# MI 5: X-ray spectrometry and analysis of works of art

Chair: B. Kanngießer

Time: Wednesday 9:30–12:15 Location: TA 201

**Invited Talk** MI 5.1 Wed 9:30 TA 201

**Das Arkanum von Meissener Porzellan: Beharrung oder Wandel?** — •Christian Neelmeijer[1], Ulrich Pietsch[2] und Heike Ulbricht[2] — [1]Helmholtz-Zentrum Dresden-Rossendorf, PF 510119, 01314 Dresden, Germany — [2]Staatliche Kunstsammlungen Dresden, Porzellansammlung, Sophienstraße, 01067 Dresden, Germany

Das Arkanum zur Herstellung von Hartporzellan in Europa geht auf ein Patent von Johann Friedrich Böttger im Jahre 1708 zurück. Seitdem ist die Porzellanmanufaktur Meissen Hersteller und Vertreiber des "Weißen Goldes". Wie streng wird auf dem dort hinterlegten Geheimnis seiner Rezeptur beharrt? Gibt es durch Variationen in den Einsatzstoffen entscheidende Modifikationen in der chemischen Zusammensetzung? Die zerstörungsfreie Materialanalyse mittels hochenergetischen Protonen an Luft gestattet es, diesen Fragen nachzugehen. Vor der Restaurierung war die nichtglasierte Porzellanmasse an Defekten von 34 gesicherten Originalen aus dem 18. Jahrhundert für den Rossendorfer 4-MeV-Protonenstrahl und das Arrangement verschiedener, simultan arbeitender Nachweisgeräte zugänglich. Über den erfassten Zeitraum von knapp 100 Jahren erweist sich die Grundzusammensetzung der Porzellanmasse (Oxide von Silizium und Aluminium) als nahezu gleichbleibend. Größere Schwankungen in den Konzentrationen der Begleitsubstanzen und der Spurenelemente verweisen auf unterschiedliche Fundorte von Feldspat, Kaolin und Quarz. Unikate von höchstem Wert sind in die Untersuchungen eingebunden, auch deren Glasuren und Malfarben.

**Invited Talk** MI 5.2 Wed 10:15 TA 201

**From micro to nano - new X-ray techniques as depth sensors for material characterization** — •Ioanna Mantouvalou[1], Lars Lühl[1,2], Marcel Pagels[1], Wolfgang Malzer[1], and Birgit Kanngiesser[1] — [1]Technische Universität Berlin — [2]Bundesanstalt für Materialforschung und -prüfung, Berlin

Due to their high penetration depth in matter X-rays render the analysis of the inside of material feasible. While for hard X-rays information can be gathered from a few tens of micrometers to even millimeters, soft X-rays are sensitive for nano-scale features. In both regimes new technological developments offer additional techniques which can satisfy the growing demand for novel analytical methods.

While soft X-ray spectroscopy is used widely at large scale facilities like synchrotrons, laboratory based investigations have up until now been hindered due to a lack of suitable radiations sources with sufficient brilliance. Laser-produced plasma sources can fill this gap. With the right choice of laser and target parameters the optimal emission energy can be tailored according to the experiment at hand.

In this presentation examples for depth resolved investigations on the micro- and nano-meter scale will be given. The application of 3D Micro- X-ray fluorescence spectroscopy (XRF) in the field of cultural heritage will be demonstrated on reverse glass paintings. Grazing incidence XRF is shown to be very well suited for nanometer depth resolved characterization of thin film solar cells. The spectroscopic possibilities of laser plasma sources as new X-ray sources are discussed with these investigations at hand.

MI 5.3 Wed 11:00 TA 201

**Investigation of the manufacturing process of attic shards by X-ray absorption spectroscopy** — •Lars Lühl[1,2], Sammia Mahlkow[1], Eleni Aloupi[3], and Birgit Kanngiesser[1] — [1]Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, German — [2]Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 44-46, 12203 Berlin, German — [3]NCSR Demokritos, Gr-15310 Aghia Paraskevi, Greece

Ceramics in general are of great historical importance because they are among the earliest evidence of human settlements. Primitive handmade ceramics that were made of coarse clay and burned at low temperatures are considered to be the first signs of tribes to settle. Up to the masterful and artistic ceramics of Greek and especially of Attic vases, the method has been refined over the centuries by polishing the surface, carving notches and especially by the use of wheels.

Attic vases are unique in its production technology due to the three-stage firing process. During the firing process the ornamentation applied on the leather dried ceramic is given its intense, glassy black colour, while the underlying ceramic coloured reddish-brown.

In order to gain knowledge about the manufacturing process, modern replica of attic shards, produced with different coarsenesses of suspension and fired with different temperatures, were investigated. The iron oxidation state was determined as an indicator for the different manufacturing procedures. The results are compared with results from historic attic shards which gave a deeper insight into the manufacturing process.

MI 5.4 Wed 11:15 TA 201

**Limits of detection of $\mu$-XRF with the SEM/EDS for RoHS relevant elements** — •Vanessa Rackwitz[1], Markus Ostermann[1], Ulrich Panne[1,2], and Vasile-Dan Hodoroaba[1] — [1]BAM Federal Institute for Materials Research and Testing, 12200 Berlin, Germany — [2]Humboldt-Universität zu Berlin, 10099 Berlin, Germany

For the determination of the specimen elemental composition most modern Scanning Electron Microscopes (SEM) are equipped with an energy dispersive X-ray spectrometer (EDS). Based on the technological improvement of low-power X-ray tubes and X-ray polycapillary optics in the last few years a new analytical tool for SEM has been developed: micro-focus X-ray fluorescence $\mu$-XRF. In order to evaluate the performance of the new $\mu$-XRF with SEM/EDS systematically, the limits of detection (LoD) for trace element concentration in a set of ten plastic reference materials were under examination. The reference materials consist of acrylonitrile-butadiene-styrene terpolymer (ABS) and have been doped with different contents of the elements Br, Cd, Cr, Hg and Pb. The interest for this kind of samples has its roots in the European Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment, RoHS. Additionally, the LoD for defined conditions can also be predicted by means of forward calculations of $\mu$-XRF spectra based on a physical model.

MI 5.5 Wed 11:30 TA 201

**Mikro-Röntgenfluoreszenz für die schnelle und empfindliche ortsabhängige Elementanalytik** — •Michael Haschke, Ulrich Waldschläger, Roald Tagle und Uwe Rossek — Bruker Nano GmbH

Die Mikro-Röntgenfluoreszenz-Spektroskopie hat sich in den letzten Jahren zu einer oft genutzten Methode für die ortsempfindliche Elementanalytik entwickelt. Die Verfügbarkeit von neuen leistungsfähigen Baugruppen etwa hochbrillante Röntgenröhren, Kapillaroptiken mit hoher Transmissions-Effektivität und Röntgendetektoren mit hoher Pulsverarbeitungskapazität eröffnen neue analytische Möglichkeiten.

Der Einfluss dieser die Eigenschaften eines Mikro-Röntgenfluoreszenz-Spektrometers bestimmenden Baugruppen insbesondere auf die Signalintensität wird diskutiert. Davon ausgehend werden die Auswirkungen dieser Verbesserung sowohl auf die Präzision einer Punktmessung als auch auf die Bestimmung von Elementverteilungen untersucht und anhand von konkreten Applikationsbeispielen dargestellt.

MI 5.6 Wed 11:45 TA 201

**Quantitative 3D micro-XRF analysis with laboratory setup** — •Timo Wolff, Wolfgang Malzer, Christian Herzog, and Birgit Kanngiesser — Institut für Optik und Atomare Physik, TU-Berlin, Hardenbergstr. 36, 10623 Berlin

X-ray fluorescence (XRF) is a wide spread analytical tool for elemental analysis. Due to its non destructive character and a relative high information depth it is frequently used various fields of science. The development of thermoelectric cooled silicon drift chamber detectors (SDD) and of X-ray optics, enabling a spatial resolution in the micrometer range, even strengthened this trend. Using a confocal setup 3D micro-XRF is possible. In this technique a second optic is mounted in front of the detector entrance to limit the field of view. The optics form a probing volume with dimensions in the micrometer range from which fluorescence is detected only. By moving the sample through this volume depth resolved information can be obtained from the sample in a non destructive way. This confocal geometry influences another aspect

of XRF, making this technique to an interesting tool: the possibility of quantitative analysis without reference samples, based on the fundamental parameter (FP) method. A new analytical description was developed and successfully tested with 3D micro XRF measurements with synchrotron radiation on standard reference samples and on archaeomtric objects in the last years. The procedure was now extended to setups with polychromatic tube excitation. Thus, for the first time quantitative 3D micro-XRF in the laboratory is possible.

MI 5.7 Wed 12:00 TA 201

**Advanced light element and low energy X-ray analysis of ceramics and ceramic-metal joints using SEM/EDX with Silicon Drift Detectors (SDD)** — •Tobias Salge[1], Orkun Tunckan[2], Ralf Terborg[1], Vasile-Dan Hodoroaba[3], and Servet Turan[4] — [1]Bruker Nano GmbH, Berlin, Germany — [2]Civil Aviation School, Anadolu Univ., Turkey — [3]BAM, Berlin, Germany — [4]Materials Science and Engineering Dept., Anadolu Univ., Turkey

An analytical aspect in EDX analysis of massive samples is to lower the spatial resolution. This makes it necessary to work with low excitation voltages to decrease the excitation volume for generated X-rays and evaluate low energy X-ray lines. In order to separate overlapping peaks, the line deconvolution algorithms incorporated into the EDX software are of crucial importance. Two representative samples will be discussed: (1) a sintered hard ceramic composed of three major phases TiB2, TiC, and SiC and (2) a Si3N4-Ti joint with a heterogeneously composed reaction layer [1]. This study demonstrates that state-of-the-art hardware in combination with modern data processing allows advanced spectrum imaging of light elements and low energy X-ray lines. Element distribution of overlapping lines at the low energy range (e.g. Ti-L, N-K) can be analyzed on the sub-micro scale by EDX in a short time by peak deconvolution. Even at low impulse statistics, spectra containing low energy lines can be accurately quantified.

References: [1] O. Tunckan (2010) Ph.D thesis. Anadolu University, Eskişehir, Turkey, 176 p. [2] Dr. R. Wäsche (BAM) is gratefully acknowledged for producing the hard ceramic sample.