Applied Surface Science
Room 101B - Session AS+SS-WeM

Applications where Surface Analysis is Your Only Hope

Moderators: Jeffrey Fenton, Medtronic, Svitlana Pylypenko, Colorado School of Mines

8:00am **AS+SS-WeM1 Accurate Ion Beam Analysis of Electrolytes via Rutherford Backscattering (RBS) and Positive Ion X-ray Emission (PIXE) of Uniform Thin Solid film of Blood congealed via HemaDrop™**, ***Yash Pershad**, N.X. Herbots,* SiO2 NanoTech LLC*; C.F. Watson,* SiO2 NanoTech LLC/Arizona State University Physics Dpt*; EJ. Culbertson,* University of California at Los Angeles

Medical diagnostics needs new methods of blood analysis using mL of blood rather than the standard 7 mL to improve care. Theranos has been recently challenged about their “finger-stick method,” where blood drops are used for complete blood diagnostics, not just glucose. They only approved by the FDA for qualitative detection, rather than accurate blood composition. Motivated by these accuracy issues, along with the great need for diagnostics from microliters of blood, we use MeV Rutherford Backscattering Spectrometry (RBS) to measure elemental composition (H, C,N, O, K, Mg, Ca, Na, Fe) in microliters of blood congealed into smooth, planar, Homogeneous Thin Solid Films (HTSF). These planar HTSF of blood are prepared with a new technology that congeal blood drops, called HemaDrop™ [1, 2] Measurements on HTSF prepared via HemaDrop™ are compared and found much more reproducible and accurate than those taken for comparison on dried blood drops, such as the so called “Dried Dlood Spot (DBS)” that can only be used in microvolume sampling for drug metabolism, not blood composition. HTSF prepared with HemaDrop™ yields reproducible elemental composition regardless of substrate used or area of analysis with < 6% sampling error. Ion damage from RBS is accounted for via the 0-dose intercept damage curve method, which graphs RBS yield of elements detected, as a function of analysis dose, using several sequential cumulative spectra. Positive Ion X-ray Emission (PIXE) is used to verify the reproducibility and accuracy of RBS. RBS and PIXE analysis on HTSF prepared with HemaDropTM using 6 microliter of blood are found in excellent agreement within the 6% sampling error. Thus, HemaDropTM successfully creates homogeneous thin solids film from blood that can be analyzed in vacuum and can also be used for Infrared (IR) spectroscopy and Tapping Mode Atomic Force Microscopy for molecular identification and counting. HTSF enable for the first time blood analysis via vacuum-based methods. IR and TMFAM are also being investigated to add molecular identification and counting.

[1] US Patent Pending, Assignee: SiO2 NanoTech, Inventors: Herbots, N, Watson CF, Krishnan A, Pershad Y, et al (2016)

[2] Electrolytes Detection by Ion Beam Analysis, in Continuous Glucose Sensors and in Microliters of Blood using a Homogeneous Thin Solid Film of Blood, HemaDrop™. Yash Pershad, Ashley A. Mascareno, Makoyi R. Watson, Alex L. Brimhall, Nicole Herbots, Clarizza F. Watson, Abijith Krishnan, Nithin Kannan, Mark W. Mangus, Robert J. Culbertson, B. J. Wilkens, E. J. Culbertson, T. Cappello-Lee, R.A. Neglia Submitted to MRS Advances, April 2016

8:20am **AS+SS-WeM2 Surface Analysis As a Valuable Tool to Study Chemistry of Metals in Environmental Problems**, ***Kateryna Artyushkova**,* University of New Mexico*; J. Blake,* New Mexico Water Science Center*; L. Rodriguez-Freire, S,. Avasarala, A. Ali, A. Brearley, E. Peterson, J.M. Cerrato,* University of New Mexico

This talk will present application of X-ray Photoelectron Spectroscopy to understand the role of chemistry of metals in several environmental problems. In the first study, the chemical interactions of U and co-occurring metals in abandoned mine wastes in a Native American community in northeastern Arizona were investigated using spectroscopy, microscopy and aqueous chemistry. Elevated concentrations of metals are of concern due to human exposure pathways and exposure of livestock currently ingesting water in the area. This study contributes to understanding the occurrence and mobility of metals in communities located close to abandoned mine waste sites. Elevated U (6,614 mg/kg), V (15,814 mg/kg), and As (40 mg/kg) concentrations were detected in mine waste solids. The power of XPS in specific identification of the chemical states of these elements as U (VI), As (-I and III) and Fe (II, III) will be presented.

In the second study, the goal is to investigate the effect of metals associated with wildfire ash from wood collected from the Valles Caldera National Preserve, Jemez Mountains, New Mexico on water chemistry. Metals and other constituents associated with wildfire ash can be transported by storm event runoff and negatively affect water quality in streams and rivers. Microscopy and spectroscopy analyses were conducted to determine the chemical composition of ash. Metal-bearing carbonate and oxide phases were detected through X-ray spectroscopy analyses.

Finally, we integrated spectroscopy, microscopy, diffraction, and water chemistry to investigate the presence of metals in water and sediment samples collected 13 days after the Gold King Mine spill (occurred on August 5, 2015). Spectroscopy, microscopy, and XRD analyses suggest that Pb, Cu, and Zn are associated with metal-bearing jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$) and other minerals (e.g. clays, Fe-oxides and oxyhydroxides) identified in sediments from Cement Creek, CO. The presence of sulfates and phosphates, Fe as 75% Fe^{2+} and 25% Fe^{3+}, and 100% Pb^{2+} in the near surface region of these sediments was detectedby XPS analyses.

Additionally, phosphates and nitrogen species were found with XPS in the sediments from Farmington, NM, downstream the Animas River. The interaction of these metal-bearing minerals with biogeochemical processes occurring downstream could cause metal mobilization into the water.

8:40am **AS+SS-WeM3 Surface Analysis Techniques – Hope Springs Eternal**, ***John Newman**, S.R. Bryan, D.M. Carr, G.L. Fisher, J.S. Hammond, J.E. Mann,* Physical Electronics USA*; T. Miyayama,* ULVAC-PHI, Japan*; J.F. Moulder, D. Paul,* Physical Electronics USA*; R. Inoue,* ULVAC-PHI, Japan*; B. Schmidt,* Physical Electronics USA **INVITED**

In today’s technologically advanced laboratories there are many dozens of different, and very specialized, analytical techniques being used to attempt to solve problems and characterize materials. When choosing the proper technique for a particular application, the needs of the study are matched to the attributes of a particular method – its depth of analysis, detection sensitivity, analytical spot size, type of information provided, and whether or not the technique is appropriate for the sample in question. For applications where the region of interest is measured in atomic layers, surface sensitive methods such as Auger Electron Spectroscopy, X-ray Photoelectron Spectroscopy, and Time-of-Flight Secondary Ion Mass Spectrometry have always been the methods of choice and, in most cases, really the only hope for a successful analysis.

However, when we look at the relatively recent technological advances in these three methods, we find that their increased capabilities expand their usefulness to much more than the traditional types of surface experiments. For example, gas cluster beams now allow for intact organic information to be obtained from depth profiles or cross-sectioned samples; higher energy x-ray beams allow for deeper analysis depths compared to traditional XPS x-ray beams; and tandem mass spectrometry technology can provide unambiguous peak identification in TOF-SIMS. This presentation will look at applications where some of these advancements are used; exemplifying how newer technologies are making these techniques our only hope for a much wider array of studies.

9:20am **AS+SS-WeM5 What Came First? The Black Ink or the Black Ink? That Is the Question**, ***Robyn E. Goacher**, L.G. DiFonzo, K.C. Lesko,* Niagara University

Determining the order of deposition of ink markings in questioned documents (forgeries) is an important forensic task. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has received attention as a possible technique for this purpose because it is a surface sensitive technique that can provide chemical images, potentially resolving the top ink from the bottom ink. Furthermore, static SIMS imaging is non-destructive, which is important for the preservation of unique evidence. Prior work demonstrated that ToF-SIMS can correctly determine deposition order of intersections between inks of dissimilar colors[1], and that the order of deposition between fingerprints and ink can be elucidated if the fingerprint is on top of the ink[2]. In order to further test the abilities and robustness of the method, intersections between similar inks need to be examined. In this study, three different black ink samples were tested (Bic^{TM}, Papermate^{TM}, and Staples^{TM} brand pens). Preliminary work produced inconsistent results, and indicated that a more thorough analysis of the primary ions striking the sample and of the polarity of the secondary ions collected needed to be done. Therefore, chemical images of the ink intersections were collected using $Ar\text{-}_{1000}{}^{+}$, $Bi_3{}^{+}$, and $Bi_3{}^{2+}$ primary ions, with both positive and negative secondary ion spectra. Data were analyzed using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR). Data analysis included consideration of regions of interest as well as full image analysis, with and without restrictions to the secondary ion mass range. The results point to issues regarding incorrect apparent order of deposition, potentially based on the interactions of inks of different types. This brings the forensic use of ToF-SIMS for determining the order of deposition in ink forgeries into question, and points to the need for further research on factors that can result in incorrect apparent deposition orders.

1. A. He, D. Karpuzov and S. Xu, "Ink identification by time-of-flight secondary ion mass spectrometry", *Surface and Interface Analysis,* **2006**, 38 (4), 854-858.

2. N.J. Bright, R.P. Webb, S. Bleay, S. Hinder, N. Ward, J.F. Watts, K.J. Kirby and M.J. Bailey. "Determination of the Deposition Order of Overlapping Latent Fingerprints and Inks Using Secondary Ion Mass Spectrometry", *Analytical Chemistry*, **2012**, 84, 4083-4087.

9:40am **AS+SS-WeM6 ToF-SIMS Analysis of Aerospace Topcoat Degradation***, **Taraneh Bozorgzad Moghim**, M.L. Abel, J.F. Watts,* University of Surrey, UK

Aircraft coatings are subjected to a multitude of environments during their service life time, including high humidity, extreme temperatures and solar radiation. The major source of degradation derives from ultra-violet (UV) radiation. With commercial aircrafts flying at altitudes between 9 and 13 km, their exposure to UV radiation and ozone significantly increases. Therefore photooxidation of an aircraft topcoat must be understood in order to monitor topcoat degradation. The main laboratory technique used to establish the degradation phenomena from UV radiation is through QUV chambers, however the effect of ozone is not considered in this method. The novelty of the approach used here, is in the use of a desktop cleaner, intended for SEM sample preparation, as the exposure method. This combines the effects of UV and ozone. The topcoat was subject to UV/ozone exposure for varying durations and analysed using time of flight-secondary ion mass spectrometry (ToF-SIMS).

The detail provided by ToF-SIMS is vital in understanding the degradation phenomena and enables a degradation mechanism to be established. ToF-SIMS produces a significant amount of data and therefore when combined with principal component analysis (PCA) a more detailed analysis of the data can be obtained. The main changes observed are the rise of inorganic components with exposure time, as the polymer resin decomposes and the inorganic pigments of the coating are exposed. However this does not describe the degradation of the organic components. Therefore by filtering out the inorganic contributions in the PCA, the changes to the organic components could be isolated and observed. This allows the positive identification of cluster ions of the reactants from the resin and those from the reaction products. In this manner it was possible to deduce the degradation mechanism.

11:00am **AS+SS-WeM10 Surface And Bulk: Are They Always The Same? X-Ray Photoelectron Spectroscopy Study***, **Tatyana Bendikov**, D. Barats-Damatov, B. Butschke, J. Bauer, J. Pellegrino Morono, T. Zell, R. Neumann, D. Milstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique (top 10-15 nm) with sensitivity down to single atomic layer. XPS provides unique information about elemental composition and on the chemical and electronic state of the element in the material. The importance of XPS analysis is essential when the top surface and bulk of the material are different in chemical composition and, consequently, in their properties.

We present here two systems where XPS analysis shows significant differences in elemental composition of the top surface, compared to bulk material characterized by various analytical techniques, such as X-ray crystallography, NMR, EPR, Raman and infrared (IR) spectroscopies, etc.

In the first system, influence of temperature on the crystal packing and secondary structure of phosphovanadomolybdic acid, $H_5PV_2Mo_{10}O_{40}$ was studied.[1] After high temperatures treatment (400-600°C) XPS analysis reveals enrichment of the top surface of the $H_5PV_2Mo_{10}O_{40}$ by amorphous vanadate/phosphate layer.

In the second system, series of iron-PNN complexes were synthesized and characterized in terms of their stability, elemental composition and metal center oxidation state.[2-3] Using example of two complexes, $[(t\mathrm{BuPNN})\mathrm{Fe(NO)_2}]^+[\mathrm{BF_4}]^-$ and $[(t\mathrm{BuPNN})\mathrm{Fe(NO)}\text{-}_2]^{2+}2[\mathrm{BF_4}]^-$, PNN= 2-[(Di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine, it is shown by XPS study that NO ligands are not stable and easily escape from the complex. This reveals changes in structure and in paramagnetic/diamagnetic behavior of these complexes.

1. Barats-Damatov D., Shimon L.J., Feldman I., Bendikov T., Neumann R. *Inorg. Chem.***2015**, *54*, 628-634.

2. Zell T., Milko P., Fillman K.L., Diskin-Posner Y., Bendikov T., Iron M.A., Leitus G., Ben-David Y., Neidig M.L., Milstein D. *Chem. Eur. J.***2014**, *20*, 4403-4413.

3. Butschke B., Fillman K.L., Bendikov T., Shimon L.J., Diskin-Posner Y, Leitus G., Gorelsky S.I., Neidig M.L., Milstein D. *Inorg. Chem.***2015**, *54*, 4909-4926.

11:20am **AS+SS-WeM11 *In Situ* Chemical Imaging of Biointerfaces Using Microfluidics and Molecular Imaging***, **Xiao-Ying Yu**,* Pacific Northwest National Laboratory

The surfaces of aqueous phases and films have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS). SALVI was recently applied to investigate biomolecules and biological interfaces in living biofilms and single mammalian cells. Specifically, a variety of hydrated protein thin films were studied, providing the first *in situ* observation of interfacial water or biological water. In the single cell study, ion transport through the ion channel in the cell membrane was mapped in wet cells. In our most recent biofilm research, characteristic fragments of the extracellular polymeric substance (EPS) were obtained for the first time, including proteins, polysaccharides, lipids, polymers, and distinct biomarkers. These species are useful to track the metabolic and electron transfer processes in the microbial communities. For example, biomarkers characteristic of quorum sensing as a result of biofilm response to environmental stressors such as $Cr_2O_7^{2-}$ exposure and subsequent dispersion of the biofilm can be observed using this novel approach. Correlative imaging was employed to achieve a more holistic view of complexed biological systems across different space scales. In addition, electron transfer mechanisms of living biofilms as the electrode material are being studied using the electrochemical version of our microfluidic reactor. Our results demonstrate that interfacial chemistry involving important biomolecules and biological systems can be studied from the bottom up all based on microfluidics. Our transferrable microfluidic reactor sets the analytical foundation toward chemical imaging of complex phenomena occurring in multiple time and length scales, or the mesoscale, underpinning chemical changes at the molecular level in the condensed phase.

11:40am **AS+SS-WeM12 Capturing the Transient Species at the Electrode-Electrolyte Interface by SALVI and Liquid ToF-SIMS***, **Jiachao Yu**, Y. Zhou, X. Hua,* Pacific Northwest National Laboratory*; S. Liu,* Southeast University, China*; Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

In situ time-resolved identification of interfacial transient reaction species were captured using imaging mass spectrometry, leading to the discovery of unexpected and more complex elementary electrode reactions and providing unprecedented understanding of the reaction mechanism on the electrode surface and solid-electrolyte interface using dynamic molecular imaging. This unique approach was enabled by a vacuum compatible electrochemical microfluidic reactor, namely System for Analysis at the Liquid Vacuum Interface (SALVI). The chemical mechanism of iodine oxidation at the electrode surface was revisited using simultaneous cyclic voltammetry (CV) and dynamic ToF-SIMS. Our dynamic ionic and molecular imaging results suggested that more complex surface reactions exist concerning the gold adlayer formation on the electrode surface, providing the discovery of more short-lived transient species and new insights of elementary electrode reactions unknown in the textbook. Such findings further illustrated the importance of truly observing electron transfer reactions in real-time with high spatial chemical mapping. This innovated approach is suitable for fundamental kinetic studies in electrochemistry at the solid-liquid (s-l) interface or the solid-electrolyte interface with many potential applications such as energy storage, material conversion, and electrocatalysis. The ability to capture and elucidate complex reaction mechanisms at the dynamic s-l interface opens a new door to control, mitigate, design, and engineer reactive pathways toward predictive material synthesis, efficient energy storage, and favorable catalytic conversion.

12:00pm **AS+SS-WeM13 Energy Storage Materials – Investigating the Surface***, **Jonathan Counsell**, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Limited

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed to also increase the energy storage density. Lithium phosphorus oxynitride (LiPON) has become the most commonly used solid electrolyte thin-film in energy storage devices. Obviously due to the widespread use of this material there is significant interest in understanding the characteristics and properties with a view towards optimisation.

Here we apply XPS and UPS to explore both the surface and bulk properties of several LixPOyNz surfaces prepared via atomic layer deposition ALD [1]. The distribution of elements below the surface is explored via ion and angular-resolved depth profiling methods. This technique has been used extensively across a broad range of applications however the damage caused by impinging ions on the structure of the analysis material has always been a concern for the analyst. More recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic oxides. Herein we discuss how, with the use of Ar250-3000+ ions, where the energy per atom can be 2.5-40 eV, it is possible to obtain more accurate information regarding the true nature of the LiPON thin-film. A comparison is made with conventional monatomic depth profiles in particular the differences in stoichiometry obtained with the two ion sources. Ion implantation is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions. We will demonstrate how the analyst can now confidently depth profile through inorganic metal oxide thin-films without the worry of reduction or preferential sputtering.

[1] Alexander C. Kozen, Alexander J. Pearse, Chuan-Fu Lin, Malachi Noked, Gary W. Rubloff, DOI: 10.1021/acs.chemmater.5b01654

Author Index

Bold page numbers indicate presenter

— A —
Abel, M.L.: AS+SS-WeM6, 2
Ali, A.: AS+SS-WeM2, 1
Artyushkova, K.: AS+SS-WeM2, **1**
Avasarala, S,.: AS+SS-WeM2, 1
— B —
Barats-Damatov, D.: AS+SS-WeM10, 2
Bauer, J.: AS+SS-WeM10, 2
Bendikov, T.: AS+SS-WeM10, **2**
Blake, J.: AS+SS-WeM2, 1
Blomfield, C.J.: AS+SS-WeM13, 2
Bozorgzad Moghim, T.: AS+SS-WeM6, **2**
Brearley, A.: AS+SS-WeM2, 1
Bryan, S.R.: AS+SS-WeM3, 1
Butschke, B.: AS+SS-WeM10, 2
— C —
Carr, D.M.: AS+SS-WeM3, 1
Cerrato, J.M.: AS+SS-WeM2, 1
Coultas, S.J.: AS+SS-WeM13, 2
Counsell, J.D.P.: AS+SS-WeM13, **2**
Culbertson, EJ.: AS+SS-WeM1, 1
— D —
DiFonzo, L.G.: AS+SS-WeM5, 1
— F —
Fisher, G.L.: AS+SS-WeM3, 1
— G —
Goacher, R.E.: AS+SS-WeM5, **1**
— H —
Hammond, J.S.: AS+SS-WeM3, 1
Herbots, N.X.: AS+SS-WeM1, 1
Hua, X.: AS+SS-WeM12, 2
— I —
Inoue, R.: AS+SS-WeM3, 1
— L —
Lesko, K.C.: AS+SS-WeM5, 1
Liu, S.: AS+SS-WeM12, 2
— M —
Mann, J.E.: AS+SS-WeM3, 1
Milstein, D.: AS+SS-WeM10, 2
Miyayama, T.: AS+SS-WeM3, 1
Moffitt, C.: AS+SS-WeM13, 2
Moulder, J.F.: AS+SS-WeM3, 1
— N —
Neumann, R.: AS+SS-WeM10, 2
Newman, J.: AS+SS-WeM3, **1**
— P —
Paul, D.: AS+SS-WeM3, 1
Pellegrino Morono, J.: AS+SS-WeM10, 2
Pershad, Y.W.: AS+SS-WeM1, **1**
Peterson, E.: AS+SS-WeM2, 1
— R —
Rodriguez-Freire, L.: AS+SS-WeM2, 1
— S —
Schmidt, B.: AS+SS-WeM3, 1
— W —
Watson, C.F.: AS+SS-WeM1, 1
Watts, J.F.: AS+SS-WeM6, 2
— Y —
Yu, J.: AS+SS-WeM12, **2**
Yu, X.-Y.: AS+SS-WeM11, **2**; AS+SS-WeM12, 2
— Z —
Zell, T.: AS+SS-WeM10, 2
Zhou, Y.: AS+SS-WeM12, 2
Zhu, Z.: AS+SS-WeM12, 2