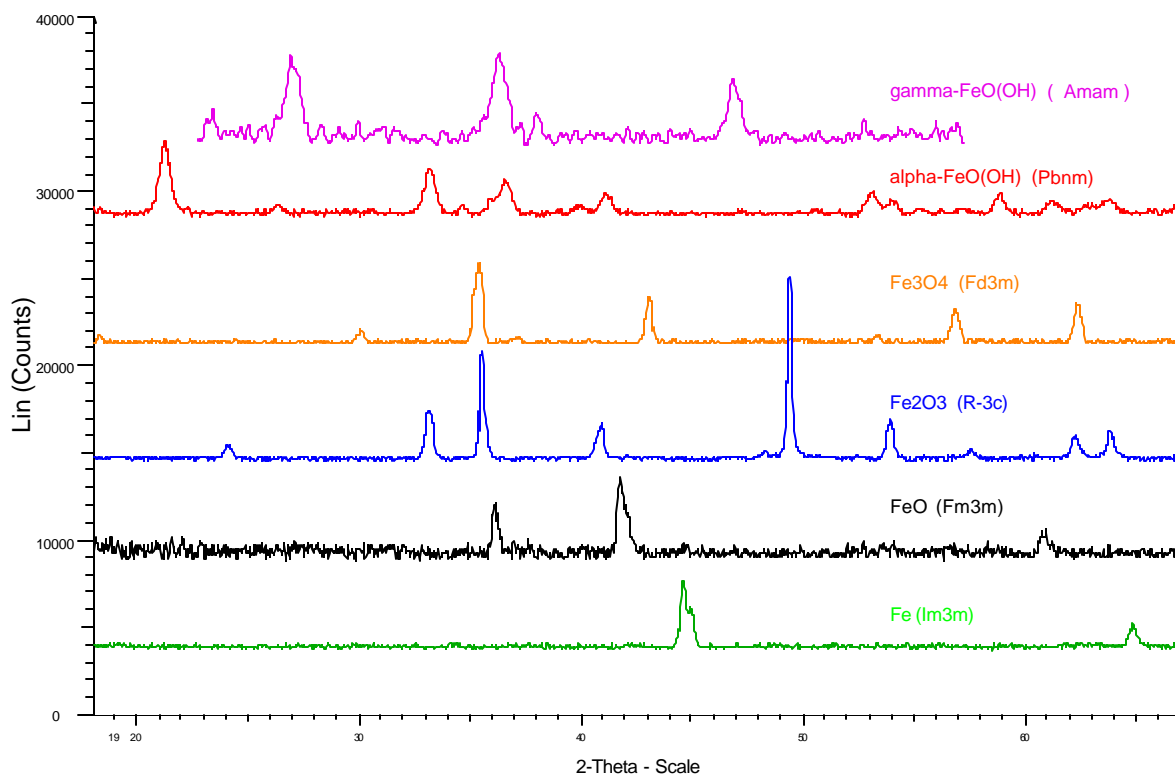


Fig. 1 X-ray diffraction pattern from iron, from iron oxides and from iron oxide hydroxides.

In comparison with other methods, X-ray diffraction examinations in these cases provide additional information about the chemical and physical properties, and make it possible for further useful discrimination of materials. XRF investigations give in these cases iron.

The type, amount, and consistency of the suspected contact trace specimen, the involved contact trace carrier, and the forensic questions raised by the criminal offense determine the diffraction method used, the strategies of measurement applied, and the sample preparation technique selected.

METHODS, STRATEGIES, PREPARATIONS, AND EXAMPLES

In our lab we have been working with a conventional automatic Bragg-Brentano powder diffractometer from Siemens since 1987, equipped with a copper X-ray tube, a variable divergence slit, a sample rotation unit, a graphite monochromator on the secondary beam, and a scintillation counter.

Three years ago we obtained a new, modern instrument, a General Area Detector Diffraction System (GADDS), introduced by Bruker AXS, with which we execute more than 90% of our measurements today. Our GADDS Microdiffraction system consists of a copper X-ray tube, cross-coupled Goebel mirrors, and pinhole collimators to produce a point-like beam, a laser-video sample alignment system, a motorized XYZ-stage, and a two-dimensional HI-STAR area detector.

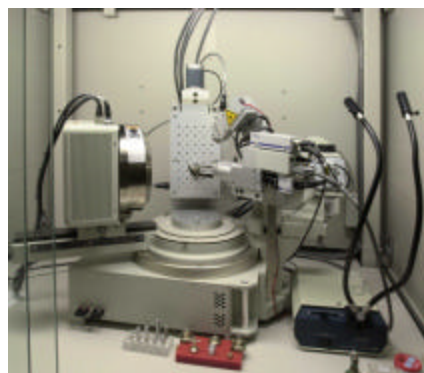


Fig. 2 General Area Detector System (GADDS).

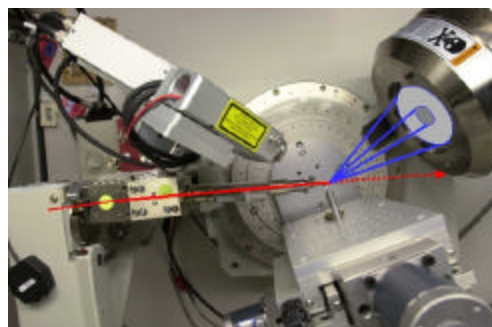
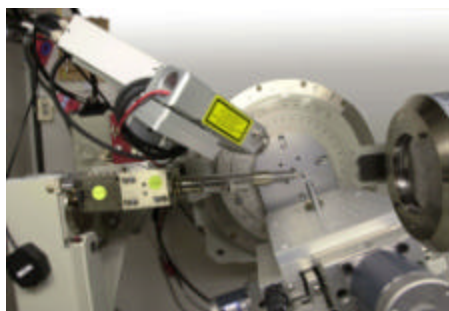


Fig. 3 System configuration, symmetrical and asymmetrical detector position with the primary beam and the scattered beam with the Debye-Scherrer cones.

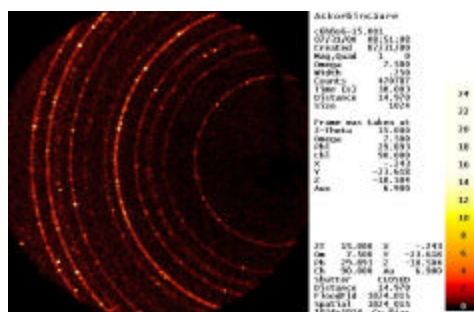
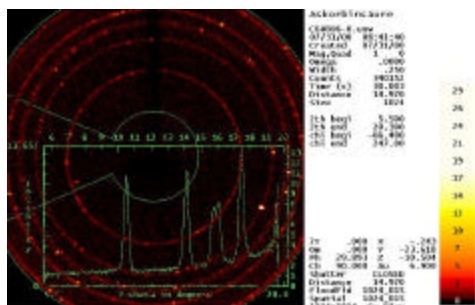


Fig. 4 Collection of diffraction data in symmetrically or in asymmetrically detector position.

Usually we measure in the asymmetrical order of the detector in 2 or 3 detector positions. The detector positions are selected so that the recorded angular ranges overlap. The individual diagrams are then merged into one spectrum. The measurements normally are performed in theta / 2theta geometry in which the sample is frequently moved by an omega scan or by an omega oscillation.

The diffracted intensity, the recorded angular range, and the angular resolution depend on the distance of the sample from the detector. A greater distance causes higher angular resolution, smaller angular range, and a lower reflex intensity.

The collimators also influence the angular resolution and determine the illuminated area of the sample. As a rule we use collimators with pinholes of 50 μm , 100 μm or 800 μm diameter. With it we measure small sample amounts as well as small sample areas. Depending on the sample preparation method, the samples are analyzed either in a transmission or reflection mode. Here the sample can be analyzed through alternative ways: for example by an at-point measuring, by a scan over the sample, or by programming the machine to select places of the sample to measure.

The state in which all material of suspected specimen is delivered, is precisely documented. Following this, the specimens are then carefully microscopically examined and described in detail. Powder-like suspected material in various matrices is microscopically sorted-out for initial examination. Here the forensically relevant constituents are separated mechanically by color value, morphology, particle size etc. The particles are ground and homogenized with a mortar of boron carbide or agate.

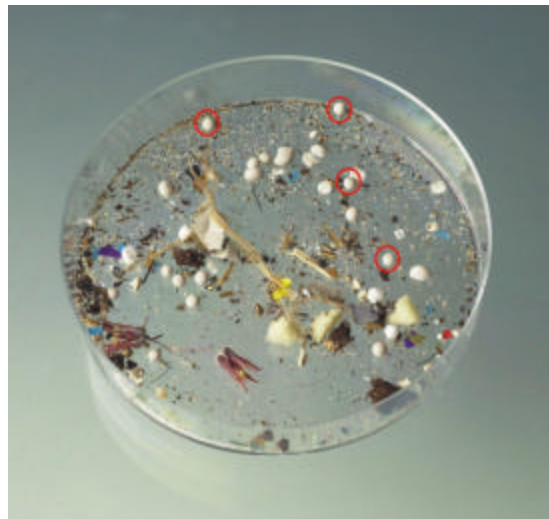


Fig. 5 “Typical” forensic sample.

In the case of large amounts of samples, the fine powder is filtered through a sieve onto a Silicon single crystal sample holder for the examination on the Bragg-Brentano diffractometer. The sample holder is sprayed before with hair spray first for better adhesion.



Fig. 6 Large amounts of samples, prepared for the Bragg-Brentano diffractometer.



Small amounts of the fine powder sample are pressed into the indentation of an acrylic glass sample holder. Our sample holders are designed so that they can be used with both the GADDS Micro-diffraction system as well as with our Eagle micro X-ray fluorescence spectrometer.

Fig. 7 Acrylic sample holder for small amounts, used for GADDS and μ -XRF.

Very small sample amounts (micro gram or less) of powdered specimen are loaded into thin walled glass capillaries. We use Mark tubes of 1.0 or 0.3 mm diameter and 0.01 mm wall-thickness. The capillary tubes are stuck with beeswax into brass hulls. The hulls can be stuck into metal pegs and screwed directly on the XYZ-stage.



Fig. 8 Mark tube in a metal peg.

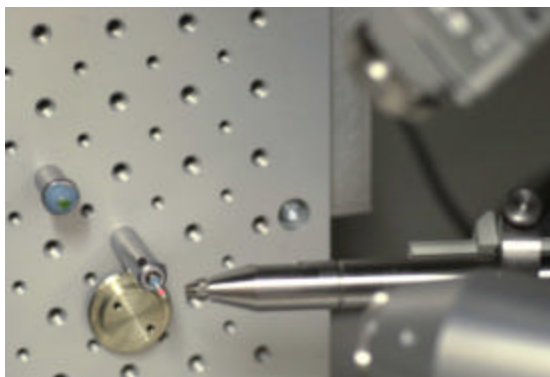


Fig. 9 Metal peg attached to the XYZ-stage.

In most cases the Mark tubes are fastened to a goniometer head. This is screwed onto an additional Phi-circle, which is fastened to the XYZ-stage. The Phi-circle is a particular attachment of our GADDS system. The specimen is adjusted with the crosshair of the video microscope and the laser spot of the video sample alignment system to the instrument center.



Fig. 10 Mark tube on a Goniometer head.

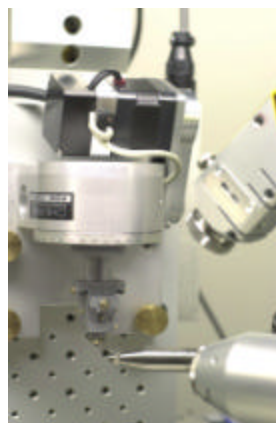


Fig. 11 Additional F-circle, fastened to the XYZ-stage.

This image shows the data frame from a fixed and from a rotated specimen. Due to the non-isotropic specimen structure – large grains and preferred orientation – the intensity distribution along the Debye – Scherrer cones is inhomogeneous in the case of a fixed specimen. In order to obtain better statistics, we prepare most powder specimen with capillary technique and we use the rotation mode with the phi - circle.

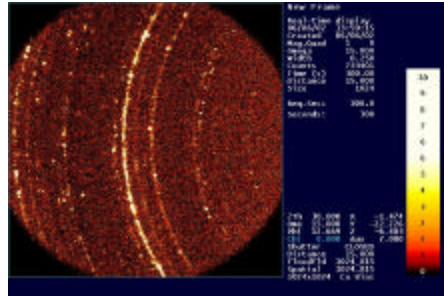
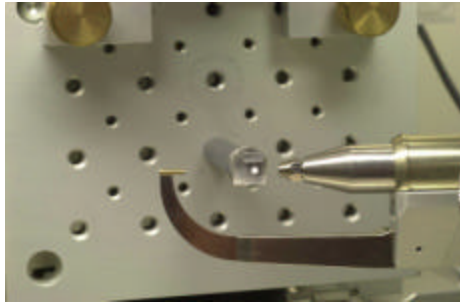


Fig. 12 Data frame from a fixed specimen.

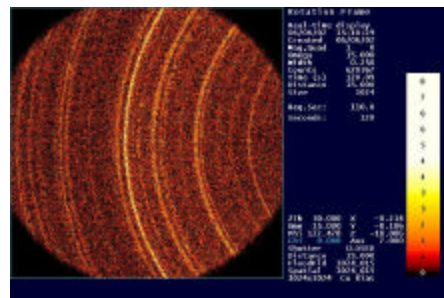
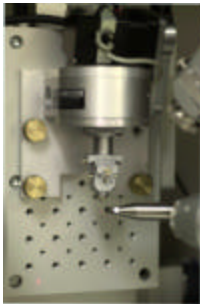


Fig. 13 Data frame from a rotated specimen.

For example in the examination of a murder we had to analyse very small amounts of the grey components of the contact trace specimen from the shoes of a suspect and the control specimen of a campfire site.

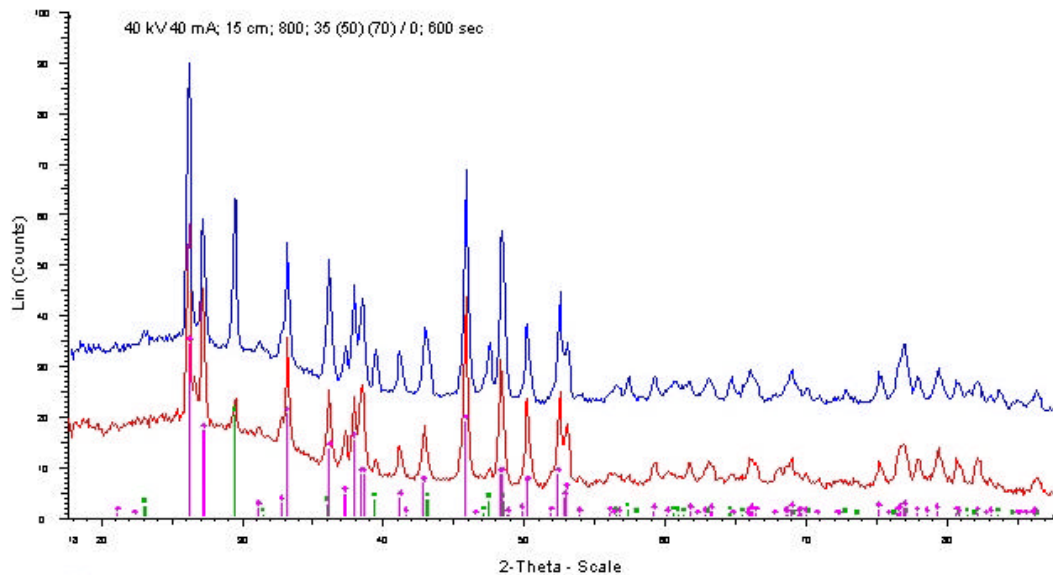


Fig. 14 Contact traces from the shoes and control specimen from the campfire site.

The result of the ICDD database search was Calcite and Aragonite. The discrimination between these compounds is only possible with XRD. The Aragonite contribution likely comes from snail shells.

To reduce the background scattering from the glass wall, powdered samples are also dusted on thin foils and fixed by a light touch of hair spray. We use 15 μm sheets of Hostaphan or 6 μm sheets of Polypropylen or 3 μm sheets of Mylar. The foil is held by Vaseline on the sample holder, and is also suitable for fixation to goniometer heads as well as on metal pegs.



Fig. 15 Preparation of small amounts of powder on a sample holder with a 3 μm sheet of Mylar.

This image represents the diffractogram of a suspected white Anthrax specimen, which was sent by mail after the attack on the World Trade Center in NEW YORK. We could identify Sucrose and Gypsum.

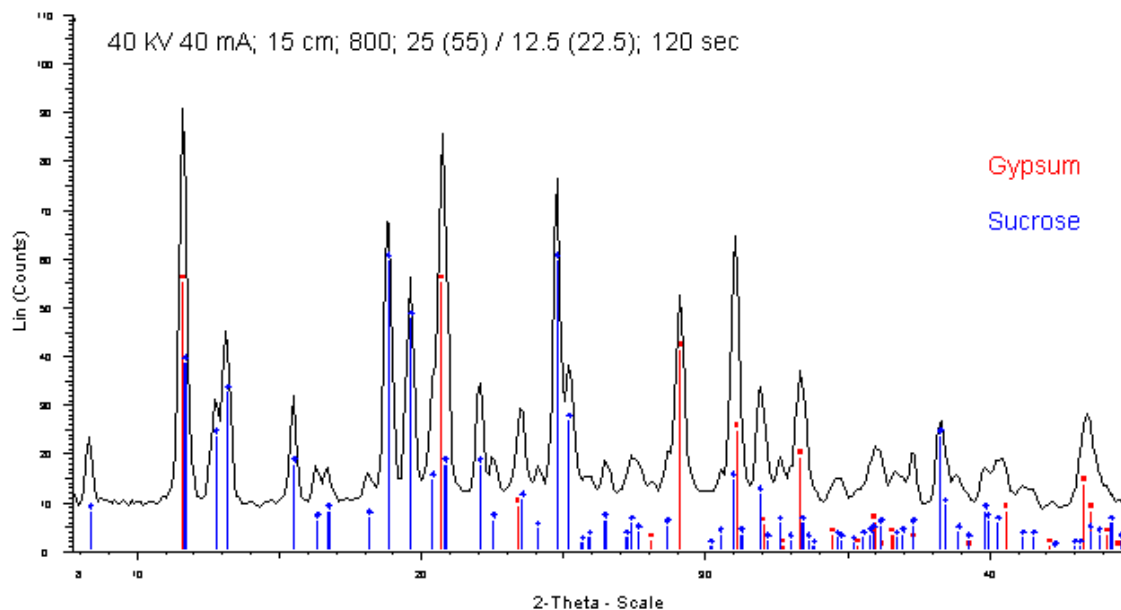


Fig. 16 Measurement of the “Anthrax” specimen.

Individual, tiny particles are placed under microscopic control with the help of a very fine needle on a strip of 3 μm Mylar, which has been previously coated with a fine trace of hair spray. The Mylar sheet is mounted on a goniometer head with a stretching device.

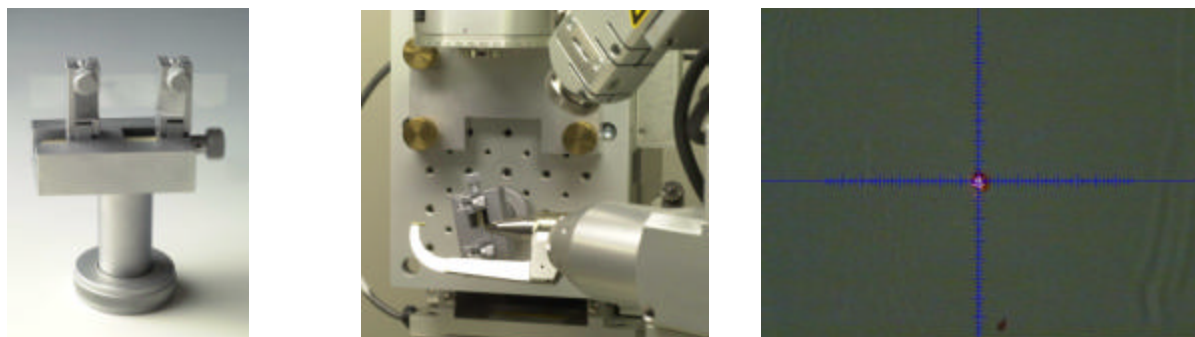


Fig. 17 Individual tiny particles on a Mylar sheet, goniometer head with a stretching device and adjusting the particle ($< \mu\text{g}$).

With this preparation technique the amount of a very tiny specimen is only limited by the capability of the specimen to be handled, that is, that with which can be handled with a very fine needle or scalpel.

In some cases we use a fine wire, a thread or a hair instead of a foil, mounted on the goniometer head with the stretching device.

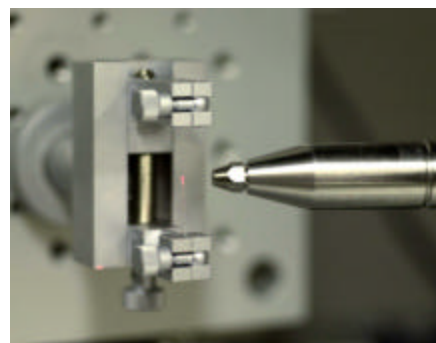


Fig. 18 Individual tiny particle on a fine wire (thread, hair, ...).

Contact trace specimens on trace carriers such as clothing, tools, etc. are analyzed undisturbed on the trace carrier itself.

For the examination of the contact trace specimen on the T-shirt with the Gadds system, the T-shirt was fixed with the help of hair spray to a small goniometer head. To reduce the background, a Silicon single crystal is fastened on the goniometer head.



Fig. 19 Examination undisturbed on the trace carrier itself, consistency of the trace specimen.

The diffraction pattern from the contact trace specimen on the T-shirt and from a control sample from the crime scene, showing the presence of the phases Ammonium Chloride, Ammonium Hydrogen Phosphate, and Potassium Ammonium Nitrate.

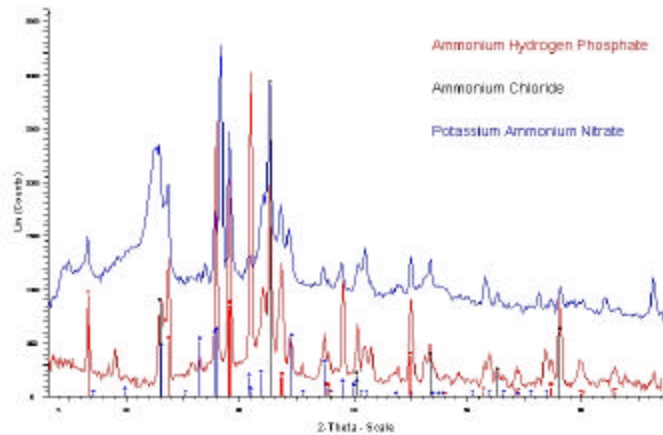


Fig. 20 Pattern from the trace specimen and the fertilizer control sample.

If possible, the contact traces are also removed under microscopic control and additionally prepared in a capillary like powder samples.

Fig. 21 shows examples for the preparation of trace specimens, which are analysed undisturbed on the trace carrier, a hammer with blue paint contact traces, a pair of pliers with emulsion paint, a car trim with automotive paint traces, and a damaged faucet.



Fig. 21 Examination of small contact traces on a hammer, adjustment the blue contact trace and measured area.

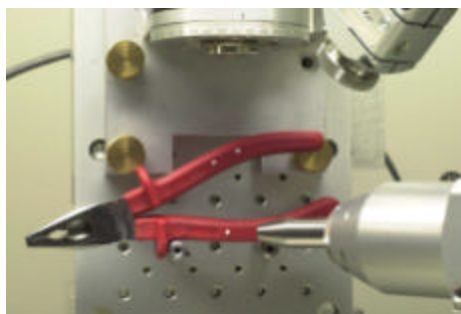


Fig. 22 Pliers.

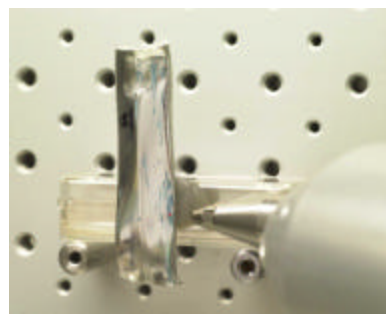


Fig. 23 Car trim.

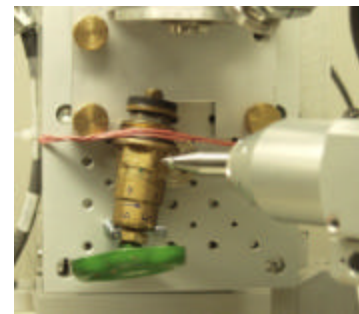


Fig. 24 Damaged faucet.

In the next case we had to examine the magnificent silver book cover and the gemstones of a very expensive replica of a bible. The book cover was fastened directly to the XYZ-stage.



Fig. 25 Silver book cover of the bible's reprint with 5 red jewels, adjustment of the book cover to the XYZ-stage, video image and adjustment of the jewel with the laser spot.

The measurement are carried out at three different detector positions, in which the jewels are scanned over an omega range of 15 degrees. The result of the ICDD database search was Almandine, a jewel from the Garnet family.

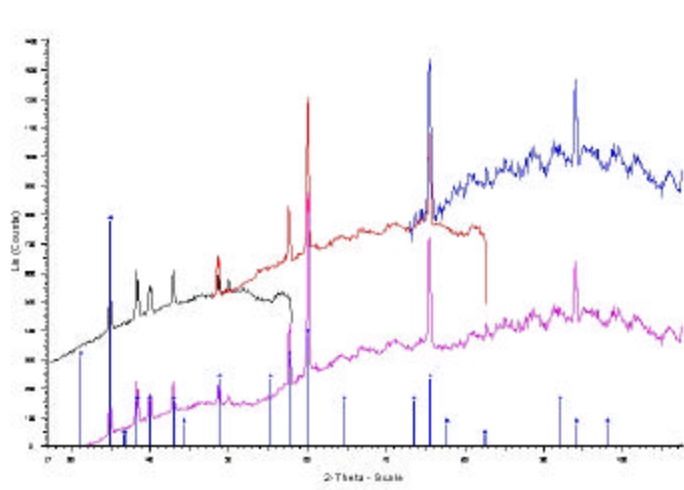


Fig. 26 Diffraction pattern of Almandine, a jewel of the Garnet family.

To identify the extenders and pigments of the single layers of an automotive paint flake, the flake was ground at an angle and fixed with modeling clay onto a small goniometer head.

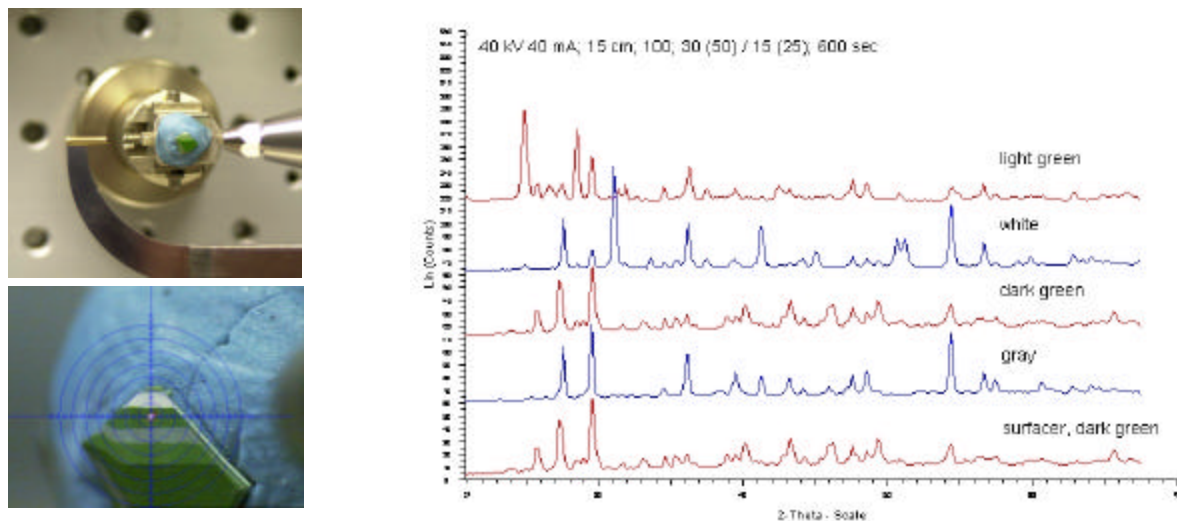


Fig. 27 X-ray microdiffraction analysis of a paint flake, grounded at an angle and mounted on a small goniometer head, X-ray of the individual layers of the car paint flake.

EXAMPLES

The first example involves a part of the forensic examinations in a criminal offense in which a bank robber was shot by a police officer. Two civilian investigators from the police department were questioning pedestrians in the city center of a small town in southern Germany. They recognized a bank robber who was being searched with a warrant. He tried to escape his arrest by fleeing on foot from the market square along the shopping street. One of the two police officials followed him. Contrary to regulation the officer had pulled his pistol and released the safety.



Fig. 28 Crime scene showing the path of the bank robber



Fig. 29 Butcher's billboard.

On the street corner the suspect threw a heavy billboard of a butcher's shop in front of the feet of his pursuer. The police official stumbled and fell on the pavement. His fall caused a shot to release from his pistol and hit the bank robber lethally.

When crime technicians checked the crime scene they found the officer's cartridge case on the sidewalk in front of the butcher's shop. The strongly deformed projectile was found on the road in front of the entrance to the butcher's shop.

The police official's pistol was kept safe and presented in the Forensic Science Laboratory for examination. By the microscopic examination of the pistol we found scratches, black tough material, and crystalline particles on the muzzle of the barrel and at the bottom of the magazine. Pyrolysis gas chromatography measurements showed, that the black material was bitumen.

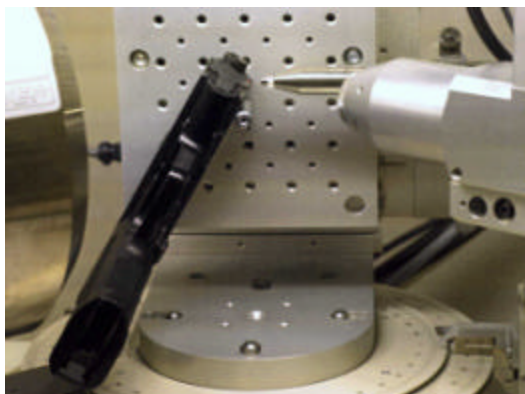


Fig. 30 Pistol mounted on the XYZ stage, contact trace specimen on the muzzle of the barrel

The X-ray diffraction analysis of the crystalline particles yielded Quartz and Calcite. These constituents are also present in the material of the sidewalk.

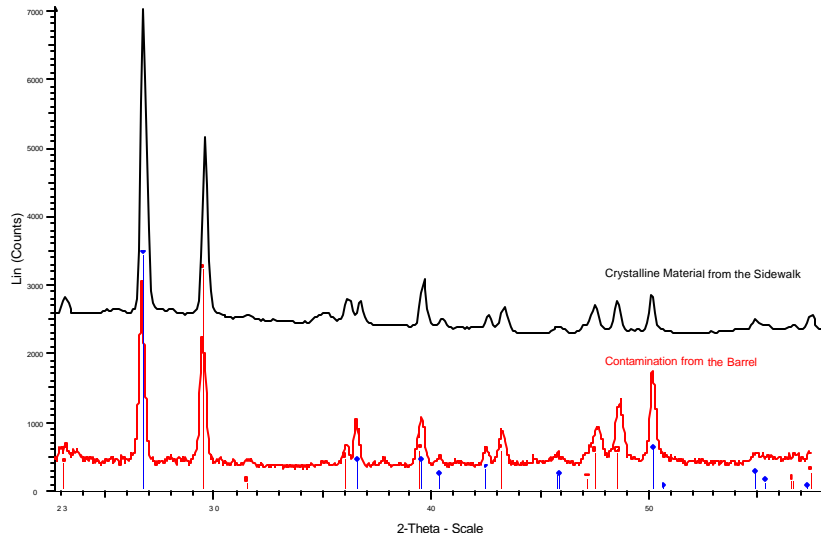


Fig. 31 XRD pattern from the contact trace and from the material from the sidewalk.

The severely deformed projectile shows considerable contact trace specimen. The analysis was carried out at various spots on the contact trace specimen. The phase analysis was carried out at various spots on the inhomogeneous contact trace specimen.

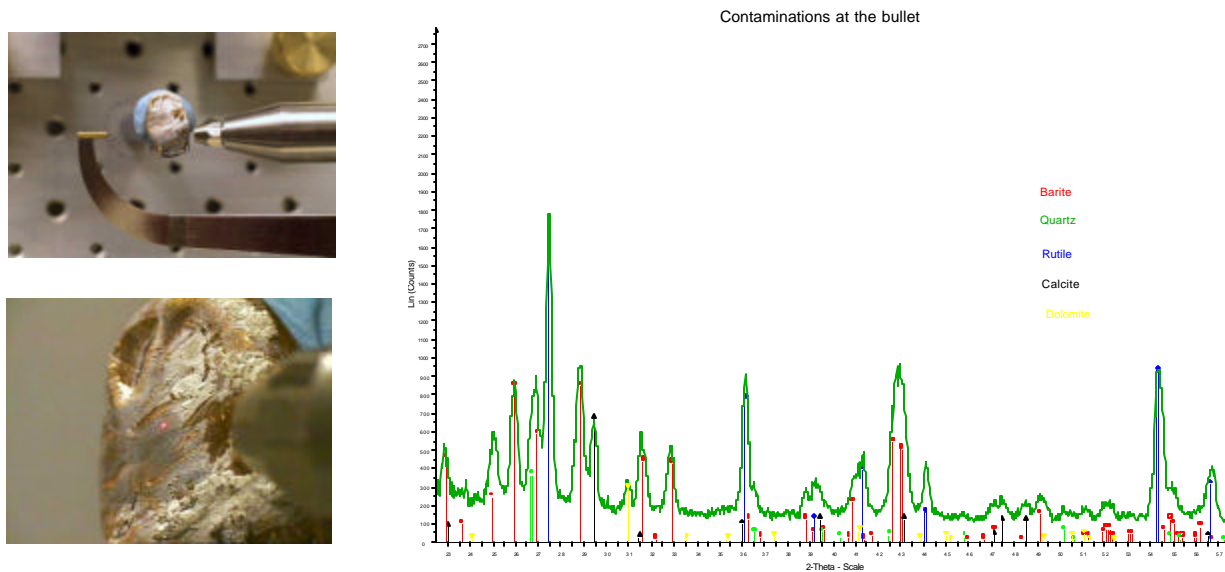


Fig. 32 Projectile mounted on the stage, measurement point, adjusted with the laser and phase analysis of the contact trace specimen on the projectile.

The phase analysis gave the best correspondence with the components Barite, Dolomite, Quartz, and Rutile. X-ray measurements on specimens from the coating of the exterior's building in the neighborhood showed that the contact trace specimen from the projectile corresponded with the material from the outside wall of the first floor of the butcher's building.

These examinations covered therefore the fall of the police official by the contact of the pistol with the sidewalk. In addition, the contamination of the exterior of the first floor of the butcher's building attested to the increase of the trajectory of the projectile. These results showed, that the shot from the pistol of the police official was an accident as the result of his fall, and was not deliberate. The police official was punished nevertheless, because he pursued the suspected with a weapon drawn and released.

In the second example we have a criminal offense in which a wife was killed and her husband was seriously injured. By X-ray diffraction examinations the reconstruction of the events of the crime will be supported.

The first ascertainments by police had shown that the perpetrator had entered the house by a window during the night. He crept quietly to the second floor, where he found the married couple in bed sleeping. The further course of events was still not known at the time of these ascertainments. The wife was killed by a shot from close proximity. The husband suffered a shot that passed directly through the right thigh. A further shot hit him on the back of his neck on the left side. A third projectile touched his right lower jaw, a fourth projectile injured him on the right neck side. The husband defended himself strongly, and further shots were fired during which he lost some teeth. Altogether eight cartridge cases and eight projectiles were later found in the bedroom. Due to the intense resistance by the husband the perpetrator fled. He was arrested in close proximity to the scene of crime the next morning. The weapon used in the crime along with further ammunition was found in his car. A T-shirt, which had very small individual grey particles in the areas that were heavily stained with blood was found by the police next to the front door of the house.

During the forensic examination of the bedroom, four projectiles were found in the wall and in the ceiling. One projectile was in the wife's blood soaked pillow. One projectile had penetrated the husband's pillow and the mattress and lay on the floor under the bed. Yet another projectile was stuck in the bed sheet of the husband, and a pool of blood had formed itself there. The eighth projectile was detected in a woollen blanket, which lay next to the husband's side of the bed. Some tiny small grey particles lay on the ground in front of the bed.

Our task was to reconstruct the crime scene with aid of these pieces of evidence. By the position of the projectiles the following picture arose: After the murder of the wife, the killer shot at the husband who was waking up, in which the projectile touched the neck and penetrated with undiminished energy the blanket and the mattress. The next shots were fired during the fight, with some hitting the wall and the ceiling. The projectile found in the sheet had probably penetrated the husband's foot and lost its force. However, the question was, how to assign the projectile from the woollen blanket.

The microscopic examination of the projectile from the woollen blanket showed extremely small contact trace specimens at the top. For the identification of this material, the bullet was mounted on the XYZ stage of the GADDs Microdiffraction system. The X-ray diffraction measurements were carried out at different places of the contact trace.

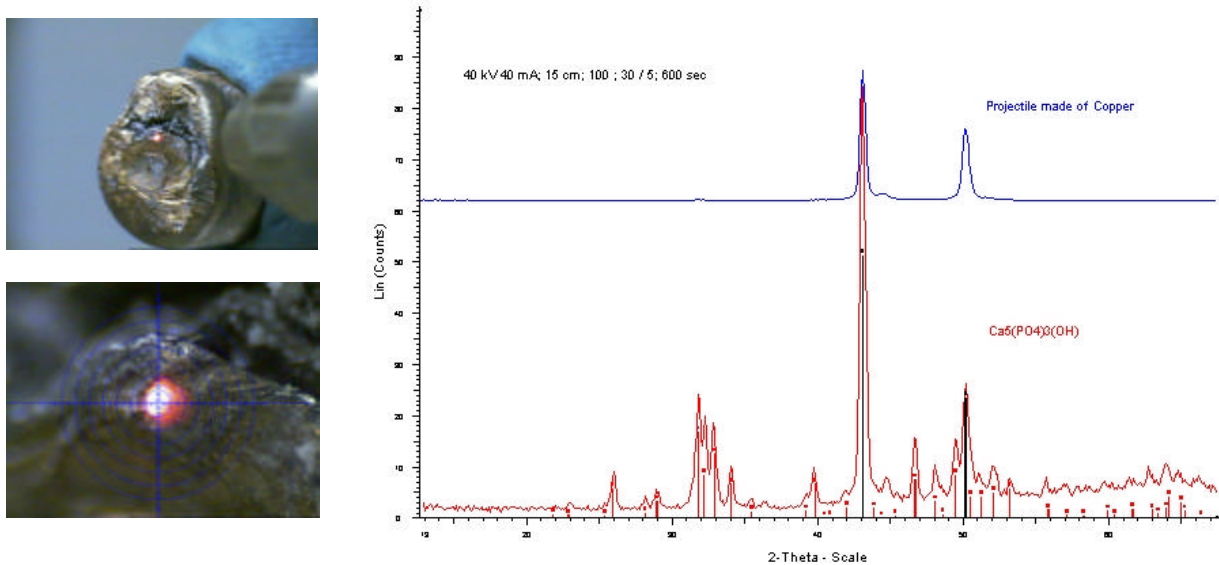


Fig. 33 Projectile from the blanket, mounted on the XYZ-stage, contact trace on the projectile, adjusted on the XYZ-stage, accurately in the instrument center with a laser beam and phase identification of the contact trace specimen from the projectile

The phase identification gave the best result with the pattern from Hydroxylfluoroxapatite. Calciumphosphate of the apatite type forms crystals of the mature tooth enamel. This indicates that this projectile entered the rear left nape of the husband and came out from the open mouth during the fight. It crushed some teeth and then fell onto the blanket. To confirm this hypothesis some of the grey particles from the floor in front of the bed were fastened using modelling clay to the XYZ-stage and analysed.

This picture represent the X-ray diffraction patterns of particles from the floor compared with the contact trace specimen from the projectile. The small picture shows one of the grey particles from the floor.

The diffraction pattern of one particle (c) corresponded with the diffraction pattern of the contact trace specimen on the projectile. However, we also found particles with other crystal structures (e.g. a, b).

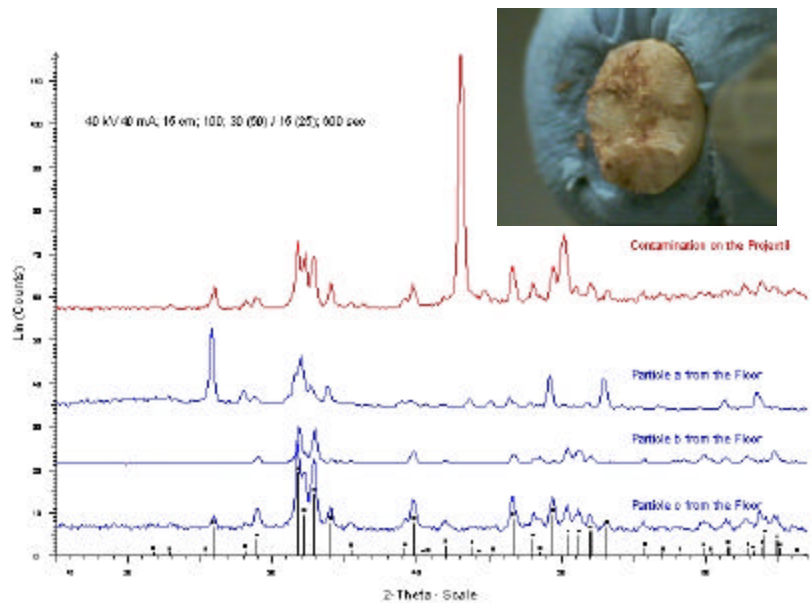


Fig. 34 Diffraction pattern of particles from the floor.

We got similar diffraction patterns during the analysis of the grey particles from the bloody areas on the T-shirt, which was found in front of the house.

This picture illustrate the crystalline structure of two particles from the T-shirt (A, B) and of one particle from the floor (c).

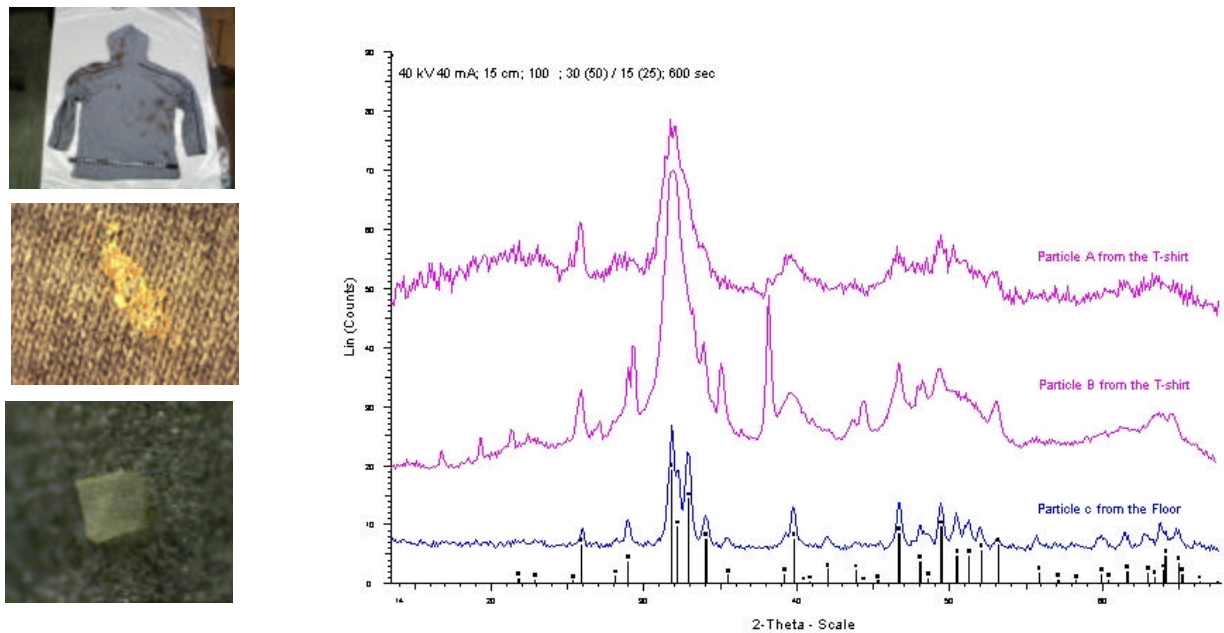


Fig. 35 T-shirt, found near the door, bloody area with grey particles, and crystalline structure of two particles from the T-shirt (A, B) and from one particle from the floor.

To understand the differences in the crystal structure of the individual particles, we examined an adult piece of tooth in comparison. The tooth was sawed apart in the upper range vertical to its longitudinal axis. The sawed off end of the tooth was embedded. The surface was then polished and cleaned. The X-ray diffraction measurements were automatically carried out step by step lengthwise along the diameter of the polished tooth area.

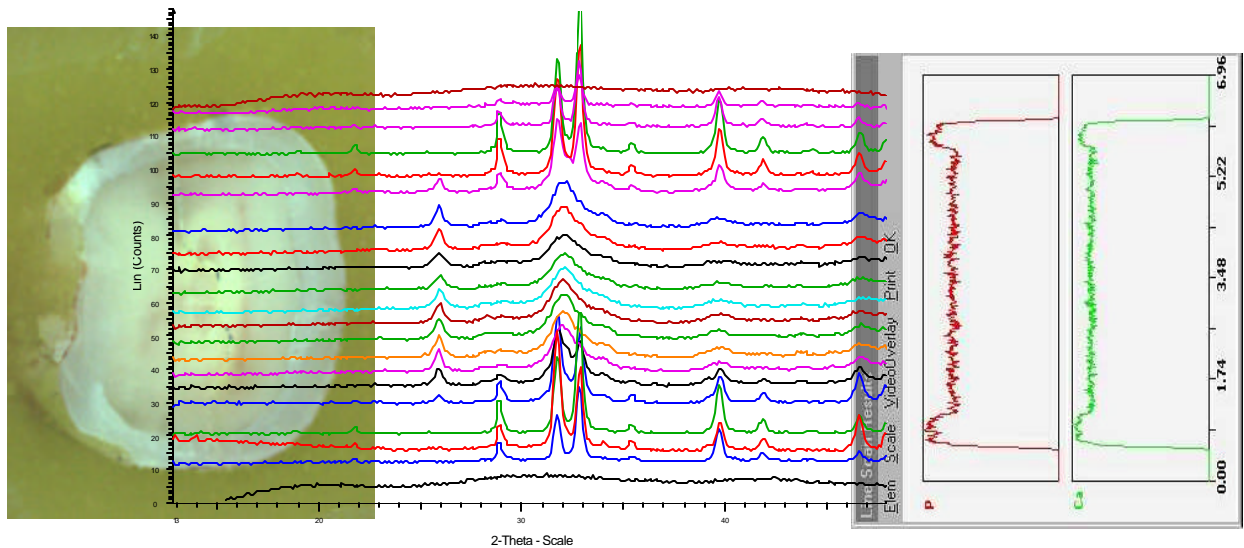


Fig. 36 Embedded tooth with its polished surface, measurements, taken vertically lengthwise along the tooth's diameter and line scan of the element analysis.

This overview of the diffraction pattern shows quite clearly, that the tooth material of the very hard tooth enamel is considerably different from that of the inner tooth material, the dentine. This change of the crystal structure is confirmed by the element analysis.

The element analysis of the outer and inner tooth material was performed with our Eagle system. The line scan along the diameter of the tooth shows a higher Calcium and Phosphor density on the tooth margin in comparison with the tooth core.

With these measurements it could be proved that the contact trace specimen from the projectile of the blanket came from a tooth. This projectile is therefore doubtless assigned as the one, which hit the left rear neck side of the husband and exited through the mouth. With this information all projectiles could be assigned. In addition, it could be shown that the grey particles from the floor in front of the bed and the grey particles from the T-shirt are also tooth material. The differences in the diffraction pattern of the individual grey particles can be explained by the different crystal structure of the tooth material in the range of the tooth enamel and that of the dentine.

In the end, the role of the T-shirt could not quite be cleared. The perpetrator presumably used it as a kind of silencer.

SUMMARY

The unique character of the diffraction patterns of crystallised material, the capability to distinguish between elements and their oxides, and the possibility to identify chemical compounds, polymorphic forms, and mixed crystals are crucial advantages of X-ray diffraction methods in the forensic science. They are non-destructive and provide us additional information about the chemical and physical properties under laboratory conditions.

We hope in future to gain further possibilities for the distinction of forensic materials through the examination of crystallite size and by Rietveld analysis with our GADDS microdiffraction system. Another project is to bring together computer-aided results of the element analyses with the Micro-RFA and the evaluation of the diffraction pattern with the PDF database.

X-ray diffraction makes it possible for further useful discrimination of materials, and it represents indeed the last resort in many criminal cases.

ACKNOWLEDGEMENTS

I thank C. Plotzki for the preparation of some specimens, J. Mönning for the digitalisation of the pictures and C. Rilling for their help with the translation. I especially thank J. Merkel for valuable discussions.

Dedicated to my academic teacher and friend Dr. Klaus Knorr for his 65th birthday.