# High-Throughput Structure/Function Screening of Materials and Catalysts with Multiple Spectroscopic Techniques

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**Abstract.** High throughput screening methodologies are expanded to synchrotron based x-ray absorption techniques. An environmental chamber, based on ultra-high vacuum equipment, has been developed allowing *in situ* studies on arrays of samples while X-ray absorption fine structure spectroscopy, Raman spectroscopy, mass spectrometry and/or X-ray diffraction can be applied simultaneously to characterize the system under process conditions in a time-resolved manner. The chamber accommodates a diverse range of samples from surface science to materials chemistry to heterogeneous catalysis. Data acquisition and data logging software is developed to handle large quantities of divers but related information. New data logging, processing and analysis procedures and programs are developed which will allow fast structure-function relationships characterization.

**Keywords:** high throughput; combined characterization techniques; instrument development; software development; XAFS; in situ, e-science.

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# **INTRODUCTION**

Combinatorial or high throughput (HTP) screening is growing rapidly in its application to optimize the composition of materials to obtain specific physical or chemical properties. X-ray diffraction methods (XRD) are now well-established for HTP characterization of crystalline bulk phases. In comparison, HTP X-ray absorption fine structure (XAFS) spectroscopy is a virtually unexplored technique. XAFS does not require long-range order and provides detailed electronic and structural information on disorded and amorphous phases, species in solution, nanostructures and thin films, all important in the materials chemistry and catalysis. XAFS is readily applied in situ and with high time-resolutions, providing opportunities for a wide range of HTP applications. The high intensity and small beam size on 3<sup>rd</sup> generation synchrotron sources, such as the ESRF (Grenoble, France) and Diamond (Chilton, UK), allow very rapid data acquisition and sample/reactor miniaturization, which are well matched to microscale HTP screening. With suitable ancillary techniques, both the structure and the function of a wide range of systems can thus be dynamically monitored under process conditions.

An environmental chamber for HTP studies has been developed, based on ultra-high vacuum (UHV) equipment, allowing XAFS and a range of further characterization techniques to be applied *in situ* and with time-resolution. New software for the acquisition and logging of the large quantities of data is being developed. In combination with new data processing techniques, which are (partially) automated, fast structure-function correlations can be derived.

# **UHV/ENVIRONMENTAL CHAMBER**

An experimental chamber is developed based on standard CF-flanged UHV equipment and allows simultaneous XAFS (in either transmission or fluorescence detection mode), Raman spectroscopy, mass spectrometry (MS) and/or XRD experiments. A picture of the chamber is shown in Figure 1, the numbers (1-5) as mentioned in the text below correspond to the different positions on/in the chamber. The chamber is constructed in complete mirror image to allow X-rays from both sides and simultaneously allow all other techniques from different sides (i.e. interchangeable) to make the chamber suitable for a wide range of beamlines and synchrotrons. All flanges are positioned such that they all direct to the same focal point, thus allowing simultaneous experiments on small samples and/or the same spot on a sample.

XAFS can be performed in either transmission (1) or fluorescence (2) detection mode. The XAFS (Be) transmission windows are of a long rectangular shape to allow simultaneous XRD. A Raman probe will be introduced *via* a water-cooled re-entrance flange with sapphire window (3) to achieve the proper working distance (21 mm) while keeping the probe isolated from the gas atmosphere and high temperatures. The Raman probe is mounted on a tripod, *i.e.* an (x,y,z)-positioning system, to allow accurate focusing of the laser onto the sample or sample area under investigation.

The different sample array devices are mounted onto the manipulator (Figure 2), ensuring a high positional and orientational accuracy. A load loack (5) at the top of the chamber allows their introduction in the chamber. Subsequently, the arrays are transferred to the bottom part of the chamber where *in situ* characterization takes place.

The arrays are confined in a holder that leads the required wiring through the manipulator out of the chamber. The wiring enables heating of the samples onto the arrays either *via* individual heaters associated with individual sample spots (in the so-called hot plate arrays [1], *vide infra*) or by applying a temperature gradient across the array. Temperatures up to ~700°C will be feasible. The arrays can be measured in atmospheres from ~10<sup>-8</sup> to ~1.5 bar of a selected gas, using a gas handling system including vacuum stop, manifolds, gauges, regulators, mass flow controllers etc.

Several viewports (on flanges and load locks) as well as a camera mounted onto the Raman probe permit observation of the arrays and accurate X-ray and Raman alignment.



**FIGURE 1.** UHV/environmental chamber, the numbers denoted are described in the text.



FIGURE 2. Positional and orientational manipulator.

### SOFTWARE DEVELOPMENT

The HTP approach, especially when coupled to combinatorial experimentation, produces large quantities of diverse but related information from a number of physically distinct sources. Appropriate escience protocols including data acquisition [2] and logging software are currently data under development. The HTP experiments are integrated with Grid-based computational and in-silico investigation. The software will enable the definition and tracking of samples (arrays and individual samples) within a laboratory, including logging of experiments carried out on the sample, and access to sample status information as well as metadata. This will be integrated with a results data service. The escience system also adds the capability to delegate access to sample and experiment metadata and result data.

Data analysis methods will be critical to the efficient completion of this research. While simple packages exist for the "batch" analysis of powder diffraction data, no similar software exists for EXAFS data. Currently, different HTP programs are under development: XMULT [3a] allows the automatic XAFS background subtraction for large numbers of spectra (arrays), using procedures derived from PAXAS [3b]. A modified version of P [3c,d] allows the simultaneous EXAFS/XRD analysis for multiple spectra simultaneously. These data processing and analysis developments will allow fast determination of structure-function correlations.

## PRELIMINARY RESULTS

A physical vapor deposition (PVD) system has been developed for the HTP preparation of thin film materials [4] and of supported metal nano-particles with controlled diameters that can be varied across a substrate surface [4b]. The obtained sample arrays are ideal for (catalytic) surface reaction studies in which metal particle sizes are an important parameter in the kinetics and mechanisms of reactions.

In a preliminary *ex situ* measurement performed at the ESRF Grenoble, ID26, it was confirmed that excellent EXAFS data can be obtained for the Au nanoparticle thin film samples supported on reduced TiO<sub>2</sub>. Moreover, the metal gradient over the array is nicely reflected in the Au  $L_3$  edge step, see Figure 3.



**FIGURE 3.** Raw XAS data obtained on a HTP thin film array, across the metal gradient deposited using PVD method.

The PVD method can be principally applied on any wafer material. Using masking techniques during the

deposition method, a large number of individual samples can be created. SiN wafers (of 35 x 35 mm total size) have been developed which contain 7x7 individual heaters (1 x 1 mm in size) consisting of Pt wire [1]. Applying the PVD method on these types of arrays creates individually addressable systems. More arrays manufactured from for example BN (to allow XRD studies) and consisting of multiple sample wells are under development. These well arrays will allow the use of robotic methodologies like Inkjet procedures to deposit for example sol-gel materials.

#### DISCUSSION AND CONCLUSIONS

An UHV/environmental chamber has been developed allowing the study of multiple samples with a range of characterization techniques including XAFS under process conditions and in a time-resolved manner. Preliminary results show that HTP studies are feasible for these microscale samples using the high intensity and beam focusing optics at 3<sup>rd</sup> generation synchrotron sources. Development in software for data logging, processing and analysis will allow rapid structure-function relationships to be derived. This HTP system will in the future be positioned as a user facility at the Diamond Light Source.

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