Software solutions for X-RAY diffraction

Interview with Dr. Alfred Wassermann, founder and managing director of RMSKempten

X-ray diffraction is the diffraction of X-rays on crystals or quasicrystals. X-rays show the same diffraction phenomena as all other electromagnetic waves. X-ray diffractometry is used in materials physics, crystallography, chemistry, and biochemistry to examine the crystal structure. Róisín Murtagh, editor at Wiley Analytical Science, interviewed Dr. Alfred Wassermann, owner and managing director of RMSKempten, to discuss X-ray diffraction (XRD) and its development over the years.

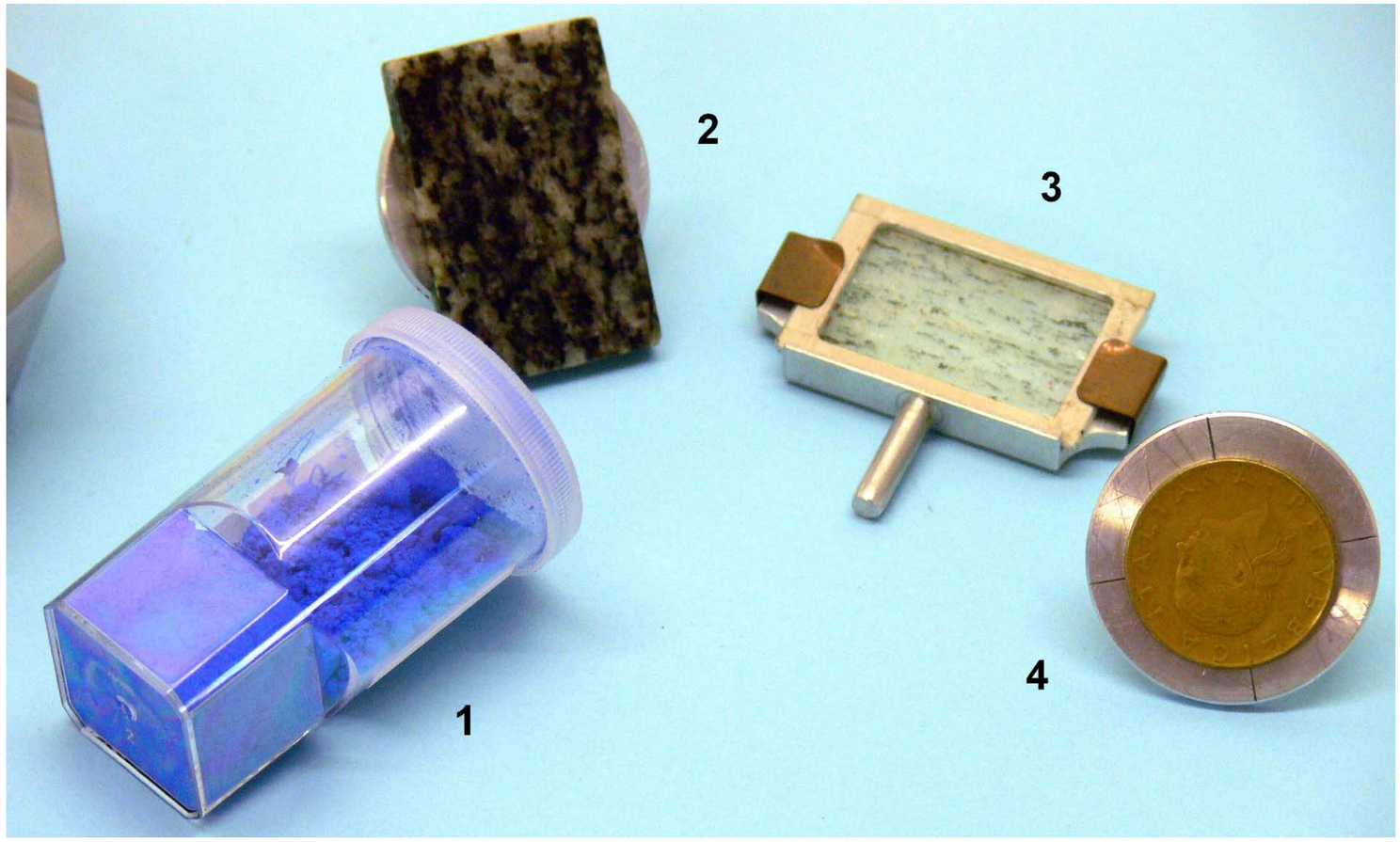
XRD device for phase analysis measurements. The measuring device with goniometer, counter, Debye-Scherrer camera, X-ray tube and sample changer is placed on top of a high voltage generator.

What is X-ray diffraction (XRD)?

Before 1912, it was not certain whether the radiation found by Wilhelm Conrad Roentgen in 1895 was particles or waves. Then, Max von Laue, together with Walter Friedrich and Paul Knipping, discovered the diffraction of X-rays on crystals and demonstrated the wave properties of X-rays. For this, Max von Laue received the Nobel Prize in Physics in 1914. In 1913, William Henry Bragg and William Lawrence Bragg (father and son) began to use X-ray diffraction to determine the structure of crystals. They elucidated the crystal structures of NaCl, diamond, zinc blende, fluorspar and calcite. Both received the 1915 Nobel Prize in Physics for this achievement. XRD is still the standard method for determining the structure of solids. The structural analysis of DNA in 1953 by James Watson and Francis Crick was not possible without the results of XRD.

The wavelength of X-rays is in the order of the spacing of the atoms in crystals. The X-rays are diffracted at the electron shells of the irradiated atoms. The diffracted waves emanating from the individual atoms interfere with each other. Depending on the distance between the atoms, there are different paths for the diffracted waves. Whether the amplitude is amplified or eliminated depends on the distance between the atoms.

Since crystals consist of three-dimensional and periodically arranged structural units, amplification only occurs for very specific angles of incidence. The Bragg equation relates the angles of incident to the distance between certain lattice planes of the crystal. This equation is the basic mathematical relationship for determining the structure from the diffraction pattern obtained from X-ray diffraction. The equation relates the wavelength of the monochromatic X-ray beam with which the sample is irradiated to the path difference between two X-ray beams diffracted at two lattice planes at a distance d. If d is an integer multiple of the wavelength, constructive interference occurs. There are only certain angles for each family of lattice planes at which this interference takes place. These angles are called glancing angles or Bragg angles. These interferences can be registered by a detector or photographic film. Since the wavelength of the X-rays used is known, the distance between the lattice planes can be calculated. If the crystal system is known, the lattice constants of the crystallographic unit cell can be derived from the lattice plane spacing.



Some examples of XRD preparation. 1 = powder for phase analysis, 2 = polished plate for texture analysis, 3 = preparation for back scattering, 4 = sample for stress measurement.

Dr. Alfred Wassermann

is the owner and managing director of RMSKempten.

He studied mineralogy at the University of Munich and graduated in 1978. He continued at the university and received his doctorate in 1983 with a thesis on the stability conditions of Åkermanite-Gehlenite solid solutions.

During this time, he founded the company RMSKempten, which aimed at the development of software for XRD and the further development of the XRD method.

In 1916/17, the physicists Peter Debye and Paul Scherrer developed a method for examining powdered samples. This represented a clear experimental simplification compared to the Laue method, which only allowed the structure determination by means of XRD on single crystals. A powder consists of randomly arranged crystallites, so all lattice planes are also randomly arranged in space and some always fulfill Bragg's reflection condition. In addition, the sample rotates about an axis perpendicular to the incident beam. X-rays generated by constructive interference form cone shells around the sample. The Debye-Scherrer method is commonly used for material testing.

SAXS, small-angle X-ray scattering, is a special form of X-ray scattering: because larger structures result in a smaller scattering angle at a given wavelength, SAXS can be used to detect mesoscopic structures, such as colloids and semi-crystalline polymers.

XRD with grazing incidence allows the investigation of thin layers.

What are the applications of XRD?

X-ray diffraction can be used in many different ways. In addition to applications in research, XRD methods are used routinely, and in some cases, fully automatically in the metal and building materials industry, geological exploration, pharmaceutical industry, and medicine for examining samples or monitoring production. Figure 1 shows some examples of XRD samples for analyses.

Phase analysis

Qualitative and quantitative determination of crystalline phases, including the determination of minerals. Every solid crystalline substance has a characteristic X-ray diffractogram due to its structure. Please see the XRD pattern of an egg shell ($CaCO_3$) in Figure 2. The diffractograms of almost all known substances are summarized in databases. If you have a powder image of a solid, you can compare it with the diffractograms of the known substances in the databases and identify the solid. This method can also be used to distinguish between different modifications of the same compound, e.g., α-Al_2O_3 and α-Al_2O_3 because they have different structures. If there is a mixture of different substances, these individual substances can be detected if they make up a proportion above the detection limit. This reliable and clear phase analysis or phase identification is the most important application of powder methods.

Determination of the lattice parameters

A lattice parameter or lattice constant, sometimes also called a cell parameter, is either a length specification or an angle that is required to describe a lattice, in particular the smallest unit of the lattice, the unit cell. The lattice parameter is either a side length of the unit cell or an angle between the edges of the cell. Modified lattice parameters are an indication of a modified structure of the unit cell, due to the inserting of other elements, lattice defects, or a destructive external influence.

Crystal structure analysis

The determination of the symmetry and the determination of the crystal structure, i.e., the determination of the atomic positions within the unit cell. This is characteristic of its physical and chemical behavior. Therefore, knowledge of the structure is of great importance.

X-ray residual stress determination

Residual stresses are stresses that remain in an object even without external loads or temperature gradients. In some cases, residual stresses result in significant plastic warping, leading to warping and deformation of an object. In other cases, residual stresses influence the susceptibility to fracture and material fatigue.

Texture analysis

In crystallography, the texture is understood as the totality of the orientations of the crystallites in a polycrystalline solid. Many properties can be highly dependent on the texture of the material and the associated microstructure. The formation of unfavorable textures during production or when a material is used can develop weaknesses or lead to failures. Consequently, considering texture can be crucial when choosing a material and its processing methods. Even after a material failure, the formed texture can help to interpret the damage analysis data.

Studies on thin layers

Thin layers are used in many areas of technology today. The applications start with relatively simple requirements in the area of finishing materials and extend to the high-tech area, such as the manufacture of active components and data carriers with the highest storage density.

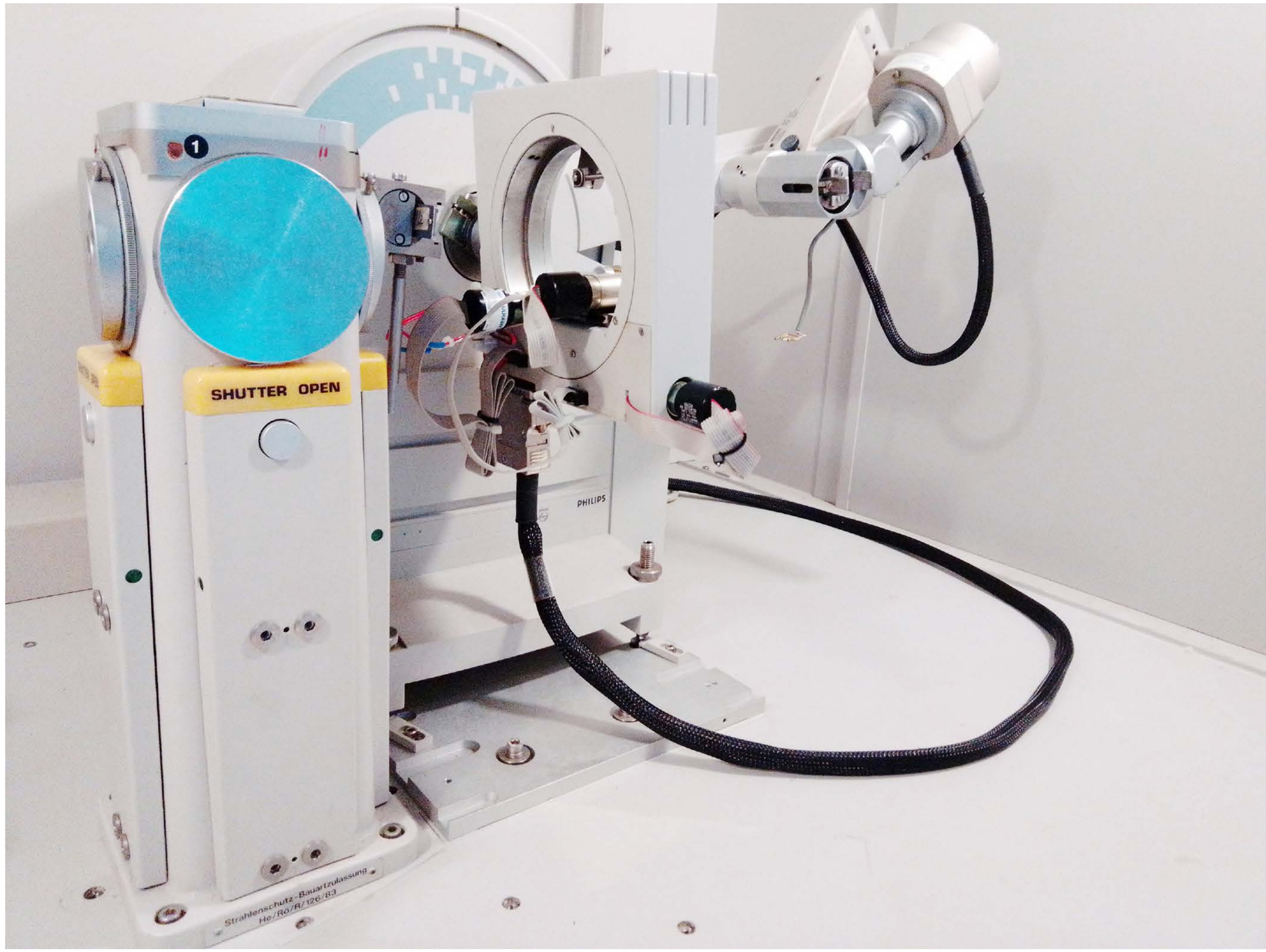
Complete XRD system. From bottom to top are the control electronics, high-voltage generator and radiation protection cabin. Through the open doors of the cabin one can see the measuring unit, consisting of X-ray tube, Euler cradle, 2 theta/theta goniometers and counting unit.

Can you elaborate on the ‘phase analysis of riverbank sand’ project?

On our website, we publish occasionally the results of XRD investigations on objects of what we consider to be of public interest. The river Iller not only runs through our town Kempten but also runs from its Alpine springs to Ulm, the town where the Iller encounters the Danube. Repeatedly, the river bursts its banks after heavy rainfall and floods large areas. After the floodwaters have drained away, the sediments that were carried along are left behind. So, the question is not uncommon “what does the river leave on its banks?” after the floods. The answer was provided by an XRD phase analysis and was not surprising: the examined samples from the bank sand correspond to the rock structure of the Allgäu Alps: quartz (SiO_2), dolomite ($CaMgC_2O_6$) and calcite ($CaCO_3$). The weathering debris of the mountains is thus transported away by the river.

When was RMS Kempten formed?

More than 40 years ago, during my doctorate, I began to create software for X-ray diffraction (XRD) on the 8-bit computers that were just coming on the market at the time. Device control and measurement data acquisition were the first applications that were soon used as standards in the former Mineralogisch-Petrographisches Institute of the Ludwig Maximilians University, in Munich. It was not long before manufacturers of the diffractometers became aware of this development. The first software package for the XRD was launched in 1981 under the name ADM, offering device control, measurement data acquisition, basic data evaluation, phase analysis, and lattice parameters refinement.



A measuring unit for Stress and Texture measurements, consisting of X-ray tube, Euler cradle, 2 theta/theta goniometers and counting unit.

In the same year, the company RMSKempten was founded, and with my first employee and lifelong friend Dr. Günter Lorenz, the business areas XRD Software, XRD laboratory (phase analysis, residual stress, and texture analysis), and Education (user training, seminars, and workshops) were brought to life.

Today, RMSKempten offers its sales partners corporate-fitted, ready-to-use software solutions for almost all applications required for the XRD.

What was the driving force behind creating your company?

During my PhD at the Mineralogisch-Petrographisches Institut of the Ludwig Maximilians University in Munich, I performed synthesis experiments to study the stability of garnets and melilite minerals as a function of pressure and temperature. For the phase determination of the synthesized minerals in these experiments, only microscopy and X-ray powder diffractometry were available at that time. X-ray powder diffractograms were recorded on film in appropriate cameras. These films were developed and the blackenings were then evaluated using photometers. Newer systems were already equipped with goniometers, (step) motors and counting units, so that an evenly running paper recorder could display a diffractogram.

The development of the first 8-bit desktop computers gave us the ability to digitize data collection and archive it to files. This paved the way for the development of software for automated device control and measurement data acquisition and its evaluation. Device control and measurement data acquisition have been the first applications that were soon used as standard in the Mineralogisch-Petrographische Institute of the LMU Munich.

The direction of my efforts was reflected in the name of the first software product: A(utomatic) D(iffractometer) M(easuring).

What products do you provide?

The main task we have set ourselves is to provide a software that makes all the steps involved in using the XRD available to the user in an easily understandable form. This starts with the device settings and leads to the measurement data acquisition via the sample control. Depending on the analysis order, the analysis is assigned to the respective sample and carried out. A reporting system tailored to the respective task collects the scope of services. It does not matter which manufacturer the controlled X-ray diffractometer came from. The user interface is always the same. In this way, laboratories that operate X-ray devices from different manufacturers can offer their employees a uniform user interface.

What services do you provide?

Our house offers XRD software, complete packages that are supplied with the X-ray system or as an upgrade to modernize existing systems. Interested customers send samples to our XRD lab. The desired analysis is carried out and the documentation and the measurement data record are handed over to the customer.

We also provide user training, seminars, and workshops. not only to those who use our software, but to all users of XRD.

What are the main challenges the clients that come to you have?

In the software area, our customers naturally expect us to integrate the latest scientific findings into the software. For us, this means that we recognize the analytical developments, follow the latest development of the measuring devices of the various manufacturers, and develop from this a newer version of our software without violating the existing standards and neglecting the already integrated applications.

In the laboratory area, we are constantly confronted with new requirements. In the environmental sector, analyses in the nano range (crystallite size) are required, and phase analyses in the micro-quantity range are required for archiometry and for art objects.

From what industries/backgrounds do your clients come from?

Customers who use our software are universities and research institutes. Our software is used for materials research and for the training of students, colleges, technical schools, and vocational training centers.

Finally, industrial laboratories for research and quality control use our software for product development and product monitoring.

What are you currently researching/working on?

We have just completed a new development of the X-ray residual stress analysis. In this project, we integrated the recent developments of so-called directional elastic grain interaction models. The interaction of an anisotropic inclusion with its surrounding matrix and the polycrystalline elastic properties of the isotropic matrix were introduced. In this new version of the software, these interaction models are used to calculate X-ray elastic constants for materials up to triclinic symmetries. In the case of texture, different grain interaction constraints exist in a specimen along different directions. Therefore, in this case, the elastic constants depend on the specimen directions. For this reason, we have included an approach for the stress factors to calculate the direction dependence. This is a new calculation method that additionally allows stress analysis over multiple lattice planes. Practical examples of direction-dependent grain interactions are the appearance of surface anisotropy in thin films and the appearance of a granular morphological texture.

In the quantitative phase analysis range, there are two approaches to arrive at a quantitative statement: the Rietveld analysis and the reference intensity (RiR) method. We are currently working on a project to bring the two methods together, ideally to unite them.

From the long-term analysis support of a laboratory customer resulted a fundamental insight into the phase relationships in the chemical system Ni-C-N. Not only are diamonds are formed in this chemistry, but also the currently highly regarded hard materials $C_{11}N_4$ and C_3N_4 as well as the well-known Ni carbides and Ni nitrides. In addition, previously undescribed phases appear to occur in this system. We are in the process of summarizing our findings so far and will publish them shortly.