Beyond SIMS
Room Great Lakes B - Session BS+FM+SS-TuA2

Cells and Tissue III

Moderators: Peter Sjövall, RISE Research Institutes of Sweden, **Michael J. Taylor**, Pacific Northwest National Laboratory

4:00pm **BS+FM+SS-TuA2-13 Nanoprojectile-SIMS in the Event-by-Event Bombardment-Detection Mode***, M. Eller,* California State University, Northridge*; S. Verkhoturov, D. Verkhoturov,* ***Emile A. Schweikert*****,** Texas A&M University

This sims technique differs from the usual approach in three ways: the nature of the bombarding ion, the mode of bombardment and that of data acquisition/processing. Bombardment is with nanoprojectiles, NP, i.e. gold nanoparticles (Au_{400}^{4+}, n/q=100; Au_{2800}^{8+}, n/q=350). A single NP impact causes emission from surface spots of 10-20 nm in diameter and up to 10 nm in depth. Bombardment-SI detection is done in the event-by-event mode, i.e. SIs form a single NP impact are detected via time-of-flight and recorded separately.The process is repeated at a rate of 1 kHz. Bombardment is stochastic over a surface of 100 to 250 µm in diameter and typically lasts for a few thousand s, amounting to testing 1 to 5% of the surface exposed to bombardment.The result is a listing of a few M mass spectra. Assuming that all impacts are equivalent the data set can be examined for correlations. Indeed, the SIs from one impact arise from collocated molecules. They reveal homogeneity at the nanoscale, which translates into the ability to identify rare defects. The approach outlined here is also uniquely suitedfor characterizing isolated nano-objects of dimensions a small as a few tens of nm. Direct or grazing impacts can readily be sorted based on the characteristics of the SIs. Results reported here have been obtained with a custom-built instrument featuring a gold liquid metal ion source and a 100 kV acceleration stage. As indicated, SI detection is via ToF either in the customary reflection mode or in transmission where specimens are deposited on a 1-2L graphene support. "Decision limit" detection is in the attomol range. The SI output is 5-10 times enhanced in the transmission mode. We show on molecular assemblies, polymer blends and membranes the ability to test molecular alignments, homogeneity and to identify defects occurring at the level of one in 10^4 to 10^5 nanospots. For nano-objects with large surface to volume ratios we demonstrate assays on individual items, the ability to count objects, as well as distinguishing functionalities and loading on asymmetric particles. On dimensions below 20 nm, non equivalency of impacts prevails, yet it is still possible to distinguish organic modifiers on a nano-object from ejecta arising from the substrate. In summary, nanoprojectile-sims has the ability to identify rare defects in synthesized films or biological membranes and is uniquely suited for molecular assays on individual nano-objects.

4:20pm **BS+FM+SS-TuA2-15 2D/3D Ion Imaging Methods using CAMECA Dynamic SIMS Instruments***,* ***Laura Créon****, S. Choi, P. Peres, S. Miwa, J. Ren, R. Liu,* CAMECA, France

Ion imaging using dynamic SIMS is one important technique for materials characterization. To perform surface imaging within a sample, the spatial position of each secondary ion must be mapped to the sample surface. Two ion imaging methods are available in CAMECA IMS 7f-Auto magnetic sector instruments: the ion *microscope* mode where spatial resolution is determined by stigmatic ion optics, and the ion *microprobe* (or scanning) mode, based on primary beam rastering across the surface, where spatial resolution is determined by the primary beam size.

The ion microscopemode allows for high sputtering rates and direct imaging using high beam current, but the instrumental transmission must be reduced and a dedicated 2D detector is required.

For the scanning ion mode, images are acquired on a standard Electron Multiplier (EM) detector with high flexibility for the image field of view (few µm^2 up to 500x500 µm^2), independently of the mass resolving power. On the IMS 7f-Auto, a lateral resolution down to sub-µm can be achieved using this mode.

It is possible to obtain 3D volume reconstruction as well as retrospective depth profiling from 2D ion image stacks recorded sequentially while sputtering in-depth.

For pure scanning probe mode, as a small beam size is required, the beam current and sputter rate are low thus limiting the achievable eroded depth within typical analysis duration.

For optimized 3D imaging capabilities in scanning mode, IMS 7f-Auto data acquisition software includes a "Sputtering between cycles" option which allows high current beam sputtering between consecutive imaging cycles. This enables 3D imaging of deep areas while keeping reasonable analysis duration.

Another method for 3D imaging consists in combining the microscope mode with scanning mode ("scanning microscope" mode), using high current primary beam and EM detector, which has advantages for the detection of atmospheric gas elements.

Different analytical protocols for 3D imaging will be described and data for different applications will be presented.

4:40pm **BS+FM+SS-TuA2-17 High-Resolution Peak Analysis in TOF SIMS: Resolving Satellite Peaks and sub-Peak Structures***,* ***Amy Walker****, L. Gelb,* University of Texas at Dallas

We present progress in the quantitative extraction of chemical information from imaging TOF SIMS data using advanced statistical methods. The detectors used in many TOF SIMS instruments undercount ions due to saturation effects; if two or more ions arrive within a very short interval (the "dead time") only the first to arrive is recorded. This changes both the total number of ions collected and their statistical distribution.We introduce a new maximum-likelihood analysis thatincorporates the detector behavior in the likelihood function, such that a parametric spectrum model can be fit directly to as-measured data. In numerical testing, this approach is shown to be the most precise and lowest-bias option when compared with both weighted and unweighted least-squares fitting of data corrected for dead-time effects. We apply the maximum-likelihood method to fit two experimental data sets: a positive-ion spectrum from amultilayer MoS_2 sample and a positive-ion spectrum from a TiZrNi bulk metallic glasss ample. The precision of extracted isotope masses and relative abundances obtained is close to the best-case predictions from the numerical simulations despite the use of inexact peak shape functions and other approximations.

We then determine the degree to which sub-peak structure at a single unit mass can be resolved. Synthetic data are generated with multiple overlapping peaks of different intensities and separations. The data quality (number of counts) required to reliably distinguish the two-peak structure from a single peak is determined as a function of these parameters.These results are then analyzed in order to establish limits on when sub-peak resolution can reasonably be attempted.

5:00pm **BS+FM+SS-TuA2-19 Innovative Approach to Safeguard Saffron Authenticity Using TOF-SIMS and Multivariate Analysis***,* ***Alice Bejjani****, O. el Ayoubi,* Lebanese Atomic Energy Commission, National Council for Scientific Research, Lebanon*; E. de Angelis, R. Pilolli, L. Monaci,* Institute of Science of Food Production, National Research Council of Italy

Saffron is a highly appreciated spice known for its aroma, color, flavor and for also its medical benefits. Therefore, it is used in food preparation, dye production and in herbal and pharmaceutical formulations. Due to the high costs and labor required for plantation and production, saffron is considered one of the most expensive products across the world and is consequently commonly adulterated. Saffron adulterations include the addition of less expensive agricultural products or synthetic components with similar color and morphology. It has been demonstrated that safflower petals and turmeric powders which are among the most frequent adulterants in saffron cannot be detected, up to 20% (w/w), by the ISO normative [1]. This work aimed to develop a rapid and sensitive method based on the Time of flight secondary ion Mass Spectrometry to discriminate between authentic and adulterated saffron with either Safflower or Turmeric at 5, 10 and 20 % (w/w). Mass spectral signatures of pure saffron, safflower and turmeric powders were acquired for the first time. Samples of adulterated saffron with safflower were easily identified via the presence of safflower unique fragments. Supervised principal component analysis was needed to differentiate between the different types of samples. The source of variations between the samples was determined and discussed.

[1] Sabatino, L.; Scordino, M.; Gargano, M.; Belligno, A.; Traulo, P.; Gagliano, G. HPLC/PDA/ESIMS evaluation of saffron (Crocus sativus L.) adulteration. Nat. Prod. Commun. 2011, 6, 1873–1876.

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