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Introduction

The SurfChem project has made a significant contribution to traceable quantitative surface chemical analysis for industrial applications by delivering new certified reference materials and test samples for specific technical applications. Regular performance tests of instruments, metrological methodology for the detection of (bio)organic surface species, ambient and non-destructive surface chemical analysis for in-line process control and new in situ characterisation techniques of catalytically active surfaces have been achieved.

The Problem

The uncertainty of measurement related to the methods of surface chemical analysis most often used in industrial environments was not accurately known and measurements from different testing laboratories were not comparable. There was an urgent need to determine the uncertainty of methods of surface chemical analysis and to develop methods with reduced uncertainty enabling comparability of analytical results. Certified reference materials (CRMs) with certified surface chemistries, composition and morphology i.e. defined thicknesses, layer and lateral structure are needed for valid and comparable surface chemical analysis at industrial end users. European instrument makers need appropriate procedures and CRMs to improve their next generation products and to develop fully new methods. End users as industrial testing laboratories need CRMs to select the most appropriate instrument on the market for their needs and new traceable methods of quantitative surface chemical analysis validated by appropriate CRMs to solve their specific analytical problems.

The Solution

We set out to solve this problem by:

- providing new Certified Reference Materials with known and stable surface chemistries as well as with defined thicknesses, layer and lateral structure for instrument development and calibration as well as verification of industry-relevant surface chemical measurements
- providing new fast non-destructive methods of quantitative surface chemical analysis for industrial in-line quality control. In particular this will include the development of advanced techniques for real time, in situ measurement of catalyst structure and activity on a localised scale to underpin the development of more efficient, selective and cost-effective catalysts
- providing metrological methods including development of new Certified Reference Materials to improve the capability and traceability of technologies widely used in industry for surface analysis such as electron and fluorescence spectroscopy, X-ray reflectometry, electron probe microanalysis or ion mass spectrometry

Impact

Results of the project were presented to ISO TC 201 SC6 "Secondary ion mass spectrometry" and ISO TC 201 SC7 "Electron spectroscopies" meetings in order to initiate formal standardisation procedure such as a New Work Item Proposal that will lead to a new or improved standard. The CRMs, other reference materials and metrological procedures developed by the project were tested by interested European industrial partners and stakeholders including instrument manufacturers, calibration and testing laboratories and instrumentation users in a range of sectors. So far 15 of the CRMs for ED spectrometer calibration have been sold to European companies, testing laboratories and universities (and one university from Canada). The technology developed by the project to study nanoparticle sintering by INPS sensor chips in industrial applications is being commercialised by Insplorion AB.

Longer-term socio-economic impacts are expected which may stabilize or even increase numbers of positions for qualified employees at European small and medium companies. The development of a consistent metrological base for quantitative surface analysis supports innovation in the industry and will, on this route, promote the development of new sustainable industrial processes cleaner and more energy and material efficient.



1 Project context, rationale and objectives

The chemical and topographical metrology of surfaces is one of the most rapidly growing fields of metrology. This is driven by the need for reliable chemical measurements and accurate and traceable surface analysis measurements in European industry for product development, for quality control in production and for the protection of intellectual property. To address this need, this project aimed to provide traceable measurement methods and certified reference materials (CRM) for surface chemical analysis in order to support next generation technologies developed by European manufactures (e.g. organic solar cells, printed organic electronics, organic light emitting diodes, biochips). The project provided prototypes of well-characterised reference materials and traceable methods to enable the comparability of results between laboratories; as this is currently a limiting factor. In addition, new quantitative methods for measuring surfaces were developed as Good Practice Guides and, based on them; New Work Item Proposals for industrial standards under ISO TC 201 "Surface Chemical Analysis" and ISO 202 "Microprobe Analysis", have been initiated.

Surface chemical analysis has made major contributions to industry with the development of new products and the solution to production problems. Surface chemical analysis has been important for example in both the science and technology of microelectronics, coatings for optical, wear and other property enhancements, bonding and corrosion for aerospace and transport, protein adhesion and toxicity for body implants, polymer surface changes for construction work, drug delivery etc. In these fields of technology the functionality of surfaces, thin films and interfaces plays an important role and substantially depends on chemical composition. In recent years, with the growing awareness of the importance of nanotechnology both surface and nanoanalysis have been featured even more widely. The applications mentioned above are integral to the development of advanced technologies in Europe's industry. In such sectors, the analysis and control of the amount of substance at surfaces by quantitative surface chemical analysis is vital not only for product development but also for trade and the protection of intellectual property, for research and development, and for quality control.

The composition of solid material surfaces and interfaces, at the atomic level, is usually very different from that of the bulk material and is often key to the way that the material behaves in its service environment in industrial applications. For example the bonding, wettability, cell adhesion and reactivity of components are all radically affected by this composition which may only represent one part in 10^9 of the atoms present at the surface. Consequently the goal of surface chemical analysis is to deliver quantitative elemental, chemical state and functional group information from the surface of materials.

However, prior to the start of this project, the uncertainty of measurement related to the methods of surface chemical analysis most often used in industrial environments was not accurately known and measurements from different testing laboratories were not comparable. This meant that the analytical results of such methods could only be interpreted in a qualitative, subjective manner and limited their value and comparability. There was an urgent need to determine the uncertainty of methods of surface chemical analysis and to develop methods with reduced uncertainty enabling comparability of analytical results. In some methods of surface chemical analysis, theoretical predictions could be used to calculate quantities, however these were not verified. Furthermore, only a few samples of known surface and in-depth composition were available for validations prior to the start of this project. The use of reference materials is the most convenient way to specify or calibrate instrumentation for surface chemical analysis and to establish traceability to the SI and enable comparability of analytical data. Therefore certified reference materials (CRMs) with certified surface chemistries, composition and morphology i.e. defined thicknesses, layer and lateral structure are needed for valid and comparable surface chemical analysis at industrial end users.

A recent trend related to nanotechnology activities in Europe is that industrial materials show more and more intended (and even non-intended) structures at scales down to the low nanometre range and chemical imaging of surfaces has become a new challenge for the development of instrumentation. This increasing activity in industrial analysis suffered from a lack of metrologically underpinned methodology and appropriate reference materials for a traceable specification of resolution power and calibration for such instruments.



There are specific needs for non-destructive methods of surface chemical analysis for fast in-line quality control in industry. One example is the identification of unwanted organic contamination at the surface of high end products used in space technology or as medical implants (even the food industry requests such analysis tools). Furthermore, new metrologically-underpinned techniques of surface chemical analysis for real time and in-situ measurements of working catalysts are needed by European industry for the development of more efficient, selective and cost-effective catalysts. Mass-market examples here are the oil and gas industry and car makers developing new catalytic exhaust cleaning systems. However, these new techniques of surface chemical analysis needed development as the metrology related to their measurements was poor prior to the start of this project.

This project was focused on the provision of reference materials for instrument calibrations and metrological methods to improve the capability of methods (EPMA, XPS, AES, SIMS, XRR) widely used in industry for quantitative surface chemical analysis. It also addressed metrology issues of industrial in-line quality control and real time in-situ measurement of catalysts all of major interest commercially and under research.

The objectives of the project were:

- The provision of new CRM with known and stable surface chemistries as well as with defined thicknesses, layer and lateral structure for instrument development and calibration, and the verification of industry-relevant surface chemical measurements.
- The provision of new, fast, non-destructive methods of quantitative surface chemical analysis for industrial in-line quality control. In particular, this will include the development of advanced techniques for real time, in-situ measurement of catalyst structure and activity on a localised scale to underpin the development of more efficient, selective and cost-effective catalysts.
- The provision of metrological methods including the development of new CRM to improve the capability and traceability of technologies widely used in industry for surface analysis such as electron and fluorescence spectroscopy, X-ray reflectometry, electron probe microanalysis or secondary ion mass spectrometry.

2 Research results

2.1 Inorganic reference materials and reference methods of surface chemical analysis

Quantitative analysis of chemical surface compositions is of key importance for the development of innovative new products. Three widely used analytical techniques to be addressed here are Energy Dispersive Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). These techniques are in the focus of the project and inorganic reference materials and test samples (prototypes) are developed for the calibration and testing of techniques and methods for quantitative surface chemical analysis used for industrial applications. Those methods are included in the business plans of ISO/TC 201 and 202 and the Surface Analysis Working Group (SAWG) at CCQM. The prototypes are developed by cooperating NMIs, here BAM and PTB, with consultation and contributions from the essential instrumentation manufactures in this specific field, Bruker Nano, Focus, ION-TOF, Kratos and SPECS. TASCAN, an independent test laboratory, made tests as well.

Reference materials and metrological methodology based thereon have been developed for EDS application specifically for a calibration of those X-Ray Spectrometers used for quantitative chemical analysis at Secondary Electron Microscopes. To reduce the uncertainty in standardless ED-Electron Probe Micro Analysis (EPMA) at Secondary Electron Microscopes caused by the unknown actual spectrometer efficiency of the EDS detector reference materials are requested by industrial laboratories with which the spectrometer efficiency of a field spectrometer can be determined. Therefore a new type of reference material for the energy and efficiency calibration of ED spectrometers has been developed. Before this innovation end-users were asked to measure a series of samples with different elements to get reference energies for the energy calibration of the detector system. The innovation has to be seen in two fields: (i) Together with the collaborator AXO a wafer based coating technology has been developed for the deposition of all elements needed to implement ISO 15632:2012 and (ii) only one single measurement has to be carried out now to get a well-defined energy and efficiency calibration of the detector of the EDS system. Since both, the absolute energies and the intensity ratios of the element peaks, are given in the certificate of the RM, the calibration can easily be performed by end-users of EDS systems. Two types of reference materials were developed:

First one for photon energies below 1 keV excited with electrons at 3 kV acceleration voltage (*EDS-TM 003*). A second one is for energy calibration ranging from 0.1 keV to 17 keV excited with 10 kV and 30 kV (Figs.1-4), respectively (*EDS-CRM*), which may be called universal in the context of its application. One conventional Si-Li X-ray detector (still in use at many testing laboratories) and one recent Silicon Drift Detector (SDD) were calibrated by PTB and BAM at the primary photon source standard BESSYII providing full traceability. Later these fully characterized X-ray detector systems were used for the precise measurement of the newly developed reference materials. With the help of the universal EDS-CRM, a traceable calibration of EDS instruments at the equipment manufacturers site as well as at the end user labs is enabled. It is used as a transfer standard to link the calibration of a field EDS to the primary photon source standard BESSYII. As requested by ISO 15632:2012 other relevant EDS parameters, e.g. energy resolution, can be characterized easily with this universal RM, too. Prototypes have been tested and validated by BAM and at interested end-user labs, to assure that typical detector configurations are also covered by the new reference materials. The universal certified reference material is a multi element specimen consisting of a C, Al, Mn, Cu and Zr layer on a Si substrate (Fig.1). It has been specifically designed to provide a high number of separated characteristic lines in the energy range 0.1 to 17 keV. For two electron excitation energies 10 and 30 keV and a take-off-angle (TOA) of 35° twelve emitted characteristic line intensity ratios are certified (see Table 1).



Fig. 1: Universal EDS-CRM prepared using a Si wafer based chip technology.

Table 1: Certified intensity ratios of the universal EDS-CRM at 10 kV excitation (left) and at 30 kV excitation (right).

$I_{cert}^{i/MnKa}$ at 10 kV	intensity ratio	$I_{cert}^{i/MnKa}$ at 30 kV	intensity ratio
C K to Mn Ka at 10 kV	4,2	Al K zu Mn Ka bei 30 kV	0,10
Mn La to Mn Ka at 10 kV *)	2,7	Zr L zu Mn Ka bei 30 kV	0,35
Mn L to Mn Ka at 10 kV	3,3	Cu Ka zu Mn Ka bei 30 kV	0,18
Cu La to Mn Ka at 10 kV *)	2,2	Zr Ka zu Mn Ka bei 30 kV	0,032
Cu L to Mn Ka at 10 kV	2,4	Zr Kb zu Mn Ka bei 30 kV	0,0056
Al K to Mn Ka at 10 kV	1,5		
Zr L to Mn Ka at 10 kV	2,8		

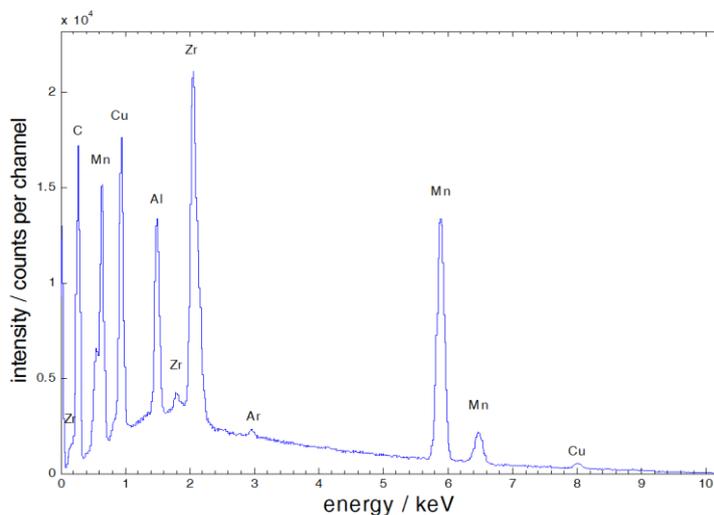


Fig. 2: 10 kV spectrum EDS spectrum of the universal EDS-CRM.

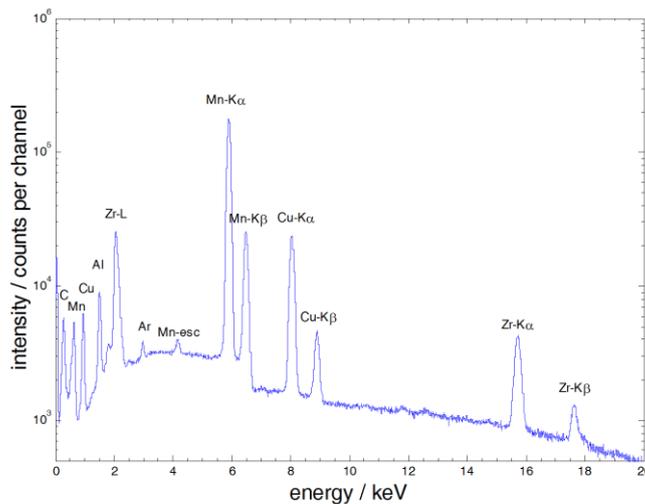


Fig. 3: 30 kV spectrum EDS spectrum of the universal EDS-CRM with Zr lines for high energy calibration.

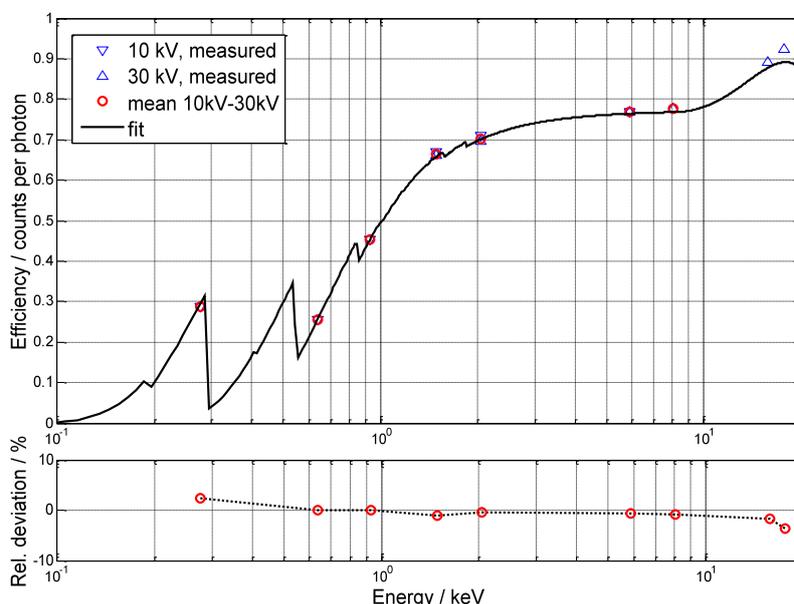


Fig. 4: EDS spectrometer efficiency for a field Si(Li) EDS system on a collaborator's laboratory with 9 experimental sampling points (X-ray emission from C, Al, Mn, Cu and Zr) determined with the help of the universal EDS CRM (Si crystal thickness: 3 mm, Ni front contact thickness: 11.8 nm, window transmittance 77% at Mn K α energy, Al layer thickness: 23 nm, mass thicknesses of C: 48.6 $\mu\text{g}/\text{cm}^2$, B: 4.5 $\mu\text{g}/\text{cm}^2$, N: 3.6 $\mu\text{g}/\text{cm}^2$ and O: 43.4 $\mu\text{g}/\text{cm}^2$).

Modern EDS systems provide increasing performance in the low energy range below 1 keV. Capability to detect X-ray lines situated below 1000 eV is reported by EDS manufacturers as state-of-the-art which enables quantitative surface analysis for a range of technologically relevant low z materials. Accordingly, the characterization of EDS performance below 1 keV is necessary, but also more challenging as for the high energy range. The C K line is taken into account in ISO 15632:2012; nevertheless, consideration of more K X-ray lines of light elements such as Be, B, N and O will step forward to supply a more complete picture of EDS behavior in the range below 1 keV. Mostly, compounds like boron nitride are used as EDS test materials in the low energy range, either for quantification, if stoichiometry can be guaranteed, or simply as B K, C K, N K and O K X-ray lines "provider" if oxidized and after carbon deposition. A set of pure materials like beryllium (Be K line at 108 eV), silicon (Si L lines at 92 eV), aluminum (Al L lines at 79 eV), lithium (Li K line at 54 eV), or magnesium (Mg L lines at 49 eV), are used by EDS manufacturers to demonstrate detection capabilities in the very low energy range. Impelled by the success of the universal EDS-TM test material it has been tried by BAM together with industrial collaborators to apply the same layer deposition technology at AXO for one set of light elements deposited as a layer on a silicon wafer. Many optimization deposition trials have been undertaken in order to ensure both the layer stability and a reasonable elemental concentration for sufficiently intense K line peaks. The optimized elemental combinations in the new test material, EDS-TM003, foreseen for EDS characterization in the energy range below 1 keV, by only one measurement at the SEM/EDS, generate X-ray spectra as in Fig. 5. The B-C-N-O layer of total thickness of about 110 nm is deposited on a Si (100) wafer. The mass fraction of carbon has been varied so that three samples of different compositions could be produced. According to Fig. 5 the optimal elemental composition corresponds to the X-ray spectrum in blue.

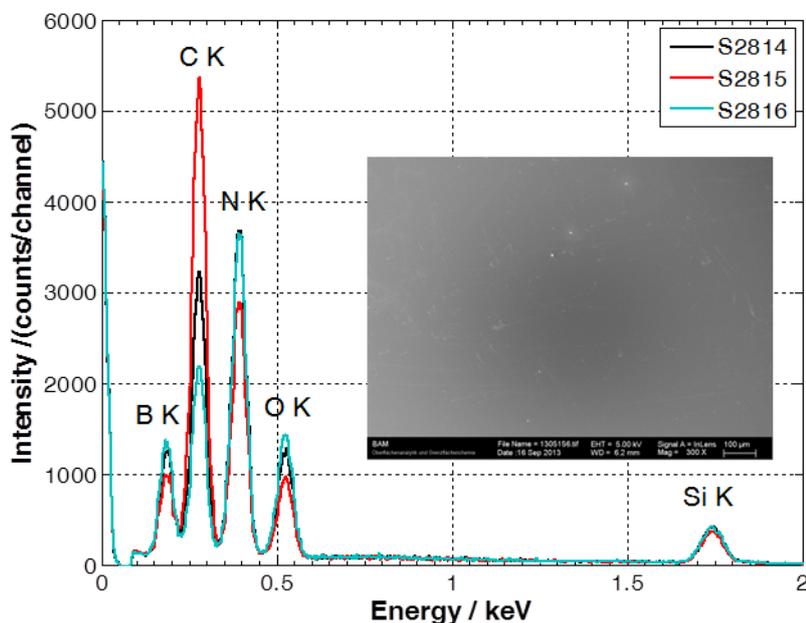


Fig. 5: 3 kV X-ray spectra of three candidates for an EDS-CRM for testing EDS performance below 1 keV. A representative SEM micrograph illustrating the very smooth surface morphology is inserted.

Another less expensive alternative has been tested with success. Some ionic liquids (see Fig. 6) with $[\text{CnC}_{1}\text{im}]^+$ (1-alkyl-3-methylimidazolium) and $[\text{NTf}_2]^-$ (bis(trifluoromethylsulfonyl)imide) as ions have been found to be useful because they may deliver X-ray peaks below 1 keV as S L and C, N, O, F K lines. They can be prepared with a flat surface, are stoichiometric and homogeneous, laterally and in depth at the EDS information depth, offer a range of elemental compositions and show sufficient stability towards e-beam damage (within typical acquisition times) and oxidation. This is the first time that ionic liquids have been considered as reference material for EDS.

A decision between the mentioned alternatives will be made after a full study of ionic liquids and one of them will be commercialized as a reference material through the BAM webshop. The universal EDS CRM is already commercially available as BAM-TM002. A specific guidance document (Guide for absolute calibration of EDS spectrometer efficiency with EDS-CRM) has been compiled that describes the best practice of an ED spectrometer calibration using these reference materials. Recently a publication in a special issue "Reference Materials for Chemical Analysis" of *Analytical and Bioanalytical Chemistry* has been published introducing the EDS CRM developed to the public (V. D. Hodoroaba, M. Krumrey V. Rackwitz, *New Reference and Test Materials as well as Procedures for Checking the Performance of an Energy Dispersive X-Ray Spectrometer (EDS) at a Scanning Electron Microscope (SEM)*, *Analytical and Bioanalytical Chemistry* **2015** 407 3045-3053, DOI: 10.1007/s00216-014-8242-5).

In summary a universal CRM to be used for the effective implementation of ISO 15632:2012 has been commercialized the first time by BAM in collaboration with AXO and PTB. The SI traceable determination of the efficiency of an EDS spectrometer at industrial stakeholders is enabled the first time by absolute detector calibration at PTB/BESSY II and the same universal transfer CRM. These new options will improve quantitative EDS analysis at industrial testing laboratories. Successful prototype reference materials for testing EDS performance below 1 keV have been approved by stakeholders to be very important for low z materials which became accessible by EDS analysis recently.

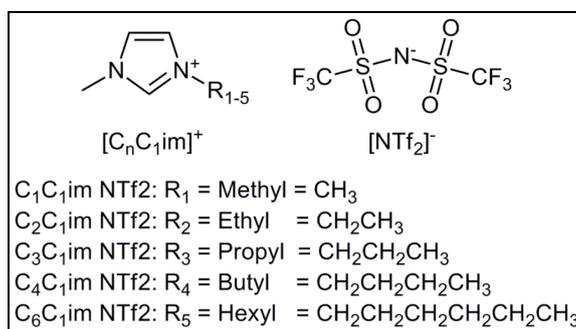


Fig. 6: A set of ionic liquids used as candidates for an EDS-CRM for testing EDS performance below 1 keV.

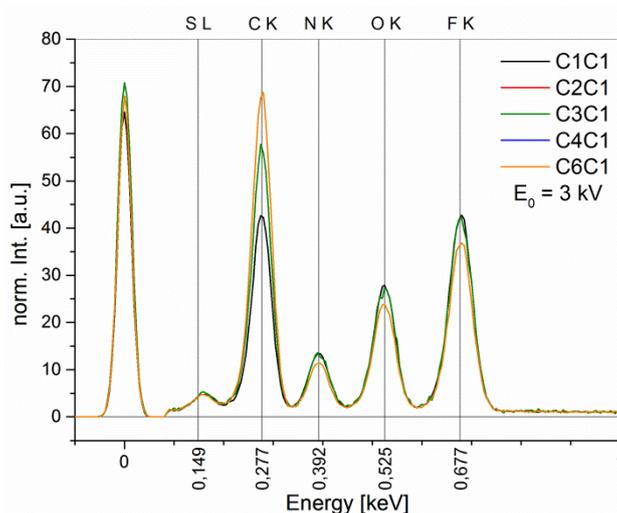


Fig. 7: EDS spectra of a set of ionic liquids (see Fig. 6) used as candidates for an EDS-CRM for testing EDS performance below 1 keV.

Imaging X-ray Photoelectron Spectroscopy (iXPS), Scanning Auger Electron Microscopy (SAM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) have large potentials to address the requirement of surface analytical technology to deliver combined information about the lateral topography and the chemical composition of nano-structured components. For the improvement of reproducibility, precision and accuracy of imaging XPS, SAM and ToF-SIMS reference materials tailored to the special demands of those methods are required. Currently no appropriate RM for imaging instruments for surface chemical analysis is available but highly demanded from the industrial users and instrument makers. The development of new standardized methods for the determination of the area seen by the instrument's ion or electron optics traceable to the length unit is another aspect accompanying the development of reference materials and is demanded by stakeholders. One overall goal of this sub-project was to metrologically underpin the fast progress in imaging surface analytical instrumentation by delivering appropriate reference materials (RMs) and methods covering the range from 10 μm down ~ 5 nm. Standardization of those methods is on the recent agenda of ISO TC 201 "Surface Chemical Analysis" representing stakeholder interests and makes only sense when appropriate test samples are available.

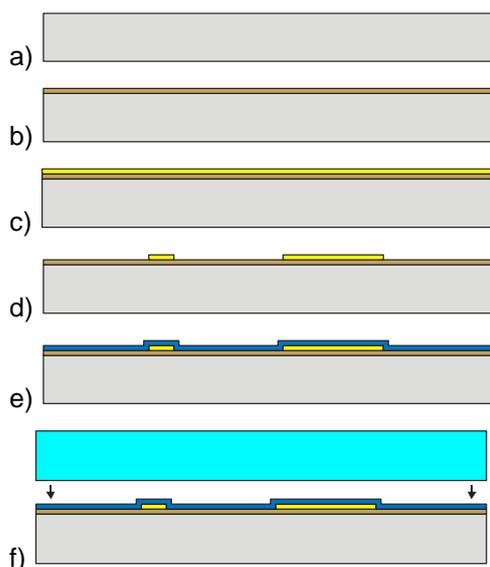
Different sample designs have been proposed, produced and tested about their qualification as RM for imaging surface analysis. For the use as RM the materials they were made of, the film thickness and the design of lateral test structures were optimised with permanent consultation of instrument makers. The production process included approaches based on electron beam writing, thin film deposition technologies and lithographic techniques at the clean room facility of PTB. Different metals were used to produce test patterns. For the production of reference samples the main challenges during production is the control of the sub μm to μm scaled dimensions of the lateral test structures and to avoid any topography at the nm scale. Substantial topography would have unwanted negative effects on the image quality because edge effects will



blur sharpness of the images produced by the instrument. Topography has been minimized after optimization of structure production methodology down to a level of a few nanometres. Metrological scanning force microscopy (SFM) has been used at PTB for characterisation of the new test structures in terms of lateral dimension and topographic flatness. With iXPS (at BAM, SPECS, TASCOS, KRATOS and FOCUS), SAM and ToF-SIMS (at BAM) the qualification of these innovative test structures to serve as RM have been tested. With the aid of this novel RM it is possible for the first time to traceably specify the lateral resolution of an individual instrument at specific settings and the μm and nm scaled area on a sample surface seen by a spectrometer’s analyser (“Field of View”).

The key challenge for the set-up of such RM is the production of metallic inlays embedded in another metallic matrix having a flat topography. After some trials the final design (cf. Fig. 10) has been realized as Cr inlays surrounded by Al. To overcome the step height at the borderline (typically ~6 nm which were state-of-the-art before the start of the project) a new processing technology was developed by PTB to reduce the step height to about 1 nm for the new RM prototypes. Measurements at the first samples at BAM and different partners from industry (such as Focus, Specs, Kratos) have proven this remaining step height to be sufficiently small for the application of these RM prototypes in lateral resolution calibration of iXPS and related surface analytical technology as SAM and Photoemission electron microscopy (PEEM). For this new processing technology a patent is pending.

A $\langle 100 \rangle$ silicon wafer (Fig. 8 a) with a silicon nitride layer (b) is used to start the production of Cr inlays surrounded by Al. The first step (c) is the deposition of the first composite of the material pair (Cr). This layer will be structured using wet chemical etching techniques (d). Then the second part of the material composite, Al, is deposited (e). In an ongoing step (f) a glass wafer (Pyrex) will be attached to the Si wafer using anodic bonding. Anodic bonding (g) is a well known fabrication process capable of attaching silicon oxide wafers to silicon wafers. It is a combination of a thermally and electrostatically induced wafer bond process. During the bond process the wafer stack will be exposed to a temperature of 300 - 400 °C. At this temperature the glass wafer starts softening which enables the material to level the topography caused by the underlying gold structures. As ongoing step (h) the silicon wafer will be removed using a wet chemical etching process (KOH). This etching process stops on the silicon nitride layer. As last step (i) the silicon nitride layer will be partially removed using a dry etch process. An only some nm thick layer remains and protects the inlay structure against oxidation. Since this process is equipped with end point detection the removal of the silicon nitride layer can be controlled very precisely. After the full removal of the nitride layer (by sputtering) the structured material composite is freely accessible for imaging resulting in a material contrast with low nm topography (cf. Fig. 9).



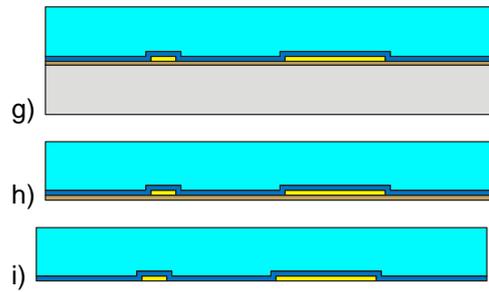


Fig. 8: Wafer based production of a Cr inlay structure in Al developed by PTB. All steps a – i are explained in the text.

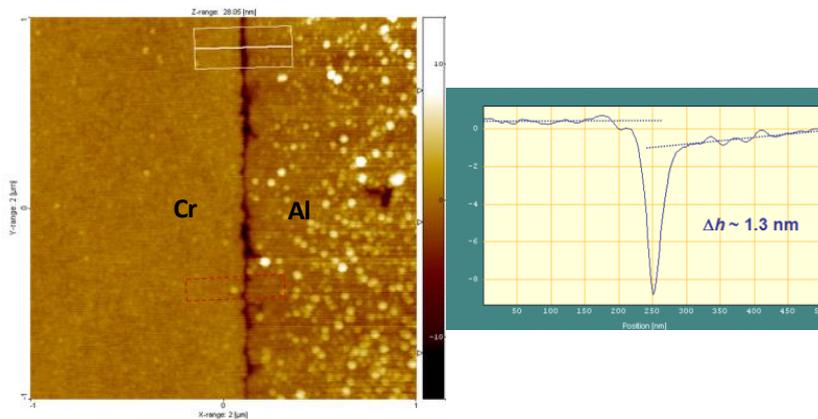


Fig. 9: Scanning Probe Microscopy image of the borderline between Cr structures embedded in an Al matrix (left side). On the right side averaged line scans across the borderline (rectangle in the SPM image left) is shown revealing a residual step height of 1.3 nm.

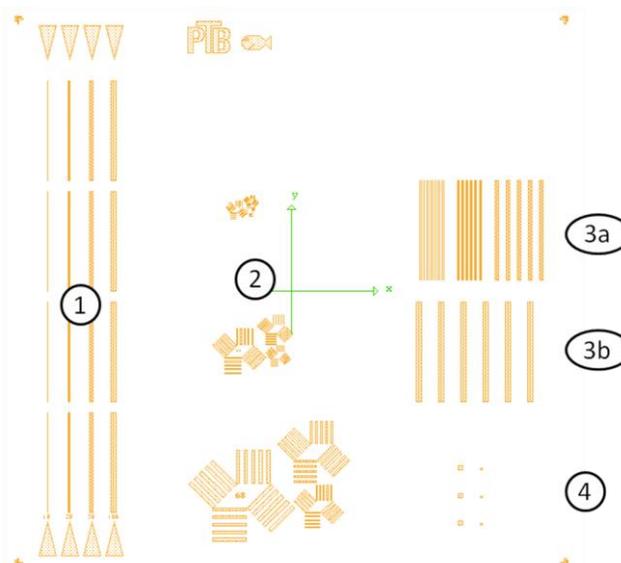


Fig. 10: Layout of the PTB test sample with Cr structures embedded in an Al matrix. There are (1) “long bars” (10, 20, 50, 100 μm in width), (2) “tilted bar boxes” (50 to 5 μm bars), (3) “bar groups” (10, 20, 50, 100 μm in width) and (4) “square groups” with A = 5, 10, 20, 50, 100 μm .



The test samples prepared by PTB have been tested extensively by project partners and collaborators. Selected results are displayed in Fig.11. At project meetings the results have been discussed and for the final product to be commercialized using BAMs infrastructure some changes will be made. The first is to add a bar pattern already used for the determination of nm scaled lateral resolution of imaging instruments for surface chemical analysis which is expanded to the μm scale relevant for laboratory iXPS instruments. This is important because this change will allow to use the test sample to implement the new ISO 18516 “Surface chemical analysis – Determination of lateral resolution and sharpness in beam based methods” which is under revision at ISO TC 201. The other point was to produce a much cheaper test sample which is only made for the determination of the Field of View in small spot surface chemical analysis using features like the “square groups” (4) shown in Fig. 10.

A prototype following the second proposal has been produced by PTB and tested by partners and collaborators. The prototype layout was designed by BAM and consists of chromium structures, dots with diameters 5-200 μm and filled squares with side length 5-200 μm on a gold layer. Figs. 12 and 13 shows the design of the prototype. With the help of this sample a regular test is enabled which determines the signal originating from outside the nominal spot size/Field of View specified for an imaging instrument at given settings. This signal is due to the fact that the primary beam or Field of View of an instrument typically has wings and the nominal size represents usually a Full Width at Half Maximum (FWHM) related to the primary beam/electron or ion optical system. However when analyzing small features as for instance μm scaled bond pads on micro chips which are smaller than the nominal size there will be signal contributions from outside the pad. This unintended contribution must be quantitatively known to the analyst. Selected results are displayed in Figs. 13 and 14. There is a strong demand by stakeholders from the industry for a respective standard development under ISO TC 201 SC7 which might be implemented using SurfChem test samples. In a preceding VAMAS inter-laboratory comparison to be launched in 2015 this second test sample will be used.

Summarizing these activities it can be stated that for the first time successful prototype reference materials (prepared by unique technology developed by PTB) and metrological methodology for a determination of the lateral resolution and the field of view of imaging instruments for surface chemical analysis have been produced at PTB and tested by BAM and almost all industrial partners of the project. Production of commercial reference materials with improved layouts, commercialization by PTB and BAM and standardization is on the horizon.

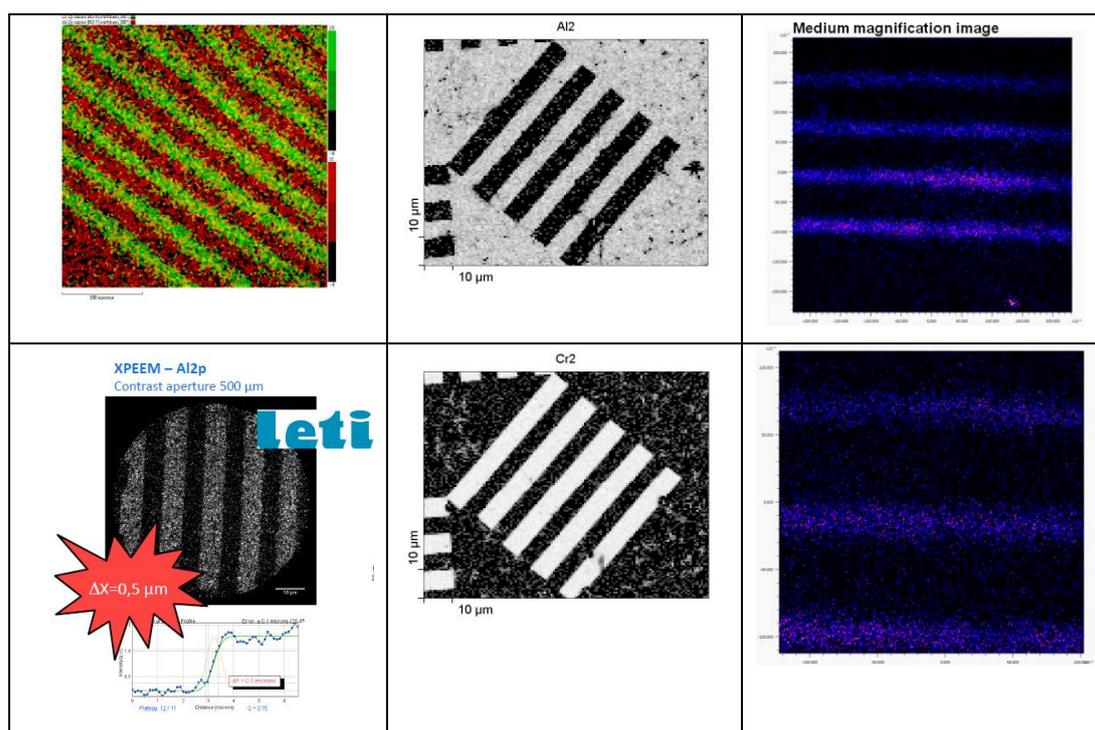


Fig. 11: Results obtained with the PTB test sample with Cr structures embedded in an Al matrix (for full layout see Fig. 10). Top left: Cr bars with a width of 30 μm imaged by a KRATOS AXIS Ultra instrument at BAM, bottom left: Al 2p PEEM image* of 10 μm Al bars measured by a NanoESCA Instrument which uses electron optical technology delivered by partner FOCUS. Image has been taken by LETI at a synchrotron radiation source and reveals a lateral resolution of 0.5 μm . Top and bottom middle: 10 μm Cr bars in Al (“tilted bar box”) imaged by a PHI 700 SAM instrument at BAM. Top and bottom right: Medium and high magnification images of 20 μm Cr bars obtained by KRATOS with an AXIS Supra iXPS instrument.
 *Courtesy by Prof. Renault, University Grenoble Alpes, F-38000 Grenoble, France - CEA, LETI, MINATEC Campus.

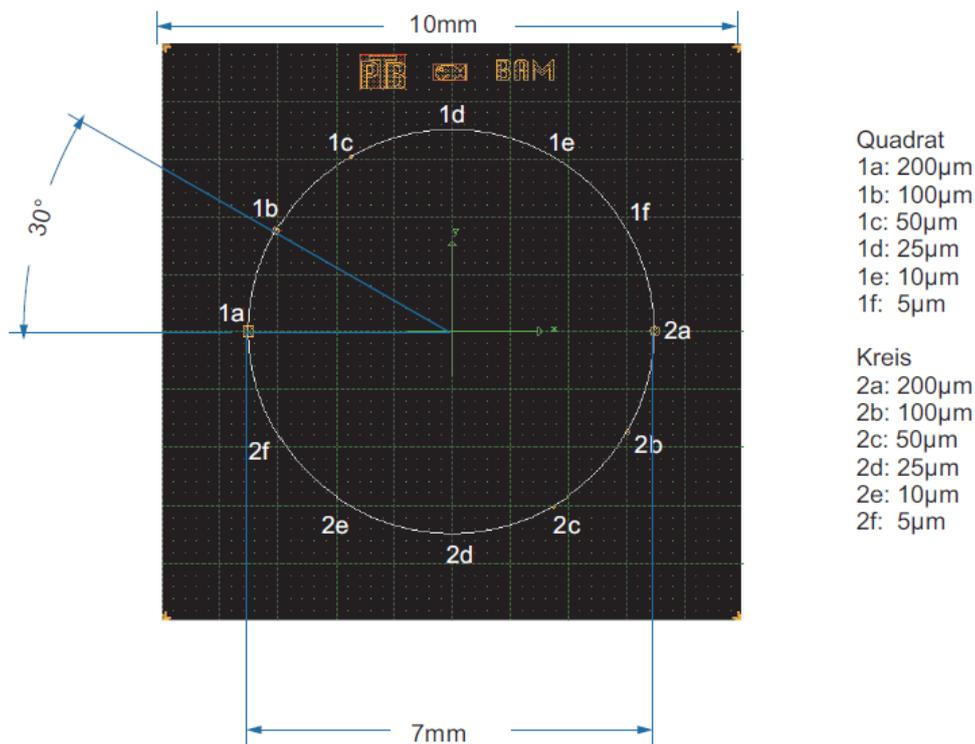


Fig. 12: Design of the PTB/BAM prototype structure having Cr dots with diameters 5 - 200 μm and squares with side length 5 - 200 μm on a gold layer. The design is made to determine signal contributions from outside the Cr structures for specific settings of the imaging instrument.

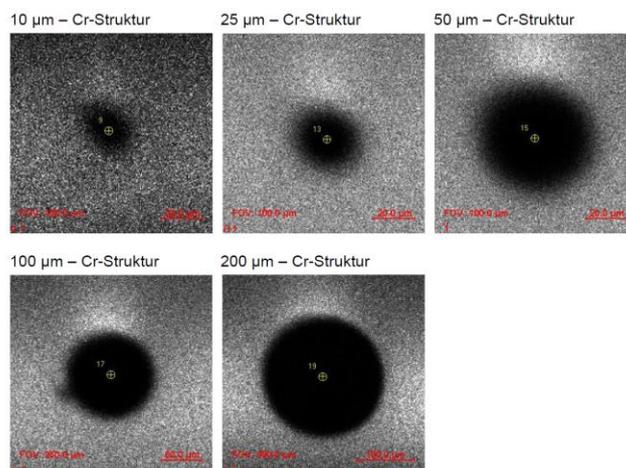


Fig. 13: Scanning X-ray Images of the 10 – 200 μm Cr dots on gold on the PTB/BAM prototype structure shown in Fig. 12. These images verify the quality of the Cr dots and have been used by TASCAN to centre the X-ray beam for XPS small spot analysis in a PHI Quanterra SXM instrument.

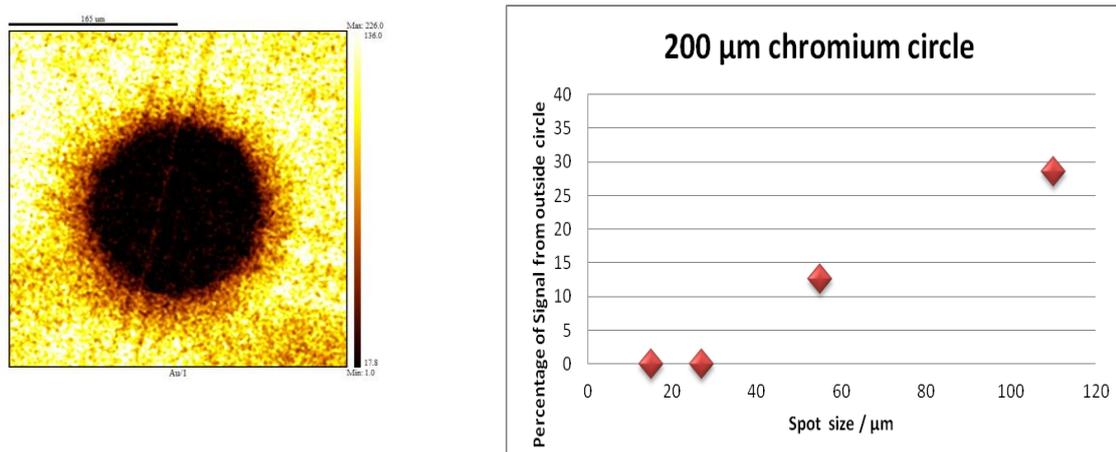


Fig. 14: Au 4f XPS image at Position “200 μm circle” (cf. Fig.12) showing the shadow of the Cr dot on the gold layer and percentage of the signal originating from outside the nominal Field of View (“spot size”) of the analyser of a KRATOS Axis Ultra instrument at BAM. The X-ray beam was centred at the 200 μm Cr spot. For a nominal 57 μm Field of View of the analyser a least 10 % of signal intensity originates from outside the 200 μm Cr dot. Only with a nominal Field of View < 27 μm no contribution from outside the 200 μm Cr dot has been measured.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are widely used techniques for quantitative surface analysis of thin films aiming on surface composition and layer thickness. The signal intensities follow an exponential law involving the thickness of the layer and an attenuation parameter which is usually referred to as the attenuation length (AL) or effective attenuation length (EAL) or as the inelastic mean free path (IMFP) of photoelectrons has to be precisely known to enable metrologically underpinned methodology for the thickness determination of thin overlayers by the Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) method at a relative uncertainty down to 5 %. A review of calculated and measured values for the effective attenuation length (EAL) and the inelastic mean free path (IMFP) of photoelectrons has been published by Powell and Jablonski [1, 2]. Seah and Dench compiled published measurements of the electron IMFP lengths in solids and provided empirical formulas for their calculation [3]. An extensive work on the calculation of the IMFPs of various materials was done by Tanuma, Powell and Penn [4]. In addition, the National Institute of Standards and Technology (NIST) hosts databases on the IMFP and the EAL: the Electron Inelastic-Mean-Free-Path Database (SRD 71) provides values for use in surface analysis by AES and XPS. The database includes electron IMFPs calculated from experimental optical data as well as electron IMFPs measured by elastic-peak electron spectroscopy. The Electron Effective-Attenuation-Length Database (SRD 82) provides values in materials at electron energies between 50 eV and 2,000 eV. However in all cases there is almost no information on the uncertainties of published values which when used substantially contribute to the combined uncertainty of quantitative data. This was the motivation to develop a methodology and undertake a metrologically underpinned determination of the EAL with the example of an nm scaled Pd layer on quartz and compare that result to the data bases.

The experiment is based on a thin Pd layer with a nominal thickness of 4 nm which had been produced by sputter deposition on fused quartz substrates at AXO-Dresden GmbH, Germany. The actual thickness was determined by PTB with traceable X-ray reflectometry (XRR) at a photon energy of 8 keV using the four-crystal monochromator beamline of PTB at the synchrotron radiation facility BESSY II, resulting in 4.4 ± 0.1 nm, respectively. This is near to the limit for photoelectrons excited in the quartz substrate to travel across

the Pd layer and to leave its surface for analysis by XPS using instruments at METAS and BAM. The instrument at BAM has an Ar ion sputter gun attached to the analysis chamber. It has been used to reduce the thickness of the 4.4 nm Pd layer even further with subsequent XPS analysis at a take-off angle of 0 degree without intermediate air exposure (Fig. 15). The actual Pd film thickness for each XPS measurement had been obtained from X-ray fluorescence (XRF) mapping (see Fig. 15), performed at the same PTB beamline at an excitation energy of 5.5 keV, by comparing the Pd L fluorescence line intensity to the surrounding virgin layer where the thickness was determined by XRR before.

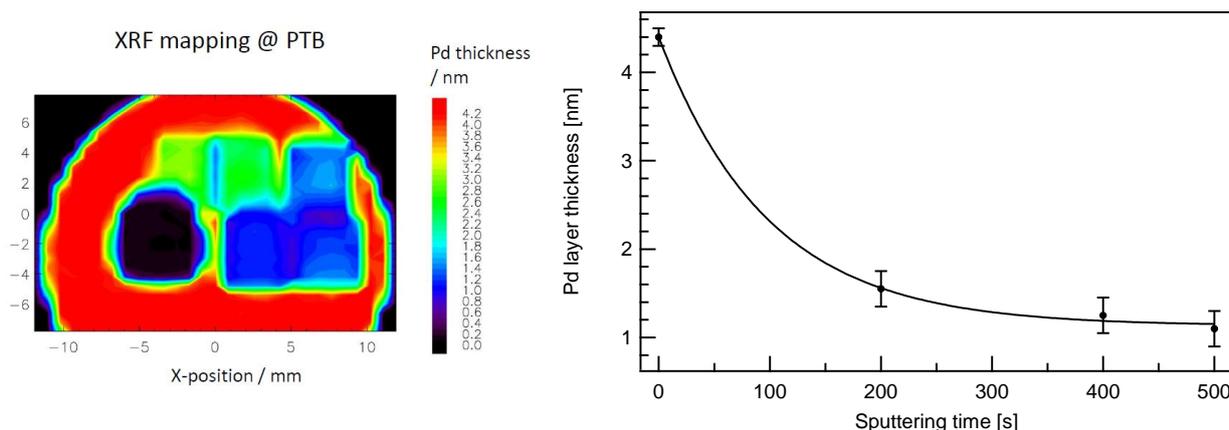


Fig. 15: XRF map used to determine sputter crater depth necessary to determine the decrease of the Pd overlayer thickness vs. Ar ion sputtering time. The solid line is an exponential fit to the data. The right sputter crater (black) goes into the substrate and has been used to determine the sputter rate; three blue ones at the right represent the craters after 200, 400 and 500 s of sputtering (clockwise).

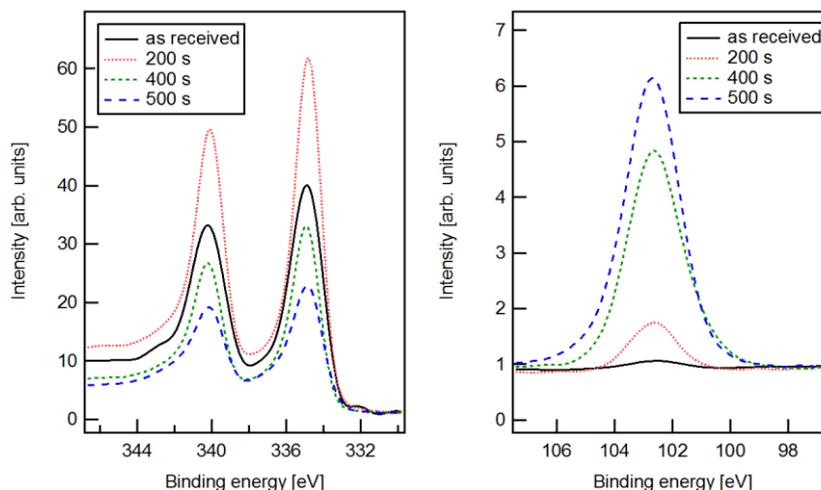


Fig. 16: XPS spectra of Pd 3d and Si2p after sputtering for 200 s, 400 s and 500 s measured at BAM using a KRATOS Axis Ultra DLD instrument. Peak areas under the Pd 3d spectra have been used to determine the EAL for Pd 3d photoelectrons in the nanoscaled Pd film.

By using following equation the EAL for Pd 3d photoelectrons excited by monochromatized Al Kalpha X-rays was evaluated at METAS from experimental data delivered by BAM and PTB to be 1.535 ± 0.476 nm.

$$I_{Pd}(d) = I_{Pd}^{\infty} \times \left[1 - \exp \left(- \frac{d}{\lambda_{Pd,Pd} \times \cos \theta} \right) \right]$$



For comparison the TPP-2M [4] model delivers 1.312 nm and a simulation using the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [5] which models spectra compared to the experimental ones delivers 1.603 ± 0.049 nm. One reason for differences between experiment and theory is related to the fact the theory needs an assumption on the density of Pd in the Pd layer which typically results in the use of bulk Pd data. The density of the nm scaled sputtered Pd overlayer on quartz used in the experiment might be somewhat different.

Summarizing this activity the project partners METAS, BAM and PTB developed a metrological procedure to determine experimental EALs together with related uncertainty. The method has been metrologically underpinned by establishing a chain of traceability to the SI by calibrated X-ray techniques at the PTB. A proof of principle has been delivered with relevance for high precision measurement of nm scaled overlayer thickness and quantitative element analysis, both by XPS.

[1] C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data 28, 19 (1999)

[2] A. Jablonski and C.J. Powell, Surf. Science Reports 47, 33 (2002)

[3] M. P. Seah and W. A. Dench, Quantitative Electron Spectroscopy of Surfaces: A Standard Data Base for Electron Inelastic Mean Free Paths in Solids, Surface and Interface Analysis, 1, No. 1, (1979)

[4] S. Tanuma, C. J. Powell and D. R. Penn, Calculations of electron inelastic mean free paths. IX. Data for 41 elemental solids over the 50 eV to 30 keV range, Surf. Interface Anal. 43, 689-713, (2011)

[5] NIST Standard Reference Database 100, NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA): Version 2.0, W. Smekal, W. S. M. Werner, and C. J. Powell, Surf. Interface Anal. 37, 1059 (2005)

2.2 Reference Materials and Methods for Surface Chemical Analysis of Organic Surfaces

Driven by recent developments in industrial technology, as for instance in molecular electronics, energy harvesting by organic solar cells or devices for medical diagnostics, there is a need for certified organic reference materials suitable for the calibration and testing of techniques and methods for quantitative surface chemical analysis. Specifically industrial testing laboratories need organic CRMs for traceable and quantitative surface chemical analysis, traceable methodology for quantitative thickness and compositional analysis of organic layers and protocols for quantification of functional groups at the very surface of organic and bioorganic materials used for biosensing and medical diagnostic devices. Ad-hoc reference materials exist and are used by convention, for example in the calibration of sensitivity factors and performance monitoring of XPS instruments. Examples include polytetrafluoroethylene (PTFE) and polyethyleneterephthalate (PET), where chemical stoichiometries can be used for establishing sensitivity factors for the elements present and line-width can be employed to monitor instrumental energy resolution. Analyses of a large number of pure organic materials with known stoichiometries have clearly established that a well-calibrated XPS instrument provides an accurate measurement of surface elemental composition for most organic materials. Uncertainty in relative sensitivity factors, electron attenuation lengths and, importantly, the algorithms used for the extraction of intensity from the data combine to give an uncertainty in composition that is typically estimated to be at the 10 % level.

Organic reference materials with certified thickness and a variety of layer stack designs prepared using organic molecules as different Irganox species and FMO (Fluorenylmethyloxycarbonyl) have been developed and tested by NPL in collaboration with partners and collaborators using complementary methods. Thermo and METAS used angle resolved XPS, KRATOS XPS with coronene depth profiling, ION-TOF, TASCAN, BAM and SP used ToF-SIMS with Argon cluster ion depth profiling, INRIM used optical spectroscopies and PTB X-ray reflectometry and X-ray spectroscopy. Organic reference films have been deposited at NPL by vacuum sublimation of organic materials onto a flat silicon wafer. The amount of material deposited during vacuum sublimation has been determined by ellipsometry and Quartz crystal microbalance (QCM). Traceability has been established by independent gravimetry, measurement by QCM and AFM step-height measurement at NPL. Samples from selected batches of the reference materials had been stored in a variety of conditions (ambient, refrigerated, and frozen, in the absence of light and under nitrogen) and analysed over the course of 6 months to establish if significant degradation of their key properties has occurred. The resulting recommendations for storage and lifetime inform the conduct of subsequent (pre-)normative studies under VAMAS TWA 2 / ISO TC 201 and the users of the CRMs.

Figure 17 displays the successful design of an organic layer stack CRM (Irganox 1010 layers in Irganox 1098) used to determine the depth resolution of ToF-SIMS and XPS for depth profiling using Argon cluster sputtering.

Figure 18 displays materials prepared by NPL and used for the VAMAS Project A3(g): Static SIMS Interlaboratory Study: organic depth profiling of mixed materials which has been launched at the end of the EMRP project. An Argon cluster SIMS depth profile demonstrates the success of the construction method. 22 participants from UK, Germany, Sweden, France, Belgium, Poland, Italy, USA, Korea and Japan participate in the VAMAS A3(g) study which is designed to enable the preparation of a New Work Item for ISO TC 201 SC6 later. The specific purpose of this inter-laboratory study is to determine the influence of the composition of a material upon the signal generated during a depth profile. The films are binary mixtures of molecular materials in which the composition is certified as a function of depth. The analysis of these samples provides information on composition-dependent sputtering yields, depth resolutions and intensities. The specific objectives of this study are: (i) to establish the degree of non-linearity in depth profile intensities with material composition. i.e. to identify the “matrix effect” and (ii) to determine whether the matrix effect is consistent between instruments and laboratories and which experimental procedures most strongly influence it.

The measurement of the amount of material in a vacuum deposited layer was a basic task for preparing organic CRMs. The accuracy of the ellipsometric thickness measurements used by NPL to certify the thicknesses was established to be within 4% through comparison with traceable XRR measurements at PTB (see Fig. 19) and resulted in a joint publication between PTB and NPL [Wernecke et al, Surface and Interface Analysis, 2014 DOI: 10.1002/sia.5371]. AFM measurements and direct weighing confirmed that the amount of material was as expected, but had poorer uncertainties. Samples were distributed to participants during the project and for the VAMAS study to establish the comparability of methods to depth profile organic materials. The work has contributed significantly to the understanding of cluster ion beam sputtering. As a result, a new work item has been proposed in ISO TC201 (Surface Chemical Analysis) on ‘measurement and reporting sputtering yields in organic depth profiling’.

Reference materials were constructed of two different kinds, in one of the mixtures a component contained nitrogen in an amide group which was possible to detect by XPS, SIMS, IR, Raman and XRF. In the second, the unique elements were both nitrogen and fluorine. For single layer mixtures, it was found that XPS and optical spectroscopies provided excellent quantification (Fig. 20) and the results are being compared to the XRF measurements (Fig. 21). Analysis of the materials by SIMS proved beyond doubt the existence of matrix effects in this technique, but also provided profound insight into these effects and demonstrated that they could be categorized and described (cf. Shard et al, International Journal of Mass Spectrometry, 2015 DOI: 10.1016/j.ijms.2014.06.027).

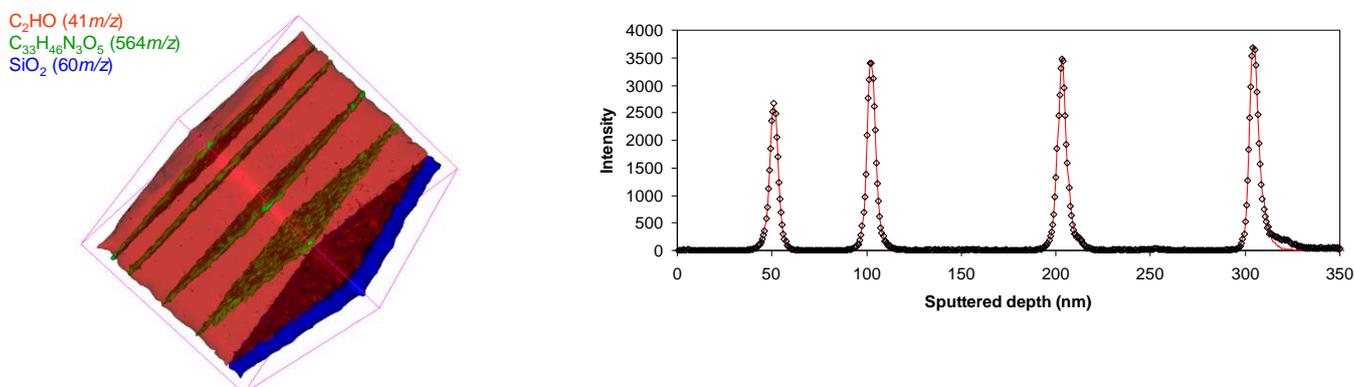


Fig. 17: Left: Successful layer stack certified reference material with narrow Irganox 1010 layers in Irganox 1098 reconstructed from ToF-SIMS data. Right: ToF-SIMS in depth profile of the obtained by Argon cluster sputtering used to determine depth resolution.

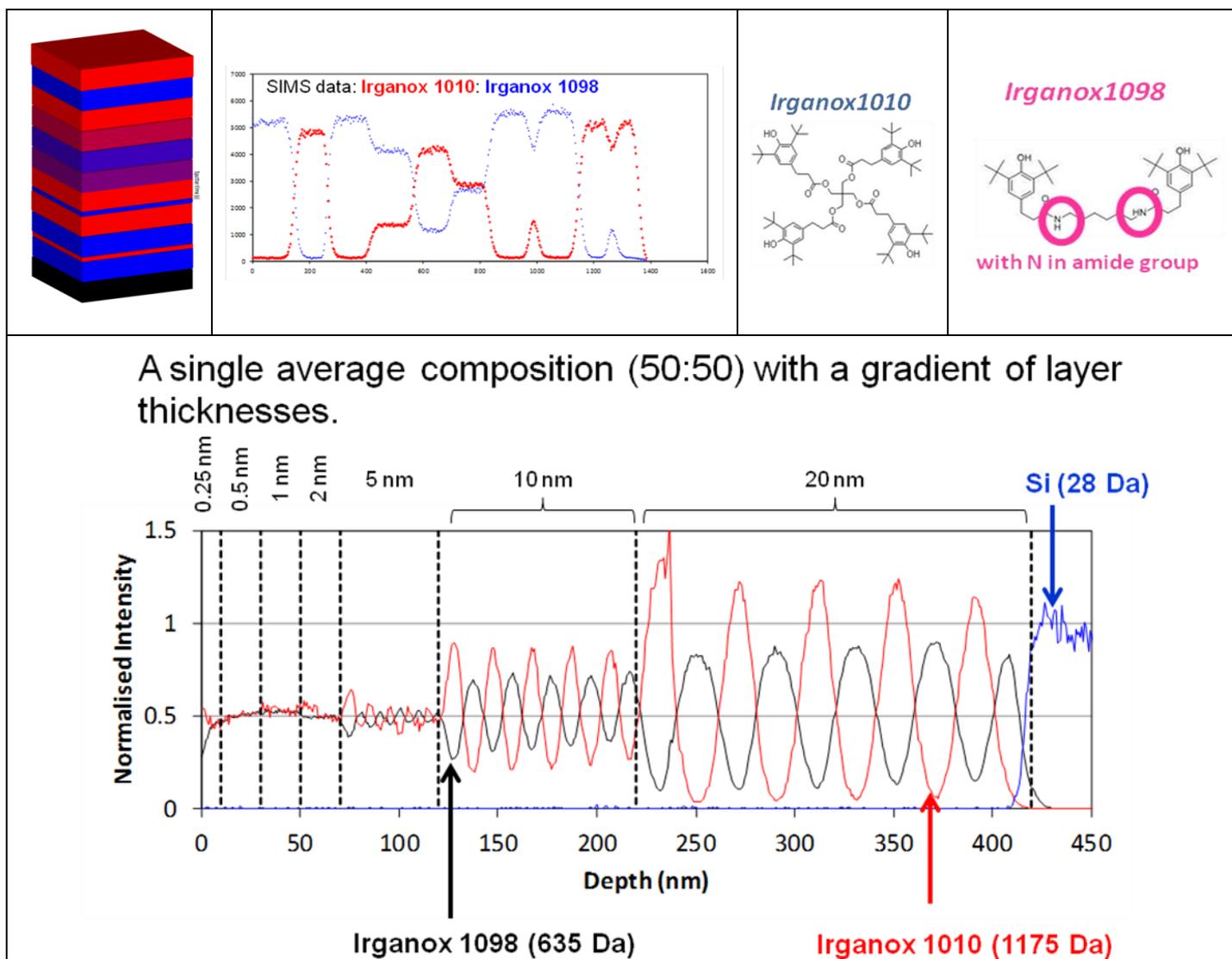
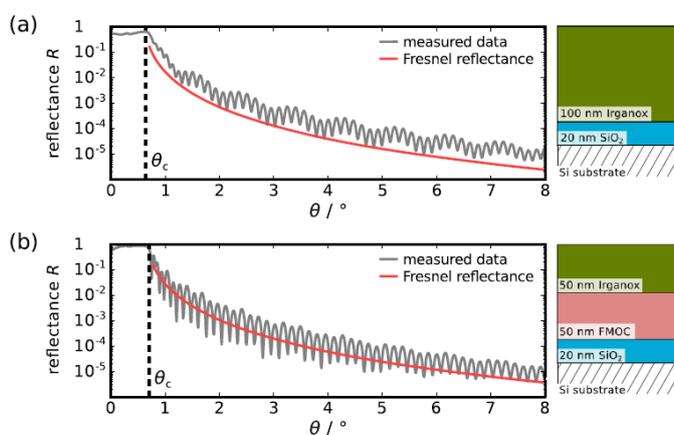


Fig. 18: Top left: Design of a CRM with a variation of thickness and compositions of Irganox 1010 and Irganox 1098 in individual layers. Top middle: SIMS in depth profile of this layer stack measured with Argon cluster ion sputtering. Top right: Molecular structures of Irganox 1010 and Irganox 1098. Bottom: SIMS depth profile measured with Argon cluster ion sputtering of a CRM with only one Irganox 1010 / Irganox 1098 mixture ratio but having a graded layer thickness.

NPL developed a technology for the preparation of stable organic reference materials for thickness determination and compositional analysis by surface analytical methods, the first time offering a chain of traceability to the SI. Two independent ways for establishing these chains have been delivered by NPL and PTB. The preparation technology is unique because it allows preparing a wider range of CRMs for different analytical tasks as depth profiling, thickness determination and maintenance of analytical hardware, e.g. control of the depth resolution obtained by different settings of cluster ion guns and matrix effects in ToF-SIMS analysis. The broad range of complementary methods used to test NPL's organic CRMs has been enabled by participation of all funded partners and almost all industrial partners.



Sample	Layer (top to bottom)	XRR thickness / nm	Ellipsometry thickness / nm
A	Irganox	107.0	104.5
	SiO ₂	20.6	20.9
B	Irganox	50.5	49.2
	Fmoc	52.3	51.2
C	SiO ₂	20.5	21.2
	Irganox	77.4	75.7
D	Fmoc	25.0	24.9
	SiO ₂	20.1	20.9
	Irganox	25.8	25.2
	Fmoc	73.6	72.8
	SiO ₂	20.0	21.0

XRR, X-ray reflectometry.

Fig. 19: Left: X-ray reflectometry (XRR) profiles measured at a photon energy of 1841 eV. (a) single layer of nominal 100nm Irganox; (b) bilayer of nominal 50nm Irganox on nominal 50nm Fluorenylmethoxycarbonyl (FMOC). Also displayed is the Fresnel reflectance (red line), calculated from the critical angle θ_c as determined from the reflectivity curve, and schemes of the layer systems. Table right: Layer thicknesses determined by power spectral density analysis of the XRR data (PTB) and from ellipsometric measurements performed before and after each evaporation step (NPL).

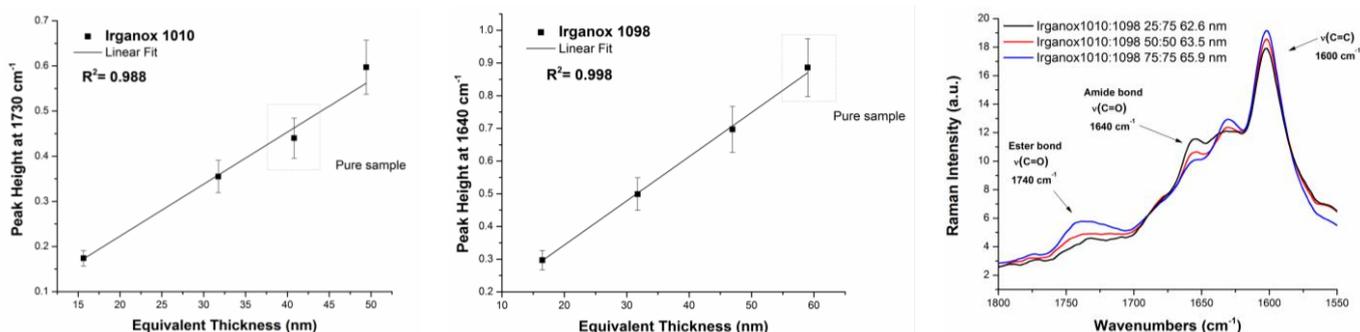


Fig. 20: Left: FTIR calibration of absorbance at two different wave numbers vs. thickness of Irganox 1010 and 1098 layers revealing a linear correlation. Right: Raman spectra with increasing intensities for amide and ester bonds which linearly correlate to increasing thickness of Irganox 1098 layers.

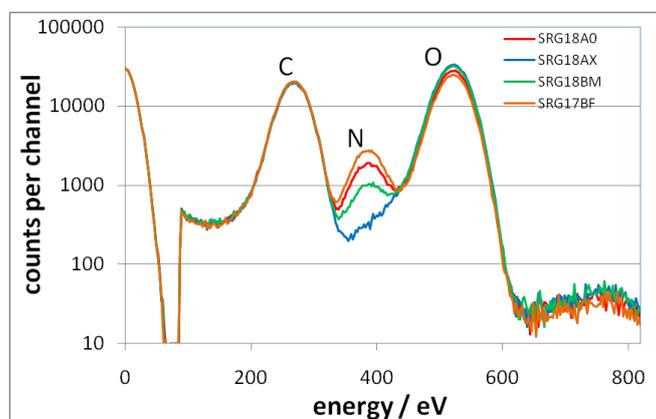


Fig. 21: Total reflection XRF spectra measured at an excitation energy of 570 eV for increasing amounts of Irganox 1098 in Irganox 1098/1010 mixed 60 nm layers on an oxidized Si wafer enabling absolute determination nitrogen which is related to amide species in Irganox 1098 and enables film thickness determination traceable to the Si.

Protocols for quantification of functional groups at the very surface of organic and bioorganic materials used for biosensing and medical diagnostic devices have been developed using two different approaches. The first relies on the design and preparation of dual functional labels that can be attached to surface functional entities to be readout by fluorescence and by a surface chemical analysis method such as XPS. The other is based on molecular labels consisting of liposomes for subsequent detection using TOF-SIMS.

Silane-modified glass surfaces which are vastly employed for manufacturing diagnostic devices as they are chemically and mechanically robust, comparatively cheap and versatile in adaption and handling. However, among the numerous methods available for glass surface silanization, only few lead to reliable surface functionalization, and a tunable control of the active functional group densities based on a better understanding of the involved processes is only rarely available. An optimum and at best controlled provision of the primary anchor points for the analytical entities on a support however governs all later optimization. A tailored density of surface functional groups for a specific application has been recognized as being of paramount importance for the optimum success of an application that is based on the covalent attachment of functional entities to a surface. Molecular labels for a determination of amino groups that fluoresce brightly and contain unique atoms suitable for surface analytical techniques as XPS and XRF have been developed by BAM, PTB and Partner Scienion. The project was able to show that reliable quantitative information on surface functional groups on flat substrates can best be obtained with surface analytical techniques like XPS in combination with chemical derivatization and by fluorescence labeling. The reliable determination of the number of surface functional groups was approached with a dual-mode boron-dipyrromethene-type fluorophore fluorescence label developed by the project which allows quantification by fluorescence and XPS on one and the same sample (Fig. 22). It has been shown that fluorescence and XPS signals correlate over at least one order of magnitude, allowing for a direct linking of quantitative fluorescence analysis to XPS quantification (Fig. 23). Employment of synchrotron-based methods (XPS, reference-free total reflection X-ray fluorescence (TXRF)) made the traceable quantification of surface functional groups possible and provided an absolute reference for quantitative fluorescence measurements (Fig. 24). For XPS, the limit of detection (LOD) has been determined to be 0.2 aminated silane molecules per nm^2 which is the same for reference free TXRF. The LOD for the microarray scanner used in the study was 0.04 aminated silane molecules per nm^2 . Protocols have been validated and uncertainty budgets established. A report describing the protocols and the comparability of methods has been published in *Analytical Chemistry* (Fischer, T, et al. *Quantification of variable functional-group densities of mixed-silane monolayers on surfaces via a dual-mode fluorescence and XPS label*, *Analytical Chemistry*, **2015**, 87, 2685-2692, DOI10.1021/ac5038501). The stability of the labels has been tested.

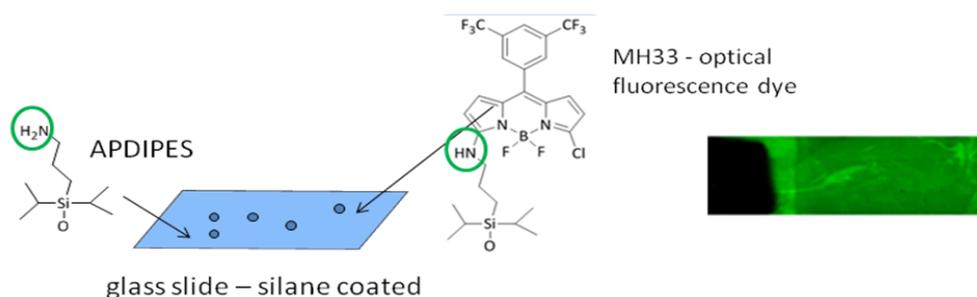


Fig. 22: Schematic illustration of the dual MH33 fluorophore label based approach for the quantitative determination of reactive amino groups on a glass slide functionalized by silane linker molecules (industrial substrate for the production of diagnostic microarrays) by fluorescence spectroscopy (fluorescence image on the right side), XPS and traceable TXRF.

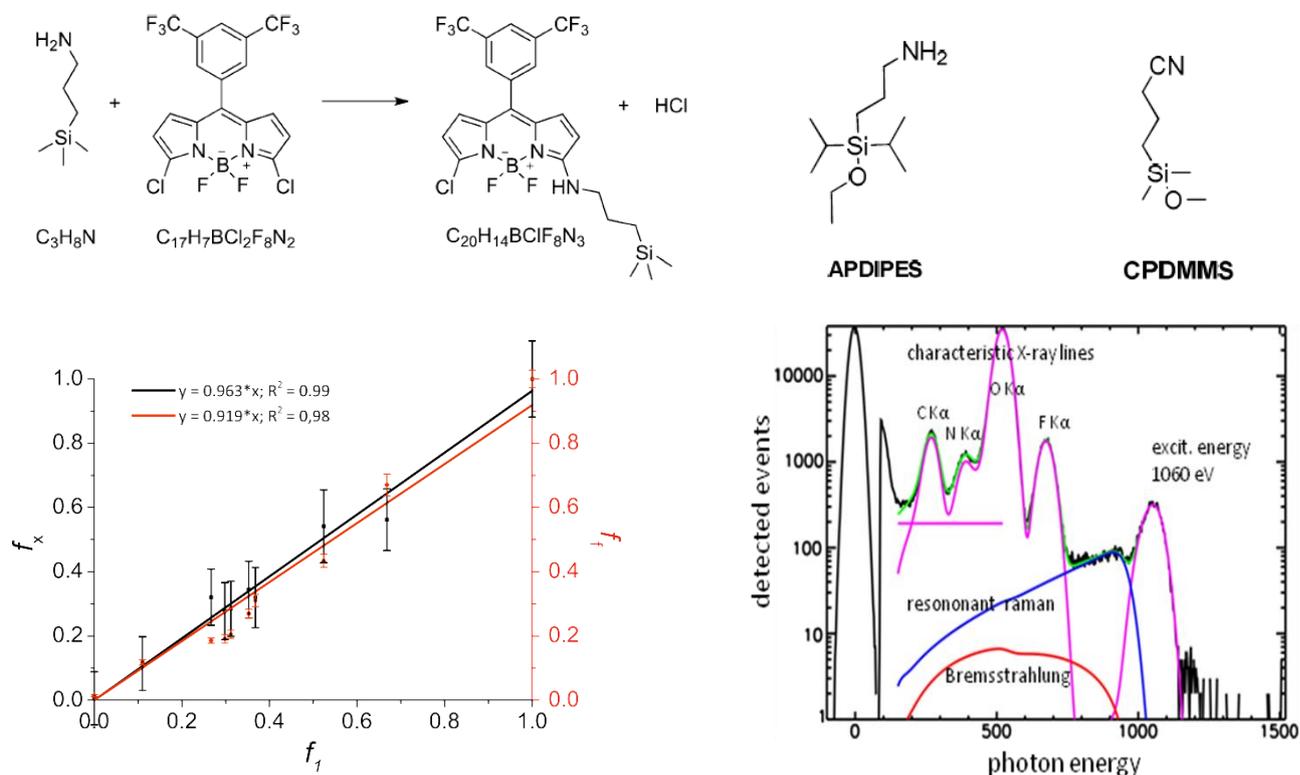


Fig. 23: Top left: Covalent labelling of a (3-aminopropyl)diisopropylethoxysilane (APDIPES) linker molecule on glass by the dual MH33 fluorophor label. Top right: Constituents of the mixture (variable composition) of silanes (CPDMS: 3-cyanopropyl)dimethylmethoxysilane) deposited at the glass slide. Bottom left: Amino fractions calculated from XPS F/N ratios after labeling (f_x , black) and normalized fluorescence (f_f , red) versus fraction f_1 of APDIPES in the APDIPES/CPDMS mixed film. Bottom right: Traceable TXRF spectrum of the labeled APDIPES/CPDMS mixed film enabling determination of absolute molecule per area numbers with a combined uncertainty of ± 0.7 by evaluating N and F K line areas. These absolute molecule per area numbers have been used to calibrate XPS and fluorescence measurements.

Using a parallel approach for the detection of biomolecules at surfaces, molecular labels consisting of liposomes for subsequent detection using TOF-SIMS and fluorescence spectroscopy have been studied. The main advantage of TOF-SIMS detection has been demonstrated showing a very high multiplexing potential, providing a possibility to screen for highly relevant functional entities (cf. Fig. 24). The liposome approach has been correlated to fluorescence detection and independent quantification of the liposome binding was provided by QCM. For low surface concentrations, the novel approach of amplification by liposome attachment and ToF-SIMS detection has been proved. SP selected liposomes suitable for surface functional entity attachment and ToF-SIMS analysis. This selection was focussed on range of liposomes providing unique ToF-SIMS signals to enable multiplexing capacity. With the performance criteria to enable effective and specific binding to the molecular analyte, and sensitive and specific detection of the surface-immobilised liposome using TOF-SIMS, antibody-conjugated liposomes made of phosphatidylcholine lipids at varying degrees of deuteration and 100-300 nm diameters in size were prepared, characterized and tested. Calibration curves of the TOF-SIMS signal vs. liposome binding determined by QCM-D have been recorded at SP in order to assess the accuracy and dynamic range of the liposome approach for probing of functional entities. The multiplexing capacity of the liposome approach has been investigated at different concentration ranges, spanning from the single molecule regime (liposome counting) to the high coverage regime.

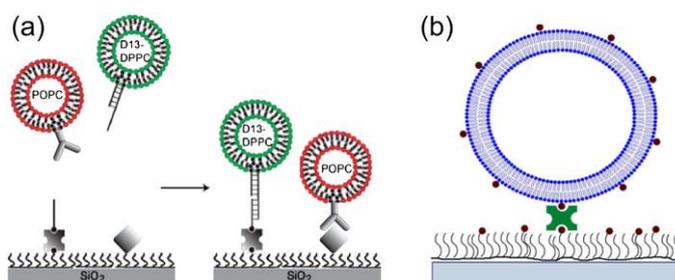


Fig. 24: Schematic illustrations of the liposome label based approach for biomolecule detection by imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS). (a) Liposome-based concept for multiplexed biomolecule detection at model surfaces. Liposomes with attached recognition elements (here, an antibody and a DNA single strand) bind to the surface only in the presence of the matching biomolecule on the surface. The surface-immobilized liposomes are subsequently detected and identified by ToF-SIMS analysis. Multiplexing is accomplished by using different liposome compositions for different recognition elements. (b) Sample system used to study the detection of specifically bound liposomes. Liposomes functionalized with biotin binds specifically to neutravidin on the sample surface. The concentration of neutravidin on the surface is varied by changing the concentration of biotinylated PEG groups in the PLL-g-PEG monolayer adsorbed on the SiO₂ substrate.

A new method for biomolecular detection, quantification and imaging at tissue surfaces, based on a combination of liposome labelling and imaging TOF-SIMS analysis (Fig. 24), was developed and evaluated. Procedures for the selective labelling of functional entities at surfaces with the liposome labels and subsequent analysis by TOF-SIMS were developed and demonstrated to be capable of quantitative analysis down to the single liposome regime (potentially representing single analyte binding events), imaging at a resolution of $\sim 1 \mu\text{m}$, and high multiplexing potential. This work resulted in two publications on the application of the liposome-based approach for biomolecular detection on model surfaces (Sjövall et al. *Surface and Interface Analysis*, DOI: 10.1002/sia.5494) and in tissue samples (Carlred et al, *JACS*, 2014, DOI: 10.1021/ja5019145), respectively. The latter one aims on the spatial localization of amyloid- β peptide deposits, the major component of senile plaques in Alzheimer's disease (AD). For the first time amyloid- β peptide was successfully mapped in transgenic AD mouse brains using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with liposome labels developed by the project (Fig. 25), simultaneously with several endogenous molecules that cannot be mapped using conventional immunohistochemistry imaging.

It is concluded that at the project partners BAM, PTB, Scienion and SP protocols were successfully developed aiming on a quantification of functional groups and biomolecules at the very surface of organic and bioorganic materials used for biosensing and medical diagnostic devices. Full traceability to the SI has been established the first time for detection of surface amines by fluorescence spectroscopy and XPS using calibration by standard-free TXRF at the PTB. Using liposome labels and subsequent detection using TOF-SIMS multiplexing capacity of the liposome approach has been fully approved, the first time down to the single molecule detection regime.

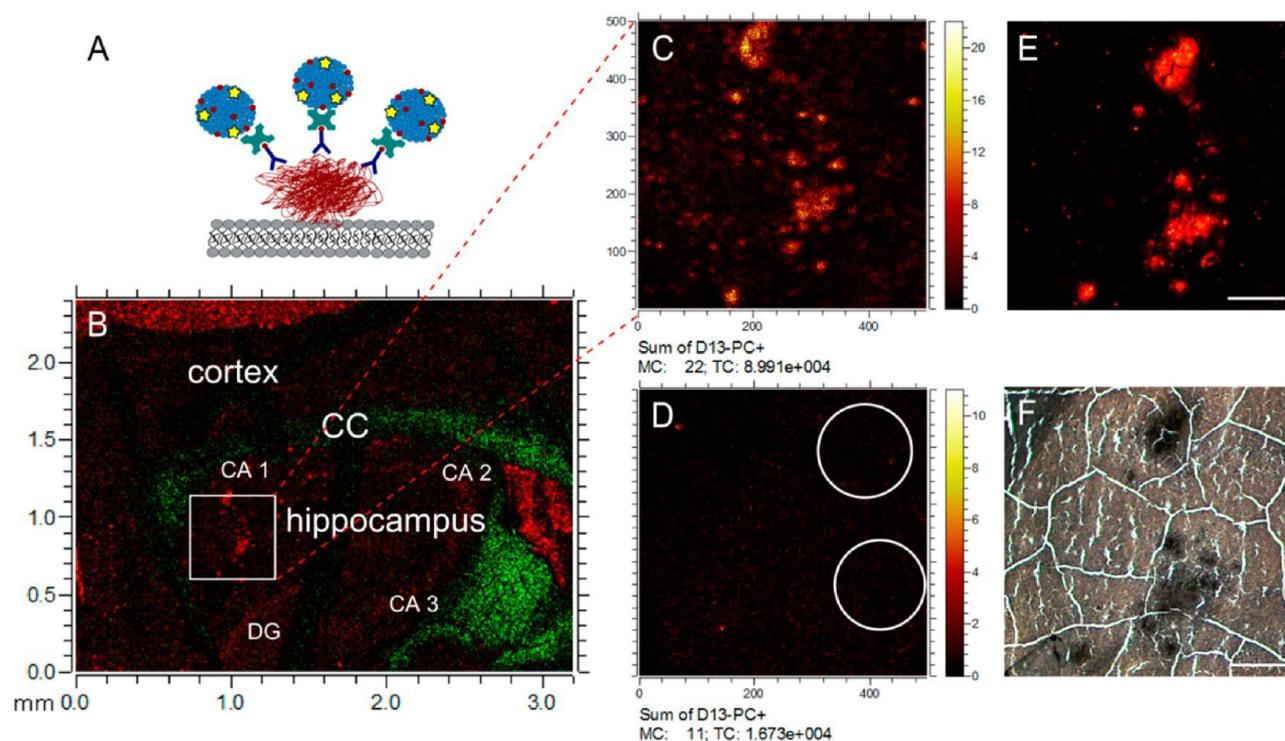


Fig. 25: (A) Schematic illustration of the protein detection principle showing the binding of biotinylated liposomes, neutravidin and biotinylated antibodies to an amyloid- β deposit in a tissue section. (B) ToF-SIMS overview image visualizing liposomes (red) and cholesterol (green) in the hippocampal region of a transgenic AD mouse brain section. Red areas above the cortex and to the right of the hippocampus indicate unspecific binding of liposomes to areas where the glass microscope slide is exposed. (C,D) ToF-SIMS images of the area indicated by the white square in (B) visualizing (C) amyloid- β deposits stained by antibody-coupled liposomes and (D) corresponding area in an adjacent tissue section incubated without the addition of antibodies (6E10). The position of amyloid- β deposits is indicated by the white circles. (E) Fluorescence microscopy image (10 \times magnification) of the same area analyzed by ToF-SIMS in (C), visualizing amyloid- β deposits stained by fluorescent lipids incorporated in the antibody-coupled liposomes. (F) Optical (bright field) microscopy image (10 \times magnification) of the same tissue sample as in (C) and (E). Scale bar= 100 μ m.

2.3 Metrology for reliable ambient and non-destructive chemical analysis for in-line process control

There is a strong demand for valid and traceable process analytical technology for product quality control in the European industry. The project addressed specific demands of high tech vacuum component and food industries. Metrologically underpinned methodology for fast in-line analytical methods based on optical spectroscopy, contact angle spectroscopy and ambient mass spectrometry has been developed by NPL, INRIM, METAS, BAM and stakeholders from the industry. For meaningful and routine analysis in industry the repeatability, reproducibility and specificity of measurements is critical and has been investigated.

Methodology that enhances the capability of optical spectroscopy for real time analysis and in situ monitoring to be used in industrial process control during product fabrication has been developed and validated. Raman spectroscopy, mid FTIR and near infrared spectroscopy have been used because they are well accepted techniques for process control, allowing the analysis of samples with a fast response, without sample destruction and giving portability for analysis in situ and in-line.

In detail, INRIM developed metrologically underpinned FTIR and Raman methodology aimed on quantitative monitoring of contaminants in clean rooms and to test the cleanliness of optical components and hardware for aerospace applications together with collaborators Thales Alenia Space and Thermo (Fig. 26). Method development was accompanied by the preparation of defined organic reference films to be used for calibration of IR and Raman equipment applied to determine organic contaminants at critical industrial

surfaces supporting the implementation of an industrial standard (ECSS-q70-05a, European Cooperation for Space Standardization).

A new methodology based on surface enhanced Raman spectroscopy (SERS) for melamine detection, a toxic molecule frequently found in milk and dairy products, has been developed at INRIM in collaboration with a stakeholder, the Public Health Institute for Food Safety in Italy (Fig. 27). The low detection limit of the new methodology for melamine detection in milk matrix enables the implementation of European regulation at stakeholders.

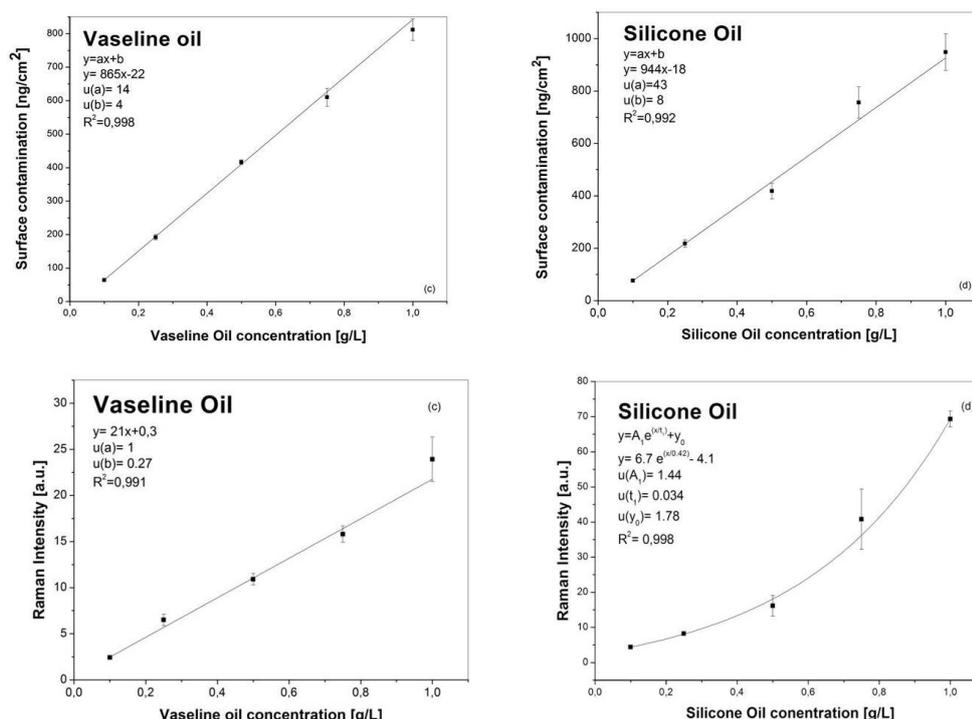


Fig. 26: Top: Calibration curve for FTIR analysis of surface contamination on industrial surfaces by Vaseline and silicone used as model contaminants. Bottom: Calibration curve for Raman analysis of surface contamination on industrial surfaces by the same model contaminants.

Food Contaminant Analysis based on Raman Spectroscopy and Gold Nanoparticles

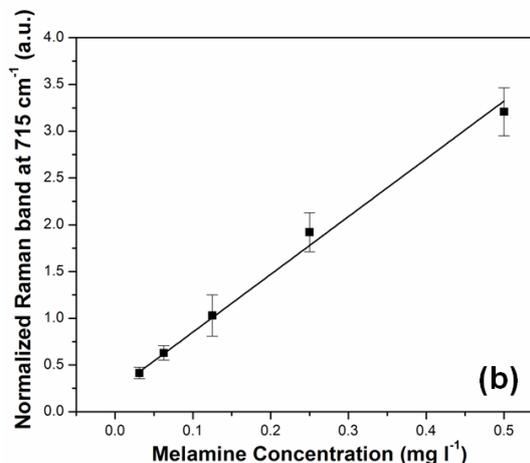
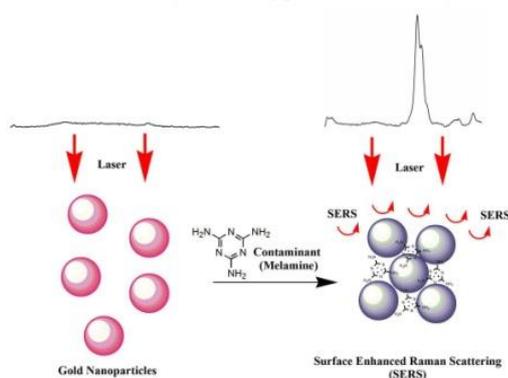


Fig. 27: Left: SERS methodology for the determination of melamine in milk. Right: Calibration curve for SERS analysis of melamine in milk.

Methodology aiming on a calibration of Contact Angle Spectroscopy (CAS) by XPS with consideration of effects of roughness has been developed at METAS and BAM together with collaborator Mettler Toledo. There is a high demand for measurable quality parameters based on CAS for industrial applications, for example the in-line process control of surface quality of electro polished and laser marked high precision weight standards. Options for a traceable correlation between contact angle and chemical surface composition (XPS) and roughness have been investigated using test samples from a production line for precision weights at collaborator Mettler-Toledo. The challenge is to minimize the surface altering in terms of roughness and chemistry but at the same time to achieve stable and machine-readable markings. The samples have been monitored by XPS, CAS, and white light interference microscopy (WLIM) at METAS and AFM and WLIM at BAM for individual steps of laser surface treatment and electro-polishing.

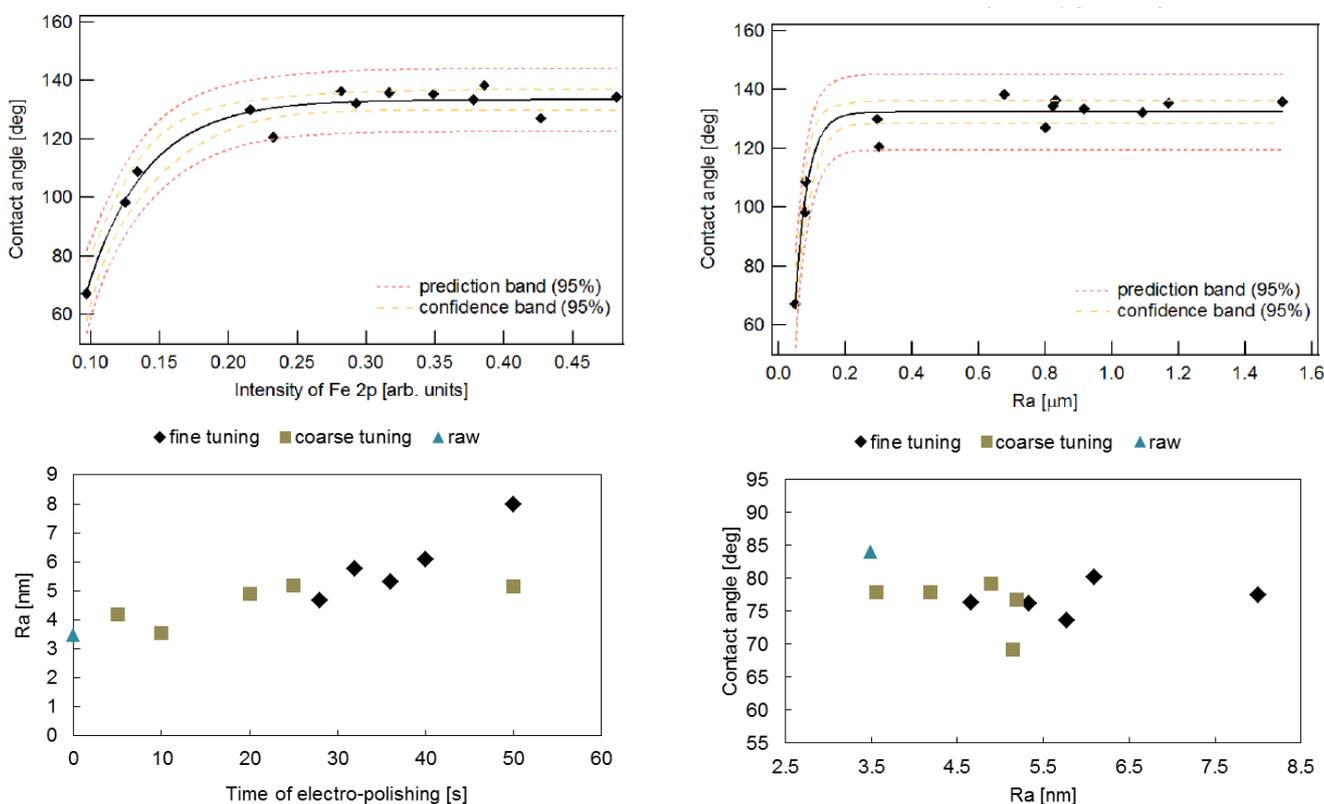


Fig. 28: Top left: Laser marked surface of high precision weight standard: Correlation of contact angle and XPS Fe 2p intensity. Top right: Correlation of contact angle and roughness for the same set of samples. Electropolished surface of high precision weight standard: Bottom left: Roughness vs. time of electro-polishing. Bottom right: Correlation of contact angle and roughness.

Fig. 28 summarizes essential results. For the laser marked surface of high precision weight standard the contact angle is a function of sub-μm scaled surface roughness up to $R_a = 300$ nm and can be also monitored by XPS using the amount of iron / iron oxides in the outermost surface layers measured. Calibration is enabled in this case. For electro-polishing the deep nm scaled roughness surprisingly increases vs. treatment time but the contact angle remains independent on R_a . Obviously the method of contact angle measurements is not sensitive enough for $R_a < 10$ nm (electro-polishing), but it can be used and calibrated by XPS and/or Profilometer measurements for $100 \text{ nm} < R_a < 400 \text{ nm}$ (laser marking). A problem was the corrugated surface obtained from surface finishing steps before applying electro-polishing. Measurement of nano roughness on corrugated surfaces seems to be a problem here which demands further investigation.

The basic metrology for repeatable and reproducible ambient mass spectrometry measurements using DESI (desorption electrospray ionisation) and PADI (plasma assisted desorption ionisation) which are emerging measurement technologies for ambient in-line application in a wider range of industries (e.g. food and pharmaceutical industry) has been addressed by NPL. The aim was to further develop the metrology of ambient mass spectrometry to meet the specific requirements for implementation in on-line monitoring by investigations of sensitivity and with repeatability and speed of measurement that match industry guidelines. NPL determined important metrology issues of sensitivity of ambient MS in order to specify the applicability of ambient MS for in-line monitoring. Stakeholders from the industry were invited to be introduced into the techniques and to deliver their samples which have been analyzed in order to figure out what molecules could be successfully analysed. The focus was on small molecules, contaminants and polymers and a better understanding on how minor components and matrix effects impact the sensitivity. It has been demonstrated that by changing the solvent composition the detection capabilities of DESI can be specifically enhanced by formation of adducts that could be easily identified.

For DESI (cf. Fig. 29) the VAMAS TWA2 Project A17 “Inter-laboratory study for desorption electrospray ionisation (DESI): intensity repeatability and constancy” has been organized by NPL with 21 participants measuring the absolute and relative repeatability and constancy for two samples, Rhodamine B (see Fig. 29) and adhesive tape. Results have been published in *Analytical Chemistry*, 2014, DOI 10.1021/ac502075t. The DESI average absolute intensity repeatability from the Rhodamine sample provided by 21 participants is 49%. It can be reduced to 12% by improvement of the protocol for measurement. The DESI average relative intensity repeatability from the adhesive tape samples provided by 20 participants is 10%. The DESI constancy of the relative intensity scale is 31%. The lack of reference samples for these new ambient mass spectrometric techniques is an important issue. NPL developed six reference sample candidates for that purpose. Results for a Rhodamine B reference show that very consistent craters may be generated and repeatabilities below 20 % may be achieved.

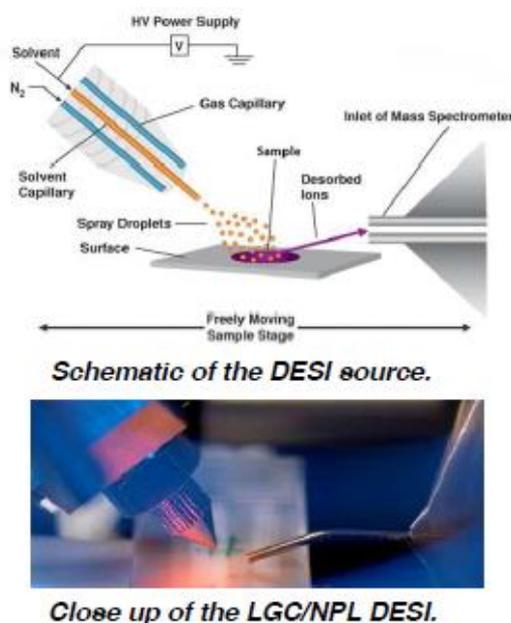


Fig. 29: DESY uses an electrospray source of highly charged aqueous spray droplets to gently desorb and ionise molecules from a sample surface. These molecules are transferred into a standard electrospray mass spectrometer through an ion transfer tube. The advantage of the technique is that it can be coupled to any mass spectrometry allowing for quantification, identification and MS/MS capability. The technique directly analyses a surface under ambient conditions.

Metrological methodologies for fast and in-line analytical methods based on optical spectroscopies, contact angle goniometry and ambient mass spectrometry were developed and validated for surface analysis in real time and in situ monitoring of industrial in-line process control during the project lifetime. The project addressed traceable optical spectroscopic methods (Fourier Transform Infrared (FTIR), Near Infrared (NIR)

and Raman), wettability testing methods and methods of atmospheric pressure secondary ion mass spectroscopy.

A number of collaborators from the industry and stakeholder institutions substantially participated in these activities. INRIM with optical spectroscopies and NPL with ambient mass spectrometry intensively collaborated using their specific methodologies to address the problem of organic contaminations of industrially relevant surfaces. METAS and BAM used complementary measurement methodology to address the calibration of Contact Angle Spectroscopy for in-line production control of surface finish of parts manufactured using different industrial technologies at a stakeholder company.

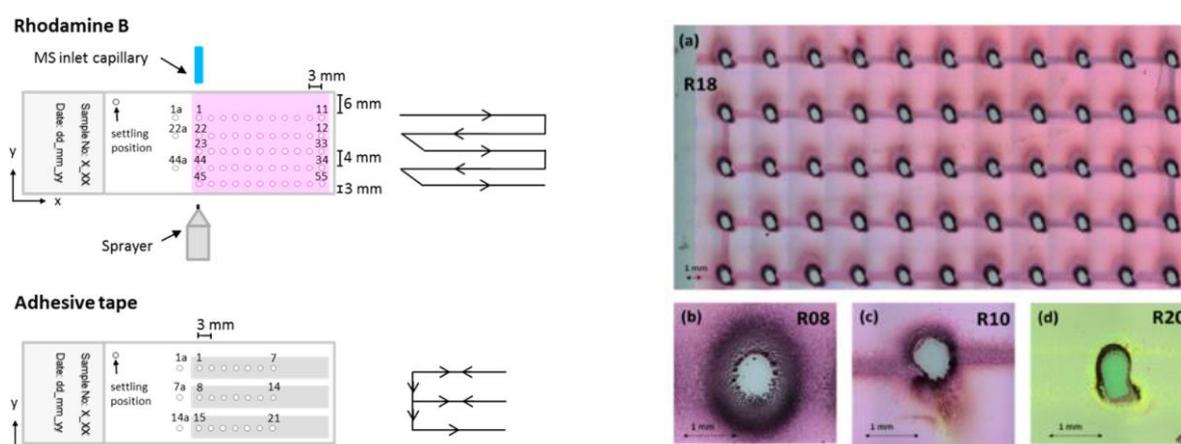


Fig. 30: Left: Schematic showing the top view of the analysis side of the reference samples: Rhodamine B and adhesive tape. The directions of the MS inlet capillary and the sprayer are indicated. The directions of analyses are specified by numbered spots and illustrated as a directional sequence. Right: DESI erosion spots on Rhodamine B samples, with high consistency and regularity in shapes and sizes.

New in situ characterisation techniques of catalytically active surfaces and supports

There are pretty new cutting-edge measurement techniques for real-time, geometrically localised characterisation of heterogeneous catalyst properties and activity such as Scanning probe microscopy, atomic force microscopy and Indirect Nanoplasmonic Sensing (INPS) on the horizon. The relationship between catalyst structure and activity is commonly poorly understood due to measurement barriers that preclude the determination of local surface behaviour under relevant reaction conditions. NPL, REG-Researchers hosted by partner Chalmers and collaborators as INSPLORION AB provided experiences and facilities for new approaches of in situ characterisation. In each case the goal was to address the major challenges associated with the widespread uptake of these techniques and ultimately present case studies demonstrating their application to characterizing relevant nanostructured surfaces.

One of the most advanced tools for in situ catalyst characterisation is the reactor scanning tunnelling microscope, which permits atomic scale topographical imaging under reactive atmospheres. However, whilst highly sophisticated, this instrumentation does not allow measurement of surface chemistry; instead chemical performance is simply measured on the bulk scale. Despite recent developments in high pressure electron microscopy, practical conditions of temperature, pressure and gas composition remain troublesome, and the approach is extremely demanding in terms of preparation and cost. Scanning probe microscopies (SPMs) offer a potential solution to the pressure-gap challenge, not least because of the ability to study samples under ambient conditions. Scanning force techniques such as atomic force microscopy (AFM) allow high-resolution topographical imaging of 2-dimensional surfaces and, with the development of novel probes, can permit the extraction of chemical information simultaneously. Two of the techniques that have been developed in this project share the common SPM approach, but are rather different in the chemical information yielded. Scanning Electrochemical Microscopy – Atomic Force Microscopy (SECM-AFM) is carried out in liquid media and relies on electrochemical detection of local reactants and products to determine catalytic activity. Proof of principle for SECM-AFM has been demonstrated by a number of academic research groups before, but the application of this new technique to catalysis had not been demonstrated before. Such liquid phase measurements have been developed at NPL to characterising

electro-catalytic processes in particular, and the primary objective of probe development was on hydrogen oxidation and oxygen reduction reactions in aqueous solutions on platinum nanoparticle catalysts. These systems are highly relevant to the fuel cell industry, wherein catalyst development and optimisation is a key challenge. Tip-Enhanced Raman Spectroscopy (TERS) can be carried out in the liquid or gas phase and gives spectroscopic information about surface chemistry, allowing the identification of surface-confined reactants, intermediates and products.

SECM-AFM is a powerful technique that enables simultaneous imaging of surface topography whilst mapping its electroactivity in an electrolyte solution with high spatial resolution. The most significant barrier to the widespread use of this technique is probe fabrication, which requires the challenging integration of an addressable nanoelectrode onto an AFM cantilever. A number of successful probe production approaches have been demonstrated but these have often not been scalable and as a result there are few commercial suppliers. In this task, new probes manufactured at stakeholder Nanoworld by a wafer-scale process were shown to generate very high quality SECM-AFM measurements. This was demonstrated by mapping the activity of patterned test substrates as well as the first application of this technique to imaging exfoliated graphene, a material of particular interest as a potential catalyst support. The latter study showcased the sub-nm height resolution of this technique by demonstrating the ability to resolve regions of single layer graphene whilst measuring interfacial activity. It was concluded that the interfacial activity of such surfaces can be strongly influenced by contaminants.

To run SECM-AFM for catalyst characterization NPL together with collaborators and stakeholders developed the necessary probes to allow local measurement of catalytic activity with nanoscale resolution. The development was successful as shown by performance tests (Fig. 31) and an application of new SECM-AFM probes for Faradaic current maps for imaging of exfoliated graphene and graphite surfaces in liquid media (Fig. 32) has been published (Andrew J. Wain et al., High-Resolution Electro-chemical and Topographical Imaging Using Batch-Fabricated Cantilever Probes, *Analytical Chemistry*, **2014**, DOI 10.1021/ac500946v). Performance test revealed for electrochemical resolution that needle probes out-perform pyramidal probes due to smaller electrode size, for topographical resolution to be similar for each probe, for image quality that pyramidal probes generally give higher quality images and for reliability that pyramidal probes much more reliable (>60% success), than needle probes (<30% success).

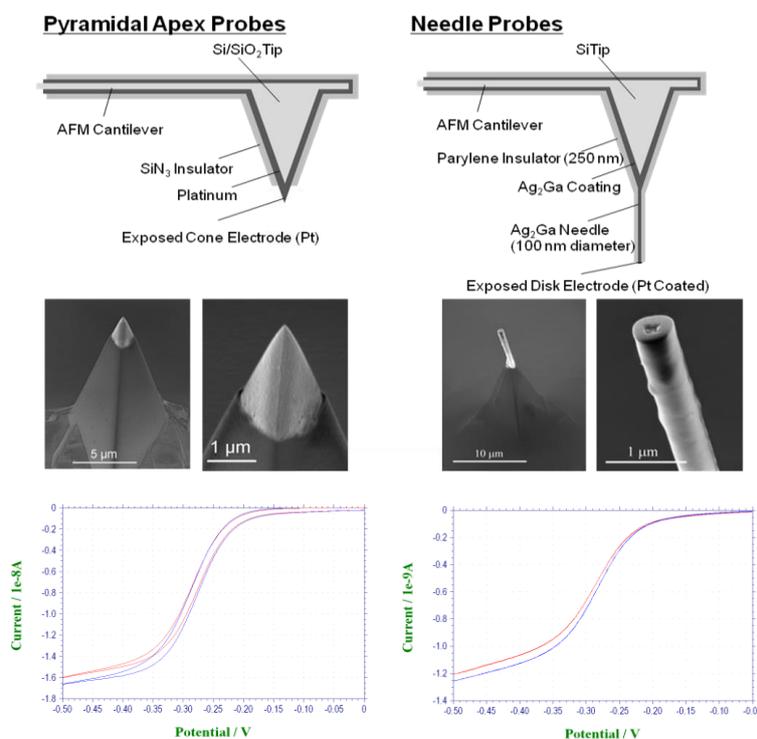


Fig. 31: New Pyramidal Apex Probes and Needle Probes for SECM-AFM measurements. Probe performance has been tested by cyclic voltammetry in 5mM Ru(NH₃)₆³⁺ solution (Ru^{3+/2+} redox couple) and Faradaic currents measured. It is ~ 10x higher for pyramidal vs needle probes.

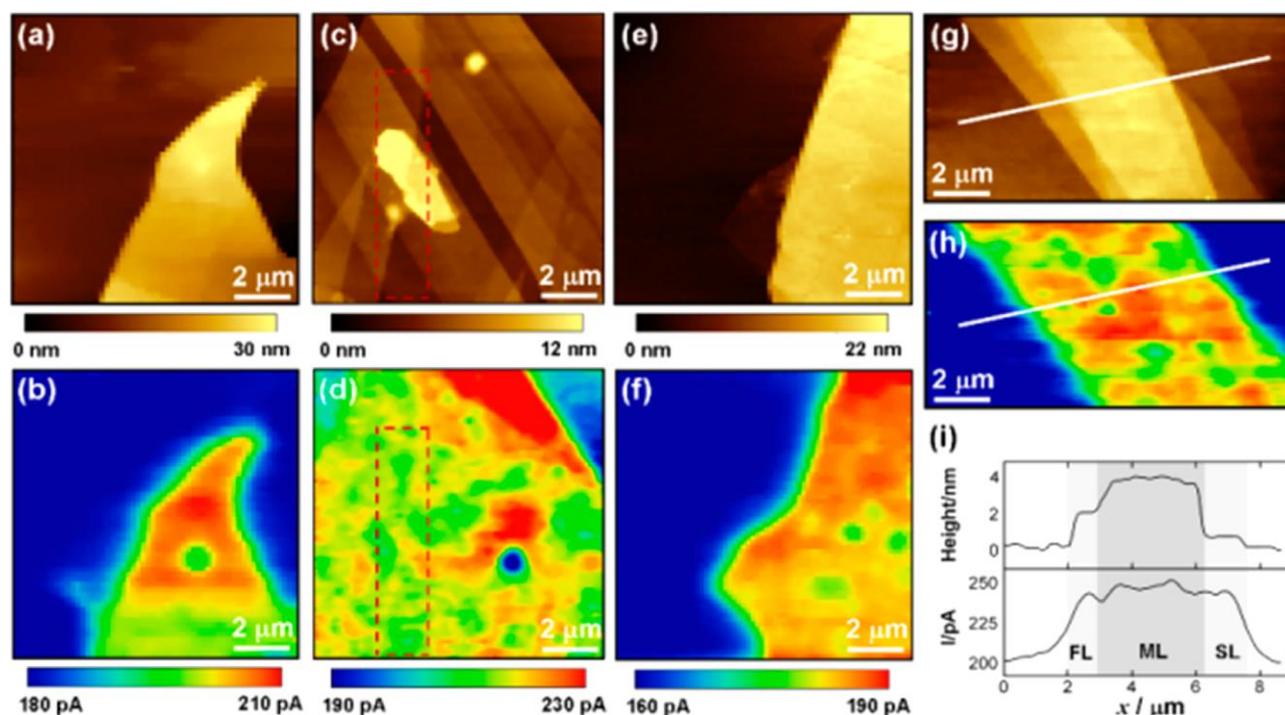


Fig. 32: Feedback mode SECM-AFM images of exfoliated graphene/graphite flakes immersed in 1 mM FcMeOH/0.1 M KNO₃ solution: Topography is shown in (a), (c), (e), and (g) and the corresponding electrochemical scans are depicted in (b), (d), (f), and (h), respectively. Line scan profiles for parts (g) and (h) are shown in (i) (shaded areas highlight regions of different graphene thickness: single-layer (SL), multilayer (ML), and few-layer (FL)). Tip bias 0.3 V vs Ag, line scan frequency 0.5 Hz, lift height 150 nm, bulk tip current typically ~200 pA.

TERS is a near-field spectroscopic approach to spatially resolved chemical mapping in which the plasmonic enhancement associated with a metal (e.g. silver) coated AFM probe is used to augment the localized spectroscopic signal, thus enabling measurements beyond the diffraction limit (Fig. 33). TERS has found a diverse range of applications but has only in a handful of cases been applied to catalytically active surfaces. Despite the well-recognized potential advantages, the application of TERS to mapping the spatial distribution of catalytic activity across a surface has yet to be realized. In this task, confocal Raman mapping of a TERS probe in contact with a polymer film containing mercaptoaniline indicated that the photooxidative coupling of this molecule to dimercaptoazobenzene (DMAB) can be catalyzed by silver at the point contact made by the tip apex. In this case, the silver on the tip is both enhancing the signal and behaving as a catalyst. In order to decouple these two properties and to enable genuine TERS mapping of a catalytic surface, alumina-coated TERS tips were employed. The alumina coating, deposited by atomic layer deposition, was sufficient to block the chemical activity of the underlying silver, without completely attenuating the localized signal enhancement. As a result, these probes enabled the high resolution (~20 nm) Raman mapping of a nanostructured silver surface, and indicated strong particle size dependence to the level of associated enhancement and reactivity. Confocal Raman mapping of an Ag TERS tip reveals catalytic reaction at the apex of the tip. Alumina coating of Ag TERS tip blocks chemical reactivity of tip without significant loss of Raman enhancement. A first demonstration of TERS mapping to distinguish between catalytically active and inactive regions of heterogeneous surfaces with 20 nm spatial resolution has been delivered (Fig. 34).

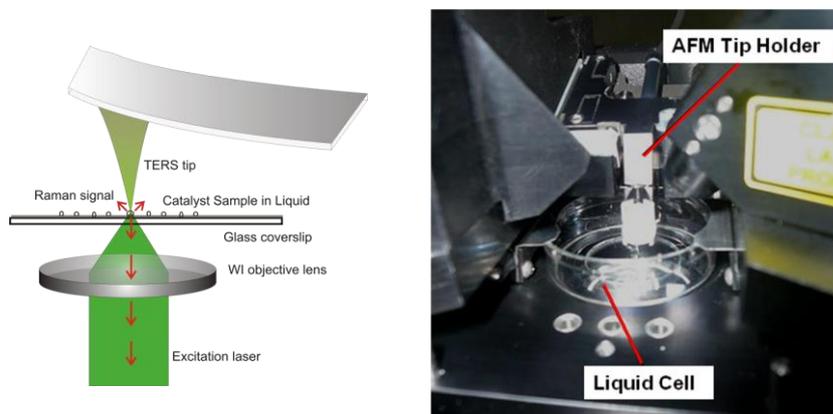


Fig. 33: Left, scheme of a TERS experiment and right experimental set-up established at NPL.

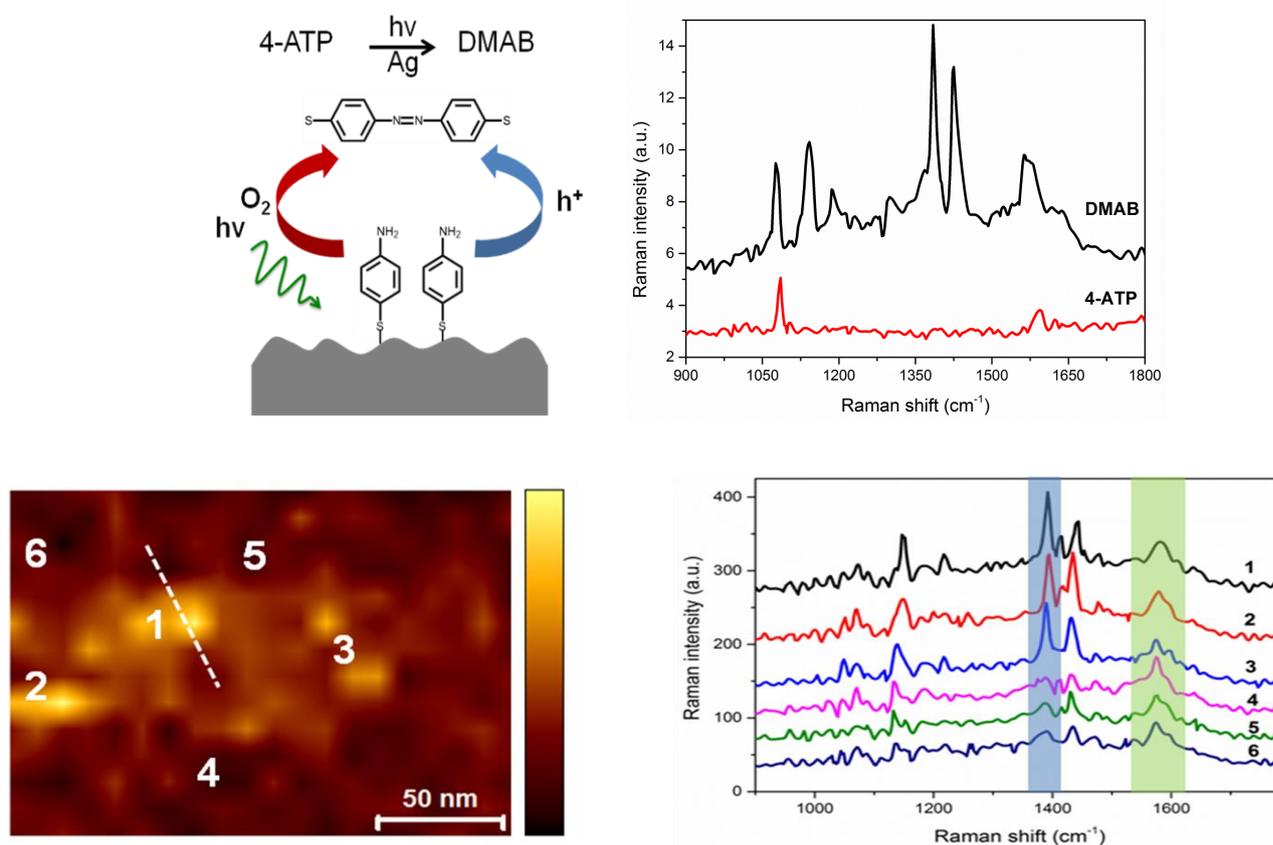


Fig. 34: Top left: Plasmon driven catalytic reaction of 4 aminothiophenol (4-ATP) oxidised to dimercaptoazobenzen (DMAB) in the presence of green laser light and 10 nm Ag nanoparticles deposited as a layer. Top right: Raman spectra of educt and product molecules. Bottom left: TERS map where the 1385 cm^{-1} peak intensity of the reaction product DMAB is used to acquire the Raman map suggesting single Ag nanoparticle resolution. Bottom right: TERS spectra taken from catalytically active and inactive surface sites at high lateral resolution, blue: DMAB peak, green: 4-ATP peak.

Another powerful technique that has received recent attention in the field of in situ catalyst characterisation, particularly from the perspective of 3-dimensional samples, is Indirect Nanoplasmonic Sensing (INPS). INPS is an optical technique developed by partner Chalmers and is based on the localised surface plasmon resonance phenomenon (Fig. 35). INPS has been used by REG researchers at Chalmers and collaborator

INSPLORION AB to probe reactions and processes occurring with catalytically active nanoparticles on relevant supports as silica and alumina and permits in-situ detection of sintering at the surface of a catalyst at real conditions, i.e. at temperatures exceeding 500 K and ambient pressure. Sintering is one of the most important processes resulting in a decay of catalytic activity and therefore a key issue for industrial application of catalysts in a wide range of industrial processes. The system selected to be studied by the REG researchers a model catalyst used to convert car exhaust gases but is also a relevant model for reforming catalysts used in the production of fuel by oil and gas industries.

The INPS technique is highly sensitive to morphological changes of nanoparticles, which can be utilised to obtain valuable information about the kinetics and mechanisms of catalytic reactions. In addition it is a very robust and remote sensing technique, requiring small analytical areas/volumes and is therefore highly compatible with realistic reaction conditions. The group at Chalmers has been supported by partner SP who delivered information on chemical changes on the catalyst surface as a result of processes leading to catalyst sintering. INPS sensor chips with SiO₂ washcoat layers were fabricated and tested reactive gas atmospheres in order to study sintering phenomena which lead, under practical conditions, to severe reduction or even breakdown of the activity of the catalyst. For reasons of stability SiO₂ washcoat layers were preferred over Al₂O₃ and TiO₂ ones. The experiments studied sintering of Pt nanoparticles at 600 °C in three simple gas atmospheres, O₂, NO₂ (see Fig. 36) and Ar, and in three complex gas environments, i.e. O₂ + NO₂, O₂ + NO and O₂ + H₂. The washcoat was found to be not stable in O₂ + NO₂ atmospheres as revealed by means of atomic force microscopy and X-ray photoelectron spectroscopy analysis performed at NPL. The optical response was calibrated by correlating it to the particles size of a nanocatalyst using a transmission electron microscope (TEM). This calibration allowed the determination of empirical equations relating the optical signal to the average diameter and based thereon, the characterization of decay of the dispersion of the active metal on model catalysts tested under real conditions.

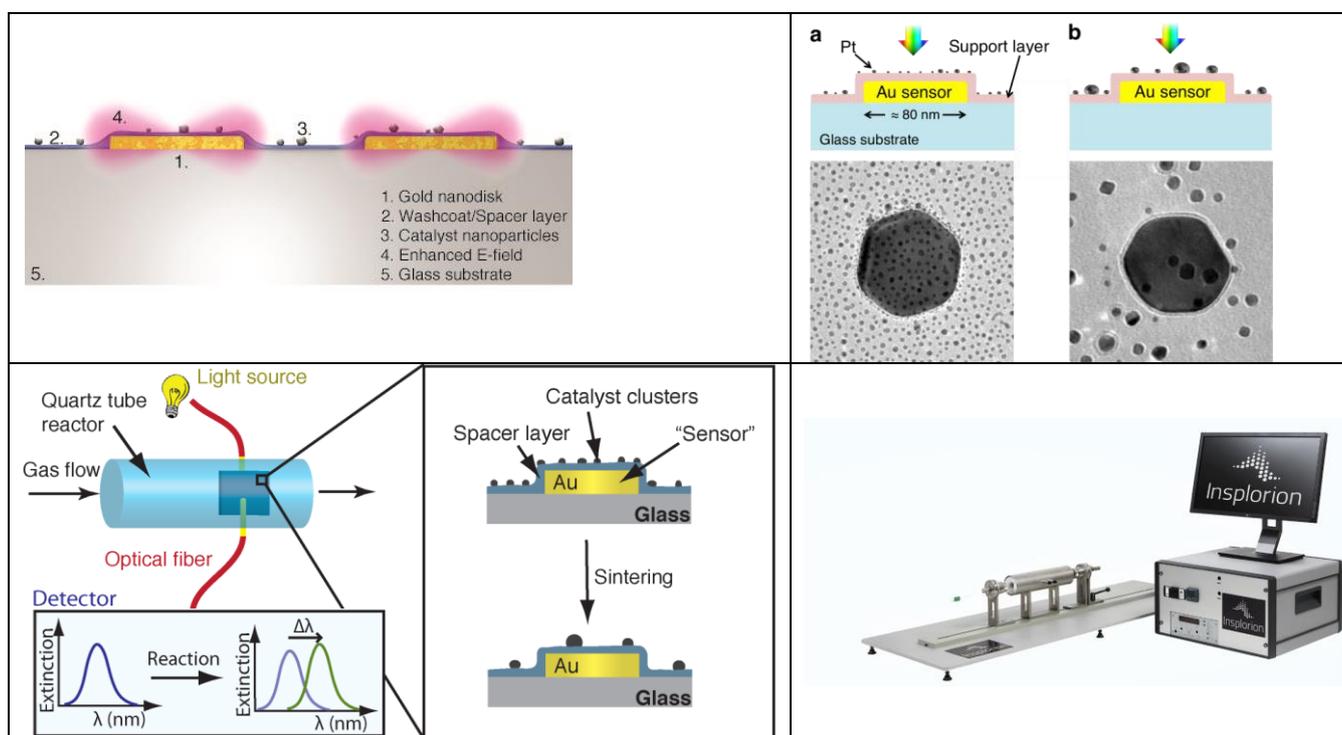


Fig. 35: Top left: An artist's view of the indirect nanoplasmonic sensing platform, which consists of plasmonic gold sensor nanodisks covered by a 10 nm thick support layer (e.g. silica), onto which the probed Pt catalyst nanoparticles are grown and exposed to reaction gas flow at elevated temperature used for sintering studies. Top right: INPS sensing platform before and after sintering visualized by TEM images Bottom left: Scheme of sintering studies where the primary measurand is the shift of wavelength $\Delta\lambda$ of the plasmon resonance which occurs when the size of the nano particles changes due to sintering in reactive gas atmosphere at elevated temperature. Bottom right: Commercial realization of the INPS platform by collaborator INSPLORION AB.

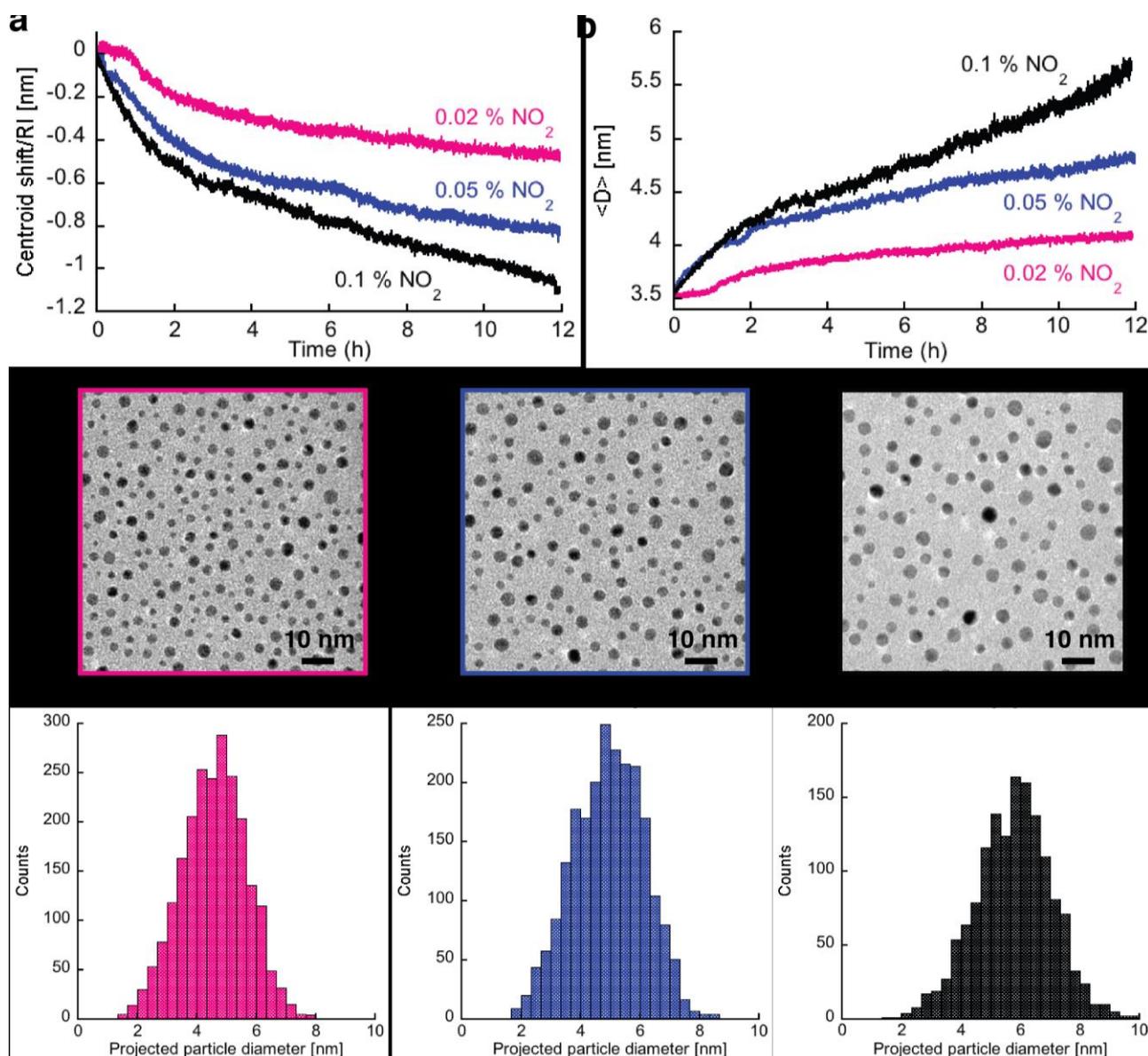


Fig. 36: Results of a successful sintering experiment with Pt nanoparticles on a silica support exposed to a reactive gas atmosphere 0.02, 0.05 and 0.1% NO₂, respectively, in Ar carrier gas at atmospheric pressure at 600 °C. Top left: INPS centroid shift signal for the sintering of Pt nanocatalyst particles. Top right: Corresponding sintering kinetics derived by fitting an empirical calibration function $\Delta\lambda = A + B\langle D \rangle$ to the initial (before sintering) and final (after experiment) mean particle diameter, $\langle D \rangle$, determined from post mortem TEM image analysis. Middle and Bottom: Post mortem TEM images of the Pt catalyst nanoparticles with corresponding histograms obtained after sintering in the three different NO₂ concentrations. Note the distinct NO₂ concentration dependence of the sintering rate and the correspondingly very different resulting mean particle diameters after 12 h of exposure.

By demonstrating the application of a variety of new advanced techniques to industrially relevant catalytic systems the first time, this research-oriented work will lead to the accelerated development of new, more efficient and more selective catalysts through a deeper understanding of the underlying surface chemistry. Validation of these new techniques has been achieved using industrially relevant model catalysts and



substrates. As a result of the exploratory nature of this work, outputs have been delivered in the form of presentations at conferences and peer-reviewed papers in highly ranked journals.

SPM related research was predominantly delivered by NPL, but with notable collaboration with the REG researcher hosted by Chalmers. Specifically, Chalmers provided well-characterized model test substrates for the development phases of both the SECM-AFM and TERS techniques. The substrate fabrication technique used was itself developed at Chalmers and so this was a particularly useful synergy. Collaborator Mantis also provided test substrates whilst stakeholder Nanoworld were instrumental to the success of the unique manufacture and provision of the SECM-AFM probes. REG researchers and collaborator INSPLORION developed the INPS sensing platform supported by partner Chalmers (preparation facilities, TEM images). NPL and SP supported the REG researchers by screening the INPS platforms using surface analysis, XPS and SIMS, before their use in the sintering experiments.

3 Actual and potential impact

Dissemination:

- The project generated 18 media articles in highly ranked peer reviewed scientific journals such as ACS Analytical Chemistry and its European counterpart, Analytical and Bioanalytical Chemistry.
- The project organized a special session on Metrology in Surface Chemical Analysis as part of the scientific program of the ECASIA13 conference which traditionally attracts many stakeholders from European industry.
- BAM hosted a training course on traceable EDS analysis for industrial stakeholders and a workshop on surface chemical analysis of organic surfaces with participation of external stakeholders.
- Partners BAM, NPL, SP and INRIM regularly attended meetings of the Surface Analyses Working Group at the International Meter Convention (2012-2014) and introduced results of the project.

Standards:

- During the project the partners participated in regular VAMAS TWA 2, ISO TC 201, 202 and 229 meetings (2012-2014) and introduced results of the project at these meetings.
- Partner BAM and collaborator Bruker Nano will contribute new knowledge on CRM based calibration and function control of EPMA using ED spectrometers to the upcoming regular update of ISO 15632:2012 *Microbeam analysis -- Selected instrumental performance parameters for the specification and checking of energy-dispersive X-ray spectrometers for use in electron probe microanalysis* under ISO TC 202.

To launch a formal standardization procedure such as a New Work Item Proposal that will lead to a new or improved standard, ISO technical committees issue Resolutions which specific technical requests. In addition they often formally request pre-normative technical work, in this area via the VAMAS infrastructure. Results of the project presented to TC 201 subcommittees have already led to such resolutions and related pre-normative inter-laboratory comparisons and will, ultimately, result in new ISO standards at a later date:

- ISO TC 201 SC7 “Electron spectroscopies” requested work on an industrial standard for identification and control of the field of view (FOV) of instruments using new 2D structured references developed by the project. ISO TC 201 SC7 further requested an inter-laboratory comparison to be launched under VAMAS TWA2 before drafting an ISO New Work Item Proposal.
- ISO TC 201 SC6 “Secondary ion mass spectrometry” requested work on an industrial standard for the use of static SIMS for organic depth profiling of mixed materials using metrologically underpinned methods and CRMs developed by the project. ISO TC 201 SC6 further requested an inter-laboratory comparison to be launched under VAMAS TWA2 before drafting an ISO New Work Item Proposal.
- ISO TC 201 SC6 “Secondary ion mass spectrometry” requested work on an industrial standard on the use of ambient mass spectrometry using new metrologically underpinned methods and NPL’s Rhodamine B reference sample. ISO TC 201 SC6 further requested an inter-laboratory comparison on *Desorption electrospray ionisation: intensity repeatability and constancy* to be launched under VAMAS TWA2 before drafting an ISO New Work Item Proposal.



Industry Impact:

- The CRMs, other reference materials and metrological procedures developed by the project were tested by interested European industrial partners and stakeholders including instrument manufacturers, calibration and testing laboratories and instrumentation users in a range of sectors (ION-TOF, SPECS, KRATOS, Focus, Scienion, Bruker Nano, TASCAN, Omicron NanoTechnology, Mettler-Toledo, Thermo Fisher Scientific, Thales Alenia Space, Insplorion, Ionoptika, 3M Germany). Companies delivered feedback on usability and appropriateness. The reference materials also received global attention from ULVAC-PHI and Panasonic (Japan).
- So far 15 of the CRM for ED spectrometer calibration have been sold to European companies, testing laboratories and universities (and one university from Canada).
- Partners PTB and BAM intend to commercialise the CRMs for the determination of field of view (FOV) of instruments. Stakeholders such as instrument makers and testing laboratories will use these materials for the specification and calibration of instruments for quantitative surface chemical analysis of structured samples, e.g., in the microelectronics, sensors and display industries.
- Layered organic CRMs delivered by partner NPL have received much interest from European and global industry for R&D and quality management of new organic displays, electronic devices and solar cells. In response to this NPL has started commercialisation activity.
- Methods of quantitative surface chemical analysis for industrial in-line quality control were developed and validated in collaboration with industrial stakeholders and accompanied by the preparation of organic reference films for the calibration of IR and Raman supporting the implementation of the standard ECSS-q70-05a (European Cooperation for Space Standardization) in the industry.
- The technology developed by the project to study nanoparticle sintering by INPS sensor chips in industrial applications is being commercialised by Insplorion AB. Insplorion expects substantial interest from the oil and gas industries.
- The new optical method for detection of melamine contamination in milk matrix has been implemented in food control covering the European legal limits published by Codex Alimentarius Commission.

Policy:

- Almost all European manufacturers of surface analytical instrumentation and private test laboratories offering services in surface analysis are Small and Medium Enterprises (SME) that cannot afford the financial and metrological infrastructure required for the development of specific CRMs, establishment of chains of traceability and pre-standardisation work. Therefore, by delivering reference materials and traceable methods, the project will directly impact European SMEs, who themselves deliver services to large European industries.
- Dissemination of the traceability concept to field laboratories through the metrology infrastructure put in place is a major outcome of the project. This will be achieved through certified reference materials enabling comparable measurement results delivered by test laboratories. The development of references for surface chemical analysis will contribute to the harmonization of measurement and documentary standards across borders, which is essential for confidence in international quality assurance, needed to facilitate global trade.

The uptake of project outputs will lead to environmental, financial and social impacts:

The environmental impact of this project comes from the development of a consistent metrological base for quantitative surface chemical analysis which supports innovation and will, on this route, promote the development of new sustainable industrial processes cleaner and more energy and material efficient thus avoiding environmental loads. One important example is the new analytical in situ methodology to study deactivation of supported metal catalysts developed by the project. These catalysts are used e.g. to convert car exhaust gases. So the project will have longer term impact on the reduction of air pollution by supporting the development of more stable and efficient exhaust catalysts. This will indirectly underpin Directive 1998/69/EC relating to measures to be taken against air pollution by emissions from motor vehicles.

The project's results will also enable cost reductions in industrial testing as the need for costly internal validations of specific analytical methods (for example for accreditation under ISO 17025) should no longer



exist because appropriate CRMs and written international standards are available now or in the near future. Furthermore, this project already delivered and will deliver reference materials and traceable methods having a direct impact on the future market strength of European SMEs, specifically the European instrument makers in the field of surface chemical analysis but also the testing laboratories who deliver services to the large European companies and the public. The shares of European instrument makers on the world market had been 45 % for AES, 60 % for XPS and 60 % for SIMS instruments with total sales of US\$195M in 2003. The output of the project will strengthen their competitiveness vs. players located in Asia and Northern America by added values of products as e.g. better daily performance control based on the project's CRMs for calibrations supported by standardisation initiated through project partners. Sales numbers and turnover at European instrument makers will be at least stabilised, most probably increased.

4 Website address and contact details

<http://www.emrp-surfchem.bam.de>

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The [SurfChem website](#) can be accessed by the public where the status of the project can be followed. A restricted area for partners has been embedded to share internal information about e.g. deliverables.

For further Information about the project please contact the project's coordinator Dr. Wolfgang E. S Unger (wolfgang.unger@bam.de).

The contact person for the development of EDS CRMs is Dr Vasile-Dan Hodoroba, BAM (Dan.Hodoroaba@bam.de).

The contact person for the development of reference samples to determine lateral resolution and the field of view of imaging instruments is Dr Ingo Busch, PTB (Ingo.Busch@ptb.de).

The contact person for the development of organic reference materials for surface analysis is Dr Alex Shard, NPL (Alex.Shard@npl.co.uk).

The contact person for the development of fluorescence markers for detection of organic functional groups is Dr Knut Rurack, BAM (Knut.Rurack@bam.de)

The contact person for the development of liposome markers for detection of bio molecules is Dr Peter Sjövall, SP (Peter.Sjovall@sp.se)

The contact person for the development of optical tools for in-line analysis is origin Dr Andrea Rossi, INRIM (Andrea.Rossi@inrim.it).

The contact person for the development of SPM techniques for in-situ analysis of catalyst activity is Dr Andy Wain, NPL (Andy.Wain@npl.co.uk).

The contact person for the INPS platform for in-situ analysis of catalysts is Prof Magnus Skoglundh, Chalmers Gotenburg (Magnus.Skoglundh@chalmers.se).



The contact persons for various traceable synchrotron based X-ray techniques are Dr Michael Krumrey and Dr Burkhard Beckhoff, both PTB (Michael.Krumrey@ptb.de), (Burkhard.Beckhoff@ptb.de).

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3. V.-D. Hodoroaba, M. Procop, V. Rackwitz, *Check and specification of the performance of EDS systems attached to the SEM by means of a new test material EDS-TM002 and an updated evaluation software package EDS spectrometer test - Version 3.4*, Microscopy and microanalysis **2013**, 19 1256-1257. DOI: 10.1017/S1431927613008271.
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7. G. Shard, S. J. Spencer, S. A. Smith, R. Havelund, I. S. Gilmore, *The Matrix Effect in Organic Secondary Ion Mass Spectrometry*, International Journal of Mass Spectrometry **2015**, 377, 599-609, DOI: 10.1016/j.ijms.2014.06.027
8. V. D. Hodoroaba, M. Krumrey, V. Rackwitz, *New Reference and Test Materials as well as Procedures for Checking the Performance of an Energy Dispersive X-Ray Spectrometer (EDS) at a Scanning Electron Microscope (SEM)*, Analytical and Bioanalytical Chemistry **2015** 407 3045-3053, DOI: 10.1007/s00216-014-8242-5
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