

**Meeting of the**

# **European Working Group for Glow Discharge Spectroscopy**

## **EW-GDS**

**Kingston University  
Kingston Hill Campus  
Kingston Hill  
Kingston upon Thames  
Surrey  
KT2 7LB  
United Kingdom**

**3<sup>rd</sup> - 4<sup>th</sup> September 2012**

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Meeting Organising Committee: Edward Steers (London Metropolitan University), Volker Hoffmann (IFW Dresden, Chairman EW-GDS), Cornel Venzago, Petr Smid (AQura GmbH, Hanau), Peter Robinson (MassCare Ltd, UK)

### Acknowledgements:

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- Horiba Jobin Yvon, Longjumeau, France
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- Mass Spectrometer Instruments. Ltd, Dewsbury, U.K.
- Nu Instruments, Wrexham, U.K.
- Spectruma Analytik GmbH, Hof, Germany
- Thermo Fisher Scientific (Bremen) GmbH, Bremen, Germany

We also acknowledge the sponsorship of the conference dinner by Nu Instruments, Wrexham, and the general sponsorship of the meeting by Evans Analytical Group, Syracuse, USA, which has provided support for the travel and attendance costs of some of the delegates.

# 1 Introduction

The Steering Committee of the European Working Group for Glow Discharge Spectroscopy wishes to welcome you to Kingston, UK for our latest meeting. We hope that the meeting will be beneficial to you whether you are using Glow Discharge as a production tool, in a research environment or if you manufacture Glow Discharge equipment. We certainly hope that your enthusiasm will help drive the development of this fascinating field, where currently there are many major instrumental developments.

The European Working Group on Glow Discharge Spectrometry (EW-GDS) was started at a meeting in Paris in 1992 as an informal “club” of those interested in depth profiling by Glow Discharge Optical Emission Spectrometry (GD-OES). It held its 2<sup>nd</sup> meeting as a post-symposium following the 1993 York Colloquium Spectroscopicum Internationale (CSI), and its scope was then widened to include bulk analysis, GD Mass Spectrometry (GD-MS) and discharge processes relevant to analytical GD Spectrometry (GDS). It held unfunded meetings at one or two year intervals, linked to major relevant international conferences. In 1997, an application for a 3 year Thematic Network (GDSNet) under the EC Measurement and Testing was successful. GDSNet ran for three years (1999-2002), had 17 partners and 18 associate partners. The main aim of the Network was to develop a more integrated approach to GDS throughout Europe. Funding was provided for general and specialist meetings, and a small amount for such activities as “round-robin” testing, but no funding was available for research personnel. During this period, EW-GDS did not conduct any separate activities.

Following the end of GDSNet, EW-GDS resumed its role of providing informal collaboration on analytical GDS activities in Europe. Following two unsuccessful attempts to establish a GD Research Training Network (RTN), it was agreed at the EW-GDS meeting following the Winter Plasma Spectrochemistry conference in Budapest in 2005 that EMPA, Thun, Switzerland, would coordinate a further proposal for an EC Marie-Curie RTN. On this occasion, it was a two stage procedure lasting almost two years, but we were successful and “GLADNET” started in January 2007, involving 16 partners. Within this Network, ten 3-year ESR (postgrad) posts and 4 ER (postdoctoral) posts were funded, and the Network led to an intensive research effort, 6-monthly training courses/ meetings of all partners and a significant drawing together of the European GD community. The 4-year Network ended in January 2011, and the EW-GDS resumed its informal coordinating role. Unsuccessful attempts were made to establish new Initial Training Networks (ITN – the successor to RTN, with somewhat more restrictive rules), in response to the 2009 and 2010 calls for proposals. The feasibility of submitting a further proposal will be discussed on Wednesday 5<sup>th</sup> September, see later.

The Payling Prize, sponsored by all GD instrument manufacturers, will be awarded for the best presentation (oral or poster), preference being given to younger scientists.

This document is intended to help you get the most from this brief meeting. Inside you will find a full list of attendees along with their contact details. There is also a detailed meeting programme and the abstracts of all oral and poster presentations.

On Wednesday 5<sup>th</sup> September, EW-GDS members will be discussing possible future collaborative projects, particularly those involving EC funding. Two schemes are of particular interest, Initial Training Networks (ITN) - - a call for proposals is already open, with a submission deadline of 22<sup>nd</sup> November - - and Industry/ Academia Partnerships and Pathways (IAPP) – a call for proposals will be made on 2<sup>nd</sup> October with a deadline of 15<sup>th</sup> January 2013. If you are interested in this discussion and have not already been invited, please contact the EW-GDS chairman, Dr Volker Hoffmann ([V.Hoffmann@ifw-dresden.de](mailto:V.Hoffmann@ifw-dresden.de))

## 2 Timetable for Meeting

|  |  |
|--|--|
| <b>Sunday 2<sup>nd</sup> September</b> |  |
| 19:00                                  | <b>Centenary Room:</b> Thermo User Dinner – Invitation Only      |
| 18:30-20:30                            | <b>Foodstore:</b> Hot Buffet Dinner – Must be ordered in Advance |

|  |  |   |
|--|--|---|
| <b>Monday 3<sup>rd</sup> September</b> |  |   |
| 7.30-8:30                              | <b>Centenary Room:</b> Breakfast   |   |
| 9.00                                   | <b>KHBS239</b> Thermo-Fisher Element GD Users' Meeting.<br>Attendance by invitation from Thermo-Fisher   | <b>KHBS 238</b> Check Presentations<br><b>ATRIUM</b> Set up Posters   |
| 11.00-11.30                            | <b>KHBS238</b> Refreshments -  | <b>ATRIUM</b> Refreshments  |
|  | <b>KHBS239</b> Thermo-Fisher Element GD Users' Meeting. (Contd)  | <b>KHBS 238</b> Check Presentations<br><b>ATRIUM</b> Set up Posters   |
| 13.00                                  | <b>ATRIUM</b> Sandwich Lunch   |   |
| 14.00                                  | <b>KHBS 026</b> Welcome and introduction V. Hoffmann   | <b>KHBS238</b><br>available for individual discussions; <b>KHBS239</b><br>available to check presentations. |
| 14.15                                  | <b>KHBS 026 Chair: V. Hoffmann</b><br><b>O 1 E. Steers.</b> Selective excitation in analytical glow discharges – an overview                                   |   |
| 14.40                                  | <b>O2 J. Whitby.</b> An Overview of Recent Glow Discharge Work at Empa   |   |
| 15.05                                  | <b>O3 V. Efimova.</b> Glow discharge as a tool for the preparation of samples for electron microscopy measurements   |   |
| 15.30                                  | Introduction to Posters  |   |
| 15.55                                  | <b>ATRIUM</b> Refreshments/ Posters  |   |
| 16.20                                  | <b>KHBSO26 Chair: R Pereiro</b><br><b>O4 D. Barnhart.</b> The Evaluation and Characterization of Alternative Gases using Iron and Titanium Reference Materials |   |
| 16.45                                  | <b>O5 C. Modanese.</b> Challenges in GDMS analyses of PV silicon materials.  |   |
| 17.10                                  | <b>O6 P. Vega.</b> Magnetically boosted radiofrequency glow discharge optical emission spectroscopy.   |   |
| 17.35                                  | <b>O7 G. Churchill.</b> Characteristics of the New Low-Flow Flat Geometry Glow Discharge Cells for the Nu Astrum GDMS Instruments                              |   |
| 19.00                                  | <b>Centenary Room:</b> Conference Dinner   |   |

| <b>Tuesday 4<sup>th</sup> September</b> |  |
|---|--|
| 7.30-8:30                               | <b>Centenary Room:</b> Breakfast -   |
| 9.00                                    | <b>KHBSO26</b> Assemble./announcements<br><b>Manufacturers' Presentations/ Chair: C. Venzago</b>   |
| 9.10                                    | <b>M1</b> MSI. E.Patel   |
| 9.35                                    | <b>M2</b> Nu Instruments. S. Guilfoyle   |
| 10.00                                   | <b>M3</b> Spectruma Analytik. M. Analytis  |
| 10.25                                   | <b>M4</b> Horiba Jobin-Yvon. P. Chapon   |
| 10.50                                   | <b>ATRIUM</b> Refreshments/ Posters  |
| 11.20                                   | <b>KHBSO26 Manufacturers' Presentations (contd)/</b><br><b>M5</b> LECO. K. Marshall  |
| 11.45                                   | <b>M6</b> Thermo-Fisher. J. Hinrichs   |
| 12.10                                   | <b>KHBSO26 Chair:P. Smid</b><br><b>O8 F. Liggins.</b> New and Improved Atomic line data for Astrophysical Applications                                       |
| 12.35                                   | <b>O9 M. Voronov.</b> Formation of electrical prepeak in pulsed glow discharge via gas heating   |
| 13.00                                   | <b>ATRIUM</b> Lunch (finger buffet)  |
| 14.10                                   | <b>KHBSO26 Chair: J. Whitby</b><br><b>010 Qian Rong.</b> Glow Discharge Mass Spectrometry Studies on Some Nephrite Materials                                 |
| 14.35                                   | <b>O11 A. Bengtson.</b> Effect of Pulsing on Hydrogen Analysis with GD-OES   |
| 15.00                                   | <b>O12 M. Kasik.</b> Sputter Rates in GDMS   |
| 15.25                                   | <b>013 Z. Weiss.</b> The GLADNET Catalogue of Glow Discharge Spectra: Part 1 finished !  |
| 15.50                                   | <b>ATRIUM</b> Refreshments/ Posters  |
| 16.15                                   | <b>KHBSO26 Chair J. Whitby</b><br><b>014 R. Pereiro.</b> rf Pulsed Glow Discharge - Time of Flight Mass Spectrometry: Investigation of the Ion Source Design |
| 16.40                                   | <b>O15 V. Hoffmann.</b> Imaging of the Glow Discharge Plasma   |
|   |  |
| 17.10                                   | EW-GDS admin. Meeting followed by the Award of the Payling Prize.  |
| 18.00                                   | Close of meeting   |

KHBS239 available for individual discussions; KHBS238 available to check presnetations.

### **3 Abstracts**

The following pages show the abstracts for the meeting presentations, organised in chronological order of presentation. Abstracts for the posters are shown at the end of the section.

## Selective excitation in analytical glow discharges – an overview

Edward B.M. Steers

*London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK e-mail  
e.steers@londonmet.ac.uk*

Glow discharges are not in thermal equilibrium, so excitation conditions cannot be described in terms of a temperature or temperatures. The populations of the various excited and ionised species depend on the individual excitation processes involved:

**Electronic excitation (EE) and ionisation (EI):** these depend on the electron energy distribution function (EEDF) and the optical excitation function (OEF) of the energy level involved. In most cases EE of atomic levels is from the ground state or a metastable state, whereas EE of ions is mostly from the atomic ground state. This is a non-selective mechanism, but since the OEF varies for different energy levels, changes in the EEDF cause changes in the relative intensity of lines.

### Collisions with metastable atoms – Penning Ionisation (PI) and Penning Excitation (PE)

**PI:**  $A_o + B_m \Rightarrow A_o^+ + B_o + e + \Delta E$  or  $A_o + B_m \Rightarrow A^{*+} + B_o + e + \Delta E$ ,

**PE:**  $A_o + B_m \Rightarrow A^* + B_o + \Delta E$

where A & B are atoms of two different elements, <sub>o</sub> signifies the ground state, <sub>m</sub> a metastable state, <sup>+</sup> an ionised atom, \* an excited state and  $\Delta E$  the surplus energy.

Provided the metastable state has sufficient energy, PI is a non-selective process i.e. a wide range of positive values of  $\Delta E$  is possible; on the other hand, PE is selective (resonant).  $\Delta E$  must be small, requiring a close energy match.

### Collisions with ions – charge transfer

**Symmetric Charge Transfer:**  $A^+ + A \Rightarrow A + A^+$

**Asymmetric Charge Transfer (ACT):**  $A^+ + B \Rightarrow A + B^{*+} + \Delta E$

No additional particle is produced, so  $\Delta E$  must be small, +ve or -ve, i.e. a resonant process. ACT becomes more important as the discharge current increases.

Energy levels can also be populated in two other ways :

**Collisions with high energy ions and atoms** – high energies ~500 eV are required, so this process is restricted to the cathode glow and excites low energy levels.

**Radiative decay from higher energy levels** – cascade effects. This becomes particularly noticeable when the higher levels are selectively excited.

The relative importance of all these processes depends on the atoms involved and on the discharge parameters – pressure, voltage and current. Thus changing the plasma gas to another pure gas or to a gas mixture can cause a major change in the observed spectrum. Small amounts of gaseous impurities can also cause major intensity changes. Examples of all these effects will be discussed in this talk.

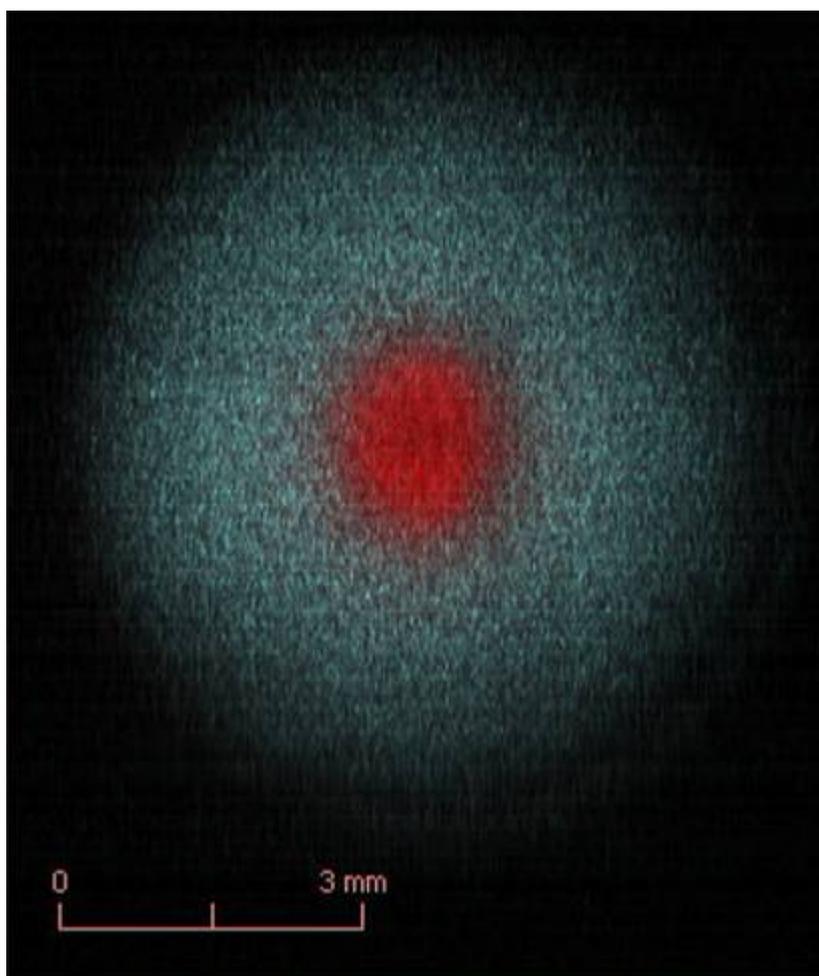
## An Overview of Recent Glow Discharge Work at Empa

James Whitby, Gerardo Gamez, Deborah Alberts, Philippe Raisin, Damian Frey and Johann Michler

<sup>1</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland. e-mail: james.whitby@empa.ch*

We describe recent work at Empa on the development and application of analytical glow discharges, including:

- a user-friendly database program to aid the selection of standards for a calibration
- use of a neon plasma to enhance halogen signals in GD-OES
- the design and performance of our imaging GD-OES instrument (push broom multispectral imaging system)
- the effects of deliberately added hydrogen gas on GD-TOFMS signals from metals



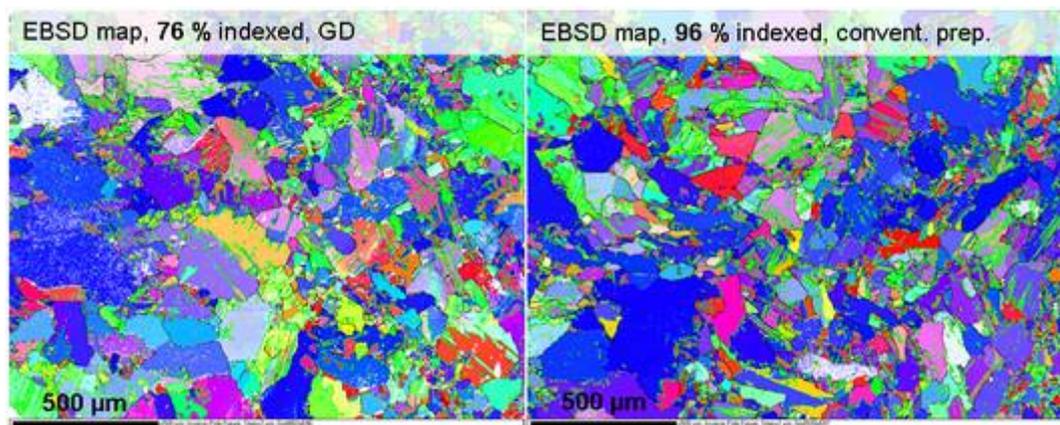
**Figure 1: GD-OES image of a copper pin (324.7 nm emission shown as red) in a nickel plate (341.5 nm emission shown as cyan). Image acquired using push-broom multispectral instrument with a pulsed DC discharge.**

## Glow discharge as a tool for the preparation of samples for electron microscopy measurements

Varvara Efimova, Volker Hoffmann, Alexander Kauffmann, Jens Freudenberger

*IFW Dresden, Helmholtzstraße 20, 01069, Dresden, Germany, e-mail: v.efimova@ifw-dresden.de, v.hoffmann@ifw-dresden.de*

Those people who work with electron microscopy (e.g. Scanning Electron Microscopy) know that existing sample preparation methods such as polishing, chemical etching, and ion beam etching are laborious and time consuming. Sputtering in the glow discharge has a great number of attractive features and thus lends itself to a fast and simple sample preparation. For example a crystalline copper surface usually prepared by vibration polishing during 24 hours needs only 5 minutes to be sputtered in the glow discharge plasma to get a similar result (please see the figures below). On the other hand glow discharge is not often used for sample preparation. Therefore, investigation of the sputter process and sputter-induced surface topography formation in the glow discharge is necessary. In the talk a study of sputtering effects in the glow discharge will be introduced. The study is a part of a research project at IFW Dresden in collaboration with the company Spectruma, which is funded by ZIM (“Zentrales Innovationsprogramm Mittelstand” - KF2466403AB0).



EBSD (Electron Backscattered Diffraction) map of the crystalline copper surface prepared by glow discharge sputtering (left) and by the conventional method (right).

## The Evaluation and Characterization of Alternative Gases using Iron and Titanium Reference Materials

DeAnn Barnhart<sup>1</sup>, Glyn Churchill<sup>1</sup>, Karol Putyera<sup>1</sup>

<sup>1</sup>Evans Analytical Group, 6707 Brooklawn Parkway, Syracuse, NY 13211, e-mail: [dbarnhart@eaglabs.com](mailto:dbarnhart@eaglabs.com), [gchurchill@eaglabs.com](mailto:gchurchill@eaglabs.com), [kputyera@eaglabs.com](mailto:kputyera@eaglabs.com)

Alternative gases have long been used in glow-discharge mass spectrometry (GDMS) to alleviate interferences that arise from the standard ionization gas of choice, in this instance argon. The research presented here explores the reproducibility of the alternative gases krypton, neon, and nitrogen on the Nu Astrum and compares and contrasts the use of krypton as an alternative gas on both the VG9000 and the Nu Astrum GDMS instruments. Additionally, utilizing titanium and iron reference standards, the propensity for the different ionization gases to produce potentially interfering species such as  $M^{++}$ ,  $MM^+$ ,  $MG^+$ ,  $G^{++}$ , and  $G^+$  from the matrix (M) and gas (G) ions is investigated. These measurements are compared to each other as well as to their counterparts in argon. Differences seen for these interferences in a titanium versus an iron matrix are also investigated. Additionally, as part of this research, the behavior of oxygen in each ionization gas for both the titanium and iron reference standards is explored.

## Challenges in GDMS analyses of PV silicon materials

Marisa Di Sabatino, Chiara Modanese, Lars Arnberg

*Norwegian University of Sciences and Technology (NTNU), Faculty of Natural Sciences and Engineering, Dept. Materials Science and Engineering, 7491 Trondheim, Norway, e-mail: [marisa.di.sabatino@material.ntnu.no](mailto:marisa.di.sabatino@material.ntnu.no), [chiara@material.ntnu.no](mailto:chiara@material.ntnu.no), [lars.arnberg@material.ntnu.no](mailto:lars.arnberg@material.ntnu.no)*

Trace elements analysis of solar cell silicon is important because it has been shown that several impurities, e.g. Fe, Cr, Ni and Cu, can dramatically reduce the solar cell performance even at level as low as part per billion in weight (ppbw). Measurements of such low levels of impurities with good accuracy are difficult, though this plays a key role for the photovoltaic- (PV) research and industry. In this work, we present a high resolution fast-flow glow discharge mass spectrometer (GDMS) as a tool to precisely measure chemical composition of solar cell silicon and the challenges of GDMS analyses for this material. GDMS technique has, so far, only been used for bulk analyses without consideration of the structure, i.e. whether it contains dislocations, grain boundaries or twins. In this study, we also aim at investigating the potential of GDMS for impurity segregation to crystal defects. This will give important information to understand and model trace element segregation during silicon solidification, and further solar cells processing.

## Magnetically boosted radiofrequency glow discharge optical emission spectroscopy

P. Vega<sup>1</sup>, R. Valledor<sup>1</sup>, J. Pisonero<sup>1</sup>, N. Bordel<sup>1</sup>

<sup>1</sup> *Department of Physics, Faculty of Science, University of Oviedo, Spain,*  
*e-mail: [vegapaola.uo@gmail.com](mailto:vegapaola.uo@gmail.com)*

Low pressure radiofrequency glow discharge (rf-GD) sources, coupled to either optical emission spectroscopy (OES) or to mass spectrometry (MS), are known to be powerful techniques for direct solid analysis of materials. Nevertheless, there is still a great interest in the development of new approaches to further improve the sensitivity and depth profile capabilities of this technique. In this sense, the application of external magnetic fields (e.g. magnetically boosted GD) has been shown to produce enhancements in the excitation and ionization efficiencies of the GD plasma. A magnetic field configured parallel to the cathode constrains secondary electron motion to the vicinity of the cathode, increasing the probability of excitation by electron-atom collisions and resulting in dense plasma in the magnetic field region.

In a previous study carried out in our laboratory, a low intensity magnetic field (7.5 mT) was applied to both, a non-pulsed and a pulsed radiofrequency glow discharge coupled to a time of flight mass spectrometer. The experiments in non-pulsed radiofrequency mode showed slight increases of analyte ion signals, depletion of Ar species-related ion signals, and non-effects neither in crater-shapes nor in sputtering rates, which indicates that the ionization efficiency and ion transport efficiency are improved when a low strength magnetic field is added.<sup>1</sup> However, in pulsed mode, the presence of a low magnetic field did not modify the analyte ion signal intensities.

In order to investigate the use of stronger magnetic fields and their effects on the GD performance, a new experimental set up based in an electromagnet device, which allows the application of an homogeneous tunable magnetic field (up to 70 mT), has been developed and coupled to an in-house rf-GDOES.<sup>2</sup> In the present work, several copper and argon emission lines have been measured in the 0-to-70 mT tunable magnetically boosted rf-GDOES, working at both pulsed and non-pulsed mode. In the non-pulsed mode, a high emission signal enhancement (up to a factor of 20) has been observed in copper atomic lines when applying the external magnetic field. Furthermore, the enhancement factor is related to the upper energy level of the corresponding emission line. In contrast, in the magnetically boosted pulsed rf mode, we have observed different behaviors at the different time domains, for instance: atomic copper lines showed a slight *prepeak* emission enhancement, which seems to be independent of the emission line upper energy level, while the signal enhancement in the *plateau* region is more pronounced and related to the upper energy level. Moreover, *afterpeak* emission of Cu I lines (only detectable when the upper energy level is higher than 6 eV) decreased.

1. P. Vega et al., *Analytical and Bioanalytical Chemistry*, 2009, **394**, 373-382.

2. P. Vega et al., *Journal of Analytical Atomic Spectrometry*, 2012, DOI: 10.1039/C2JA30106G.

## **Characteristics of the New Low-Flow Flat Geometry Glow Discharge Cells for the Nu Astrum GDMS Instruments.**

Glyn Churchill<sup>1</sup>, DeAnn Barnhart<sup>1</sup>, Karol Putyera<sup>1</sup>

<sup>1</sup>*Evans Analytical Group, 6707 Brooklawn Parkway, Syracuse, NY 13211,  
e-mail: [gchurchill@eaglabs.com](mailto:gchurchill@eaglabs.com), [dbarnhart@eaglabs.com](mailto:dbarnhart@eaglabs.com), [kputyera@eaglabs.com](mailto:kputyera@eaglabs.com)*

A new low-flow flat geometry discharge cell has been developed by Nu Instruments for the Astrum Glow Discharge Mass Spectrometer (GDMS). Certified Reference Materials, such as titanium (BS-T2A) and iron (BS-56G), and a production grade 4N5 purity titanium reproducibility material were analyzed using both a low-flow coaxial “pin” cell and this new flat sampling cell on the Nu Astrum instrument. These results were compared and contrasted to ascertain the performance characteristics of the new low-flow flat sampling cell versus the more conventional coaxial geometry on this newest generation of GDMS instruments. Additionally, sputtered crater shapes of select titanium samples utilizing varying voltages were investigated for bottom flatness with the aim of reducing layer smearing, for instances in multi-layered samples. The known advantages of increased abundance sensitivity on the Nu Astrum in comparison to the previous generation of VG9000 models were also investigated.

## Advances in GDMS

### Ekbal Patel

*Mass Spectrometer Instruments Ltd, Victoria Mills, Mill Street East, Dewsbury . West Yorks U.K.  
email: [ekbal@massint.co.uk](mailto:ekbal@massint.co.uk)*

GDMS is a well known proven technique for bulk analysis of solid materials. The VG9000 and Concept GD Instrument were initially the only two Instruments based on magnetic sector high resolution Instruments with low flow source. Both Instrument were configured from other products and inherited some weaknesses.

With introduction of GD90, considerable work has been done on the source region to enable ease of operation, maintenance and simplification of source. This has improved the cooling efficiency of the cell enabling low melting samples such as gallium to be performed easily. The design configuration enables using pin or flat samples without any changes to the cell. The high transmission Autoconcept platform with ion optics capable of attaining 160,000 or better resolution has enabled the replacement of the source slit.

The RF system developed has now opened new opportunities and increased the application areas of the Magnetic sector GDMS. It is the first fully automated system with simple changeover between DC and RF. Further improvements in sensitivity and resolution have now been made. Typical examples of analysis are Al<sub>2</sub>O<sub>3</sub> powder, rare earth sample, insulators and thin layer materials.

## **Performance characteristics of the Nu Astrum, a new high resolution GD-MS**

Sergey Ryabov, Andrew Burrows, Steve Guilfoyle

*Nu Instruments, Unit 74 Clywedog Road South, Wrexham LL13 9XS, UK  
[sergey@nu-ins.com](mailto:sergey@nu-ins.com), [andyb@nu-ins.com](mailto:andyb@nu-ins.com), [steveg@nu-ins.com](mailto:steveg@nu-ins.com)*

Glow Discharge Mass Spectrometry is an extremely sensitive technique for the characterisation of many materials. The ability of GD-MS to accurately and precisely quantify elemental composition from matrix level to sub ppb (part per billion) level is more or less unique and therefore in some application areas it is considered to be the gold standard. Superalloys, metal composites and semiconductor materials are all required extensively in the aerospace, electronics and computer industries. GD-MS is an ideal technique to characterise these materials and has been a mainstay of the analytical community for several decades.

Nu Instruments have recently launched a new GD-MS Instrument, the Nu Astrum. This instrument is an entirely new design, though taking some cues from its predecessor the VG9000, which is still the most widely used GD-MS instrument. The Nu Astrum is a double focusing instrument capable of resolution greater than 10,000 RP. The sample cell and extraction optics have been designed to ensure minimal cross contamination between samples and also to reduce cleaning time and operational costs. Both pin and flat sample cell arrangements are available, allowing a wide variety of sample sizes to be analysed. By cryo-cooling the sample region, the gas background is also significantly reduced, meaning easier identification of analytes due to reduced gaseous molecular species. In addition, a totally new software suite has been purpose designed for the needs of the GD-MS analytical community.

We present initial data for several types of material, taken both from measurements made at the Nu Instruments factory and also by the first users of the Nu Astrum. The data shows that the Nu Astrum is suitable for the analysis of a range of materials. We also describe some of the potential further developments under consideration for the future.

## **New Techniques in GDOES (Glow Discharge Optical Emission Spectrometry) Open Up New Fields of Applications**

Michael Analytis, Marina Henniger

*Spectruma Analytik GmbH, Fabrikzeile 21, D-95028 Hof Germany,  
e-mail: [info@spectruma.de](mailto:info@spectruma.de)*

A survey will be given on the overview of unique tools and new applications from Spectruma. Hereby it is shown the particularly importance of the usage of pulsed RF (radio frequency) discharges for the measurements of  $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$  layers in solar industry and lithium-ion battery. Application of pulsed glow discharge strongly reduces the sample heating and provides the quantitative depth profiling (QDP) in the nanometer to micron range. Thanks to this tool both non-conductive and conductive samples can be analysed.

In a third application from medical science sector the universal sample unit (USU), a special GD-source, is presented. With the USU non flat, rounded and samples with any other special geometries can be measured. Layer thickness, coating weight, oxidation level, roughness of base material and many more figures can be read out.

## Isotopic depth profiles by GD spectroscopies: GD-OES and PP-TOFMS

Patrick Chapon, Sébastien Legendre, Agnès Tempez

*Horiba Jobin Yvon, 16-18 rue du canal 91160 Longjumeau Cedex*

*E mails : [patrick.chapon@horiba.com](mailto:patrick.chapon@horiba.com), [sebastien.legendre@horiba.com](mailto:sebastien.legendre@horiba.com), [agnes.tempez@horiba.com](mailto:agnes.tempez@horiba.com)*

Access to transport mechanisms within materials can be studied through isotopic depth profiles. With OES detection, Deuterium (D) mainly has been measured; with TOFMS all isotopes are readily available.

D in OES is measured at the wavelength 121,534 nm and is well separated from the most intense H line at 121,567 nm.

The capability to detect D together with H and all other elements in a depth profile is interesting as it provides unambiguous determination not affected by residual background and is used notably for corrosion studies of fusion reactors materials. In a recent paper <sup>[1]</sup> Nakamura *et al.* have studied with GD-OES the deuterium behaviour at the interface of different metals (SS304, F82H and nickel) oxidized under high temperature heavy water.

PP-TOFMS<sup>TM</sup> measures all masses at any depth in a depth profile from H (mass 1), D (mass 2) to U (238/235) and beyond (for molecular fragments) and is therefore well suited for obtaining isotopic depth profiles for thin and thick layers. Baron Wiechec *et al.* <sup>[2]</sup> for instances have looked with PP-TOFMS<sup>TM</sup> at amorphous anodic alumina permeated by linear pores using <sup>18</sup>O tracers.

Through a review of published works, we will present the possibilities and issues of GD spectrometries for isotopic depth profiles of thin and thick layers.

- 1) H. Nakamura, *et al.*, “Deuterium behavior at the interface of oxidized metal under high temperature heavy water”, *Fusion Eng. Des.* (2012), doi:10.1016/j.fusengdes.2012.02.044
- 2) A. Baron Wiechec *et al.*, “<sup>18</sup>O distributions in porous anodic alumina by plasma profiling time-of-flight mass spectrometry and nuclear reaction analysis” *Surface and Interface Analysis* (2012) doi 10.1002/sia.5032

## New Developments in Radio Frequency Glow Discharge and Near Surface Depth Profile Analysis

Kim Marshall, Ted Casper, Sara Casper, Greg Schilling, and Diane Goodman  
LECO Corporation, Saint Joseph Michigan  
([kim\\_marshall@lecotc.com](mailto:kim_marshall@lecotc.com))

Glow Discharge Optical Emission Spectroscopy (GD-OES) has become an important tool for elemental analysis. GD-OES is used for both quantitative bulk analysis and compositional depth profile analysis (CDP). The radio frequency (RF) glow discharge is indispensable because it is required for the analysis of non-conductive materials or layer materials, where at least one layer is non-conductive. It is clear that, for both DC and RF glow discharge, the emission source is the heart of the technique. Additionally, it can be shown that the so-called plasma parameters (lamp voltage, current and pressure) control, either directly or indirectly, all of the sampling and excitation processes [1,2]. In the work presented here a new refinement to RF lamp control is presented and compared with our earlier “True Plasma Power<sup>®</sup>” approach.

A second development that will be presented expands upon earlier work showing that GD-OES can be utilized for the analysis of surface layers of only a few nanometers in thickness [3]. The precision and apparent accuracy with which these ultra-thin layers can be determined with this technique are impressive. This is particularly so when the speed of the GD-OES analysis is compared to the analysis times of traditional depth profiling techniques like Auger Electron Spectroscopy, Secondary Ion Mass Spectrometry, or X-ray Photoelectron Spectroscopy. These methodologies require tens of minutes or even hours for each analysis while GD-OES can complete a similar analysis in under a minute. A comparative study of the magnetic data layers on various terabyte hard disks will be presented. This study provides a framework to ascertain the types of information that can be provided by GDS for process control. Determining and controlling these ultrathin and complex coatings is key to the quality control of these devices [2,3]. This work will demonstrate that GDS is well suited for aiding in the process control of such commercial surface coatings.

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## Element GD: Overview of Applications and New Developments

Joachim Hinrichs, Lothar Rottmann

*Thermo Fisher Scientific (Bremen) GmbH, Hanna-Kunath-Str.11, 28199 Bremen, Germany  
e-mail: [joachim.hinrichs@thermofisher.com](mailto:joachim.hinrichs@thermofisher.com)*

The ELEMENT GD high resolution GD-MS uses a high power, fast flow DC concept for rapid sputtering and highest sensitivity. The current status is being presented, based on the main applications of the ELEMENT GD, i.e. the production control of high purity metals, Nickel super alloys, and solar cell silicon. Besides the standard flat sample geometries, examples for other sample shapes will be shown.

The typical power of 30 – 50 W applied to the source in its standard continuous mode produces sputter rates on the order of 100 nanometers per second. At such conditions, any surface contamination is quickly removed, eliminating the need for intensive cleaning of the sample surface and shortening pre-sputter times before analysis. Nevertheless, for depth profiling of layered samples at the nanometer scale this standard setup is less favorable.

Examples for thin layer analysis will be presented as an application for the newly developed pulsed GD source. The pulses used are of 10-100  $\mu$ s duration, maintaining the high instrumental sensitivity, while at the same time using much less discharge power. Initial experiments show that it is possible to achieve a depth resolution of <10 nm while still achieving ppm level detection power. For the analysis of major components in layered systems, the GD power can be further decreased to give even higher depth resolution at a lower overall sensitivity.

## New and Improved Atomic line data for Astrophysical Applications

Florence Liggins and Juliet C. Pickering

*Imperial College London, Space and Atmospheric Physics, Prince Consort Road, London SW7 2BW,  
e-mail: fs111@ic.ac.uk*

Atomic line data are used in combination with stellar atmospheric models in order to produce synthetic stellar spectra from which, when compared with observations, physical parameters such as the temperature, composition, and kinetics of a star can be determined, parameters key to understanding stellar and galactic chemical evolution. A new generation of ground and space-based telescopes and spectrographs, ranging from the far infrared (FIR) e.g. Herschel's HIFI, to the vacuum ultraviolet (VUV) e.g. the Hubble Space Telescope's STIS, set a new standard for these atomic data requirements; the increase in both spectral resolution and accuracy of these instruments expose the poor quality, or in some cases complete lack of, required laboratory atomic wavelength and energy level data.

Laboratory spectroscopy of singly ionised iron-group elements, observed in hot star spectra, is being carried out at Imperial College using the improved VUV Fourier transform (FT) spectroscopy technique (Thorne *et al.*, 1995) which allows a high chromatic resolving power ( $>10^6$  at 200 nm) and accuracy ( $1:10^7$ ) as well as a broad spectral range due to its unique low wavelength cut-off of 140 nm. In order to carry out a full term analysis, whereby new or improved energy levels are found, a suitable source is required that emits lines from as many energy levels as possible. The source used for this work is a glow discharge hollow cathode (HC) source recently designed and manufactured at Imperial College and based on a similar source used by the atomic astrophysics group at Lund University. This source's increased stability allows a higher working current to be used, for example up to 1 A using an iron cathode and 800 mA with manganese.

Besides the relative difficulty in preparation of a hollow cathode sample, these sources have advantages over the Grimm source, for example, in that they produce higher radiation intensity due to higher atomic density and increased dwell time of sample atoms. For a term analysis, it is imperative that a high intensity is achieved in order that weaker lines, typically due to transitions from high energy levels, are enhanced and the higher photon flux allows for higher accuracy in the wavelengths obtained. By linking to higher energy levels, typically those that are as yet unobserved, new and improved energy levels can be established and thus wavelengths calculated for transitions that are ordinarily unobtainable in laboratory conditions, e.g. spin-forbidden transitions, increasing the accuracy and completeness of available atomic line data for astrophysical applications.

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## Formation of electrical prepeak in pulsed glow discharge via gas heating

Maxim Voronov<sup>1</sup>, Volker Hoffmann<sup>1</sup>

<sup>1</sup> IFW Dresden, Institute for Complex Materials, Helmholtzstraße 20, 01069, Dresden, Germany, e-mail: [VoronovMV@mail.ru](mailto:VoronovMV@mail.ru)

A microsecond Pulsed Glow Discharge ( $\mu\text{s}$  PGD) in a Grimm-type source is characterized by the so-called “prepeak”, which is a spike in both electrical current [1-5] and emission intensity [6,3] at the leading edge of the discharge pulse. The prepeak is followed by synchronized vibrations of the current and the emission. To understand the nature of these phenomena, a microphone was inserted into the discharge chamber. Acoustical waves were detected and found to be in correlation with the measured vibrations [7]. This points to a thermal mechanism for prepeak formation: the gas is heated in the leading edge of the discharge pulse and then expanded.

To prove this suggestion, a Monte-Carlo based model was developed to simulate the evolution of Ar concentration, temperature, and flow in time and space. Potentially, the model could be used for gas simulations in a wide range of different applications. Here, the model is incorporated into an existing but modified model of the  $\mu\text{s}$  PGD in a Grimm-type plasma excitation source[8]. Simulation have revealed a rapid increase of the Ar temperature, which takes place near the Cathode Dark Space (CDS) in the first few microseconds of the discharge and is accompanied by a corresponding rapid decrease of the Ar concentration, see Fig. 1. The fall in Ar concentration limits the electrical current in the discharge. In this way the formation of the prepeak is explained.

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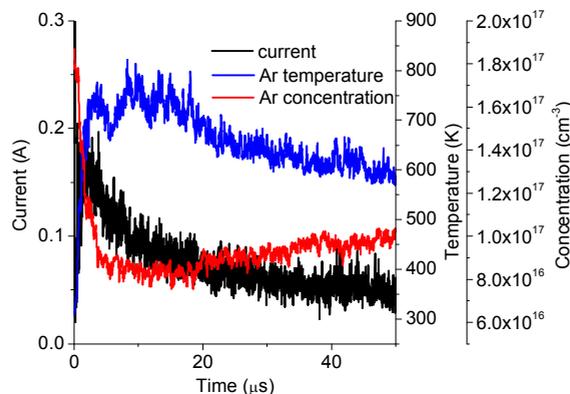


Fig. 1. Some calculated parameters of a PGD in a Grimm-type source with a 4 mm diameter anode. Initial pressure 8 mBar, a voltage of 1500 V of rectangular form is applied to the cathode at time zero.

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## Glow Discharge Mass Spectrometry Studies on Some Nephrite Materials

Bilige Siqin<sup>1</sup>, Rong Qian<sup>2</sup>, Shangjun Zhuo<sup>2</sup>, Fuxi Gan<sup>1, 3</sup>, Min Dong<sup>2</sup>, Yanfen Hua<sup>2</sup>

<sup>1</sup> Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, P. R. China, e-mail: sqbl03@yahoo.com.cn

<sup>2</sup> Shanghai Mass Spectrometry Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China, e-mail: qianrong@mail.sic.ac.cn

<sup>3</sup> Fudan University, Shanghai 200433, P. R. China

### Abstract

Glow discharge mass spectrometry (GD-MS) was applied to study the nephrite minerals formed by different metallogenic mechanisms and geological environments from deposits in China, Canada, New Zealand and Russia. The GD-MS analysis and multivariate statistic analysis results indicated that two types of nephrite minerals of different metallogenic mechanisms could be classified by some typical elements. It was shown that serpentine-related nephrite minerals had higher concentrations of Cr, Co and Ni than dolomitic-marble-related nephrite minerals. Meanwhile, nephrite samples from Wenchuan had higher concentrations of Mn, V than other deposits and nephrite samples from Xiaomeiling had higher concentrations of Sr, K and Na than other deposits, which were consistent with their geological environments. The GD-MS research results indicated that both metallogenic mechanisms and geological environments could affect the elemental concentrations in nephrite minerals.

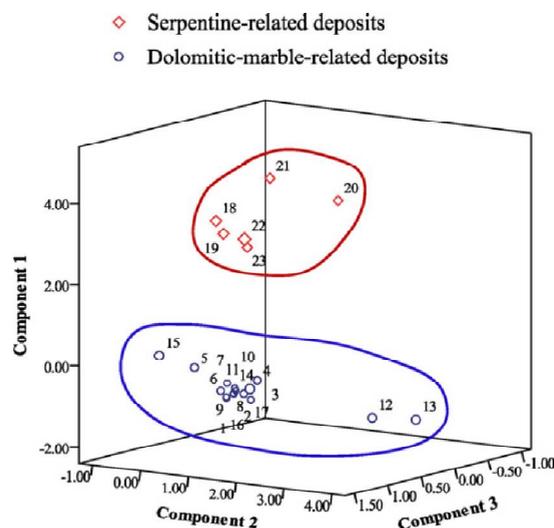


Fig. Three-dimensional diagram of principle component analysis on nephrite minerals of different formation.

## Effect of Pulsing on Hydrogen Analysis with GD-OES

Arne Bengtson<sup>1</sup>, Mats Randelius<sup>1</sup>, Simone Weyler<sup>2</sup>

<sup>1</sup>*Swerea KIMAB AB, Isaffordsgatan 28A, SE-164 40 Kista, Sweden, e-mail:*

*[arne.bengtson@swerea.se](mailto:arne.bengtson@swerea.se), [mats.randelius@swerea.se](mailto:mats.randelius@swerea.se)*

<sup>2</sup>*ThyssenKrupp Steel, Dortmund, Germany*

GD-OES has been used for depth profile analysis of hydrogen in various applications for decades. Provided that hydrogen is a major element in the surface layer (e.g. a hydride or a polymer coating), this is considered to provide an essentially valid picture of the hydrogen in-depth composition. However, there is a strong industrial interest in determination of trace amounts of hydrogen, e.g. in various zinc alloy coatings on steels. The major technical reason is that hydrogen embrittlement can be very detrimental to the quality of coated steels used in e.g. the automotive industry.

Previous work has shown that it is very difficult to measure trace levels of hydrogen with GD-OES, due to a high and unstable background signal. Hydrogen is always present in the glow discharge plasma to some extent, primarily in the very beginning of the discharge when e.g. adsorbed water is released from the walls of the discharge chamber. The heating of the source due to the discharge current causes further release of hydrogen that continues for several minutes; the impact of this process on the time evolution of the hydrogen background can be both non-reproducible and differ between sources. In addition, the presence of hydrogen in the plasma affects both spectral backgrounds and emission yields of other analytes [1].

When pulsing a GD source, the reduced average power results in less heating. This is one reason to expect a reduced background from hydrogen, but additional effects related to dissociation and excitation processes may also play a role. In this work, a radio frequency (RF) GD source has been pulsed with duty cycles of 25, 50 and 75 percent, at frequencies between 100 and 3000 Hz [2]. The samples studied were steels coated with both zinc-based metallic coatings (trace levels of hydrogen) and organo-metallic coatings (hydrogen a major element). The results indicate that the hydrogen background is indeed reduced by pulsing, but so is the emission yield (EY) of hydrogen. Further work is in progress, and the available results will be presented and discussed.

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## Sputter Rates in GDMS

Martin Kasik

*EAG Laboratories, 6707 Brooklawn Pkwy, Syracuse NY 1322, USA,  
e-mail: [mkasik@eaglabs.com](mailto:mkasik@eaglabs.com)*

GDMS analytical techniques are discovering more and more applications in characterization of near surface regions, thin films and advance coatings. Good understanding of sputter rates for various materials and the ability to estimate sputter rates prior to the analysis for often unique customer samples are crucial for proper planning of testing and experiments. Calculated sputter rates and measured sputter rates are compared for wide range of materials and also for different GDMS instruments.

Sputter rates are the results of an interaction between glow discharge and a sample. Some relationships between the sputter rates, glow discharge parameters, and sample properties are discussed and demonstrated which includes the Bouman equation.

## The GLADNET Catalogue of Glow Discharge Spectra: Part 1 finished !

Zdeněk Weiss<sup>1</sup>, Edward B.M. Steers<sup>2</sup>, Volker Hoffmann<sup>3</sup> and Juliet C. Pickering<sup>4</sup>

<sup>1</sup> LECO Instrumente Plzeň, spol. s r.o., Plaská 66, 323 25 Plzeň, Czech Republic.

<sup>2</sup> London Metropolitan University, 166-220 Holloway Road, London N7 8DB, UK.

<sup>3</sup> Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany.

<sup>4</sup> Blackett Laboratory, Imperial College, London SW7 2BW, UK.

Information about progress of work on a new catalogue of glow discharge emission spectra will be given. This work started some time ago as Project P16 of the GLADNET Analytical Glow Discharge Network, funded by the EC under its Sixth Framework Programme (FP6). The recently finished Part 1 of the catalogue contains spectra of iron (2554 lines), copper (323 lines) and zinc (85 lines), in the range from 155 nm to 540 nm, in argon and neon discharges. Strengths of emission lines are expressed by emission yields. They are corrected for the instrument function and are proportional to true intensities, with proportionality factors reflecting sputtering rates of the respective pure metals in the given gas. Emission yields presented in the catalogue are consistent over the whole spectral range mentioned above, between different elements and between both discharge gases.

Glow discharge spectra differ significantly from emission spectra produced by another excitation sources such as arc/spark or ICP and there is no other systematic resource of this kind, that would be devoted to glow discharge spectra. Emission lines listed in the catalogue are classified by type (atomic, ionic) and by excitation energy, if that information was available. From this data, it is possible to draw a wealth of information relevant both to practical analytical work (selection of analytical lines in different applications and at different experimental situations, magnitude of line interferences) and fundamental studies (populations of individual excited levels, excitation mechanisms, planning of experiments - prospective overlaps of lines observed at certain resolution, etc.). Methodology and data processing strategies involved in the preparation of the catalogue will be reviewed.

## rf Pulsed Glow Discharge - Time of Flight Mass Spectrometry: Investigation of the Ion Source Design

Rosario Pereiro<sup>1</sup>, Cristina Gonzalez<sup>2</sup>, Marcos Bouza<sup>1</sup>, Lara Lobo<sup>1</sup>, Beatriz Fernandez<sup>1</sup>, Jorge Pisonero<sup>2</sup>, Nerea Bordel<sup>2</sup>, Alfredo Sanz-Medel<sup>1</sup>

<sup>1</sup>*Department of Physical and Analytical Chemistry, Faculty of Chemistry, University of Oviedo, Julian Claveria, 6. 33006 Oviedo, Spain, e-mail: [mrpereiro@uniovi.es](mailto:mrpereiro@uniovi.es); [mbouza86@gmail.com](mailto:mbouza86@gmail.com); [laraloborevilla@hotmail.com](mailto:laraloborevilla@hotmail.com); [fernandezbeatriz@uniovi.es](mailto:fernandezbeatriz@uniovi.es); [asm@uniovi.es](mailto:asm@uniovi.es)*

<sup>2</sup>*Department of Physics, Faculty of Science, Calvo Sotelo, University of Oviedo, 33007 Oviedo, Spain, e-mail: [cristinagonzalezgago@hotmail.es](mailto:cristinagonzalezgago@hotmail.es); [pisonerojorge@uniovi.es](mailto:pisonerojorge@uniovi.es); [bordel@uniovi.es](mailto:bordel@uniovi.es)*

Considering the promising analytical capabilities brought about by coupling pulsed radiofrequency glow discharge (GD) to time of flight mass spectrometry (TOFMS) [1], further research is still welcomed aiming to achieve the best performance of this direct solid analysis tool. In this context, and having in mind that the development of an optimum GD design is crucial, we developed and analytically evaluated an in-house ion source (“UNIOVI GD”) which has been interfaced to an orthogonal TOFMS. In the UNIOVI GD design (based on the Grimm-type GD), and following previous investigations, it has been searched for a simple design as well as for a short distance between sample and MS skimmer cone.

In this work, specific details about the UNIOVI GD design will be provided, paying special attention to differences with a previous GD chamber [2] which will be here called as “GD.1”. Pulse shapes of argon species and analytes have been studied as a function of the discharge conditions and results compared with those achieved with the GD.1, both coupled to TOFMS. Different behaviour and shapes of the pulse profiles have been observed for the two GD sources, and the results will be discussed.

Analytical performance characteristics have been evaluated both for the analysis of conductors (stainless steel samples) and insulators (glass), in terms of limits of detection (LODs), calibration graphs, selectivity and crater shapes. The proposed UNIOVI GD ion source showed special good performance for the analysis of glass samples, offering LODs about one order of magnitude better than with the GD.1 design, less polyatomic interferences and flatter crater shapes.

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## Imaging of the Glow Discharge Plasma

Volker Hoffmann<sup>1</sup>, Maxim Voronov<sup>1</sup>, Till Wallendorf<sup>2</sup>, Swen Marke<sup>2</sup>, Steven J. Ray<sup>3</sup>, Andrew P. Storey<sup>3</sup>, Gary M. Hieftje<sup>3</sup>, Tobias Steingrobe<sup>4</sup>, Wolfgang Buscher<sup>4</sup>, Carsten Engelhard<sup>4</sup>

<sup>1</sup>IFW Dresden, Institute for Complex Materials, P.O. Box 270116, D-01171 Dresden, Germany, <sup>2</sup>IfU Diagnostic Systems GmbH, Gottfried-Schenker-Strasse 18, D-09244 Lichtenau, Germany, <sup>3</sup>Indiana University, Department of Chemistry, Bloomington, IN 47405, USA, <sup>4</sup>University of Münster, Institute of Inorganic and Analytical Chemistry, Corrensstrasse 30, D-48149 Münster, Germany

Early research [1] revealed that the achievable lateral resolution of continuous glow discharge optical emission spectroscopy is quite poor, but the application of pulsed glow discharges improved the situation [2] and extensive investigations are going on in order to exploit this information for material analysis. A recent paper reviews these activities, where IFW investigated the possibilities of a new acousto-optical imaging spectrometer (AOS) in combination with glow discharge sources [3,4].

The AOS employs a compact UV/VIS/NIR chromatically compensated optical design that combines a wide wavelength range high resolution acousto optical tunable filter (AOTF) with a wide wavelength range image amplifier based on a microchannel plate. The time resolution of the image amplifier is down to 1 ns. The spatial resolution of the optical system is about 0.1 mm at a distance of 150 mm from the light input window. Over the wavelength range 250-800 nm the spectral resolution changes from 0.1 – 0.6 nm. Due to electronic tuning the access time to any wavelength is about 200 microseconds. These characteristics allow the measurement of discharge images for a wide range of different tasks including RF and DC micro- and millisecond pulsed discharge evolution and phase-correlated investigations of light emission during the RF cycle. In comparison with imaging spectroscopy measured by a monochromator, the developed AOS has both advantages and disadvantages. The short time for setting a specified wavelength allows the measurement of the evolution of several lines simultaneously, which is not achievable with a monochromator. However, interfering phenomena also exist with the AOS: a relatively high background image, etaloning (light interference pattern existing in the detected image), and a spatial shift of the image with wavelength. Ways to remove these effects are discussed.

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## APPLICATIONS OF A PULSED GD-MS.

Joachim Hinrichs and Lothar Rottmann

*Thermo Fisher Scientific, Hanna-Kunath-Str. 11, 28199 Bremen, Germany;  
Joachim.Hinrichs@thermofisher.com*

The ELEMENT GD high resolution GD-MS employs a DC power supply for the determination of sub-ppb trace metal concentrations in solid conductive samples. Due to the source design, the glow discharge is of relatively high power (typically 30 – 50 W) producing rapid sputter rates of 100 nanometers per second. At such conditions, any surface contamination is quickly removed, eliminating the need for intensive cleaning of the sample surface and shortening pre-sputter times before analysis. Nevertheless, this standard setup is less favorable for applications looking at low melting point samples that require very high detection power at a reduced energy input.

In this presentation the development of a pulsed, low power DC source will be described. With this new source the ELEMENT GD is operated at a much lower power of 3 – 4 W, while maintaining the same instrumental sensitivity as for a continuous DC source running at ten times higher power. When combined with enhanced Peltier cooling, sub-ppb detection limits are achieved in solid Gallium samples.

Depth profiling of layered samples will be presented as a second application for the pulsed GD source. Initial experiments show that it is possible to achieve a depth resolution of <10 nm while still achieving ppm level detection power. For the analysis of major components in layered systems, the GD power can be further decreased to give even higher depth resolution at a lower overall sensitivity.

## Characterization of the spatial distribution of excited species at the prepeak and afterpeak time domains, in pulsed RF-GD-OES

R. Valledor<sup>1</sup>, J. Pisonero<sup>1</sup>, Th. Nelis<sup>2</sup>, N. Bordel<sup>1</sup>

<sup>1</sup>University of Oviedo, C/ Calvo Sotelo s/n 33007 Oviedo (Spain); e-mail: [rebeca\\_val@hotmail.com](mailto:rebeca_val@hotmail.com)

<sup>2</sup>Bern University of Applied Sciences, Quellgasse 21, 2501 Bienne (Switzerland)

Radiofrequency Glow Discharge (rf-GD) spectrometric techniques are powerful analytical techniques for direct solid analysis of bulk and coated materials, for conducting and isolating samples. The combination of GD with optical emission spectroscopy (GD-OES), or with mass spectrometry (GD-MS), provides exceptional capabilities to perform high resolved depth profiling. Moreover, the development of pulsed-GD sources has opened new possibilities in GD techniques due to the interesting properties that they present such as less thermal effects, and different time-domains along the GD pulse which are related to different excitation/ionization mechanisms of the species present in the plasma [1].

In commercial rf-GD-OES instruments, the average emission intensity of the whole plasma is acquired and fundamental studies with this disposal give useful but limited information about the plasma. In this work, an in-house experimental set-up provided with a hollow anode source has been developed in order to allow spatially resolved measurements of the glow discharge emission. Side-on as well as end-on observation of the plasma plume can be performed. The detection system consists of a spectrograph with an intensified charge coupled device (iCCD) synchronized with the rf-generator, allowing time resolved data acquisition. A system of lenses focuses the emission coming from different positions along the plasma plume axis, at distances where the sampler can be found when coupling the GD to a mass spectrometer.

Temporal and spatial distributions of different species have been investigated in pulsed-rf-GD, to characterize the ionization/excitation processes that take place in the plasma. Emission intensities are measured at different positions of the plasma plume, and also at different times along the rf-GD pulse. In particular, argon and analyte (copper) emission has been evaluated during prepeak and afterglow temporal domains, at different RF pulse frequencies. These results will help to understand in more detail the GD plasma dynamic and, thus to improve the performance of the GD instruments in which the mass transport plays an essential role.

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## Investigation of the spatial and temporal distribution of plasma excited species produced in Laser Ablation- Glow Discharge

R. Valledor<sup>1</sup>, M. Tarik<sup>2</sup>, J. Pisonero<sup>1</sup>, N. Bordel<sup>1</sup>, D. Günther<sup>2</sup>

<sup>1</sup>Department of Physics, University of Oviedo, c/ Calvo Sotelo s/n, 33006, Oviedo, Spain; e-mail: rebeca\_val@hotmail.com

<sup>2</sup>ETH Zürich, D-CHAB, Laboratory of Inorganic Chemistry, Wolfgang-Pauli-Str. 10, 8093 Zürich, Switzerland

Laser Ablation (LA) has been used as sampling technique especially with Inductively Coupled Plasmas (ICP) over the last years. Combining LA with Glow Discharge (GD) also offers important analytical features: sampling and excitation/ionization steps are separated in time and space, leading to low matrix effects. In addition, LA provides the possibility of high lateral resolution, and both conductors and insulating materials can be analyzed without the need for radiofrequency powered GD. Mass spectrometric studies have shown the capabilities of the GD to post ionize the ablated material. In particular, the use of a Time of Flight Mass Spectrometer (TOFMS) allows quasi-simultaneous analysis of elemental and molecular information when the aerosol is injected at certain time domains in a pulsed GD [1-3]. However, further research is needed in order to fully understand the processes involved in the LAGD interaction.

In this sense, OES would allow to visualize the expanding plasma plume. Therefore, in this work, an in-house developed LA ms-pulsed GD-TOFMS instrument [3] has been adapted to allow the observation of the region defined by sample, cathode and anode. An iCCD provided with an objective has been used to obtain 2D images of the emission within this region at different temporal domains during the GD pulse (prepeak, plateau and afterglow). Optical bandpass filters have been used to select the wavelength range of interest in order to evaluate Al, Cu and Ar emission (sample ablated material, cathode material and filling gas, respectively).

The relative delay between the LA event and the emission measurement along the GD pulse has been found as a crucial parameter. No post excitation of the ablated material has been observed when the LA sampling takes place during the pulse. In contrast when the LA process takes place just before GD pulse termination and the emission is recorded during the afterglow, the overall emission of the LAGD plasma has been found to increase up to 65% with respect to the GD plasma alone at about 5-6 mm from the cathode. Different Cu, Ar and Al transitions have been evaluated in order to check for the enhanced species in the LAGD plasma.

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## The 'Hydrogen effect' upon the analysis of copper, iron and titanium as observed by Glow Discharge Time-Of-Flight Mass Spectrometry (GD-TOFMS)

James Whitby<sup>1</sup>, Sohail Mushtaq<sup>2,3</sup>, Peter Horvath<sup>1</sup>, Edward Steers<sup>2</sup>, Juliet Pickering<sup>3</sup>, and Johann Michler<sup>1</sup>

<sup>1</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland. e-mail: [james.whitby@empa.ch](mailto:james.whitby@empa.ch)*

<sup>2</sup>*London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, U.K.*

<sup>3</sup>*Blackett Laboratory, Imperial College, London, SW7 2BW, U.K.*

The effects of hydrogen gas (in argon) at concentrations of up to 0.4 % v/v upon ion signals from a direct current glow discharge have been observed using a time-of-flight mass spectrometer for samples of copper, iron and titanium. Contrary to the usual effect observed by GD-OES, for all three metals the analytical signal increased as low concentrations of hydrogen were added and then became approximately constant. Sputter rates decreased slightly as hydrogen was added. This increase in the signal and reduction in sputter rate is consistent with previous reports using a similar technique (Menendez *et al.*, 2005; Saito, 1995). Somewhat unexpectedly, the signals due to both  $\text{ArH}^+$  and  $\text{H}_3\text{O}^+$  decreased dramatically over the range of hydrogen concentrations studied, as well as the signal due to  $\text{Ar}^+$  (decrease of up to five orders of magnitude). For all three metals, the signals due to the dimer ion ( $\text{Cu}_2^+$ ,  $\text{Fe}_2^+$ ,  $\text{Ti}_2^+$ ) increased (x100) as hydrogen was added, as did the signals due to oxides ( $\text{TiO}^+$ ,  $\text{FeO}_2^+$ ).

The addition of hydrogen substantially changes the nature of the charged particles detected at the mass analyser, and it is clear that despite previous modelling work for hydrogen-containing argon discharges (Bogaerts and Gijbels, 2002) we do not yet understand in detail what gas-phase processes are most significant in determining the analytical signal for GD-MS measurements. Some authors have suggested that the addition of hydrogen increases the concentration of metastable argon atoms, whilst others have claimed exactly the opposite. Part of the explanation for this may lie in our previous suggestion that reactions in the flow tube are significant for GD-MS signals (Mushtaq *et al.*, 2011). Although this study does not answer this question directly, it does support the idea that the deliberate addition of hydrogen gas may sometimes be beneficial for analytical purposes (Hodoroaba *et al.*, 2003).

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## Effect of added molecular gases H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> (0-1%) on the Thermo Element GD ion signals with an argon discharge

Viktoria Weinstein<sup>1,2</sup>, Edward B.M. Steers<sup>1</sup> and Glyn Churchill<sup>3</sup>

<sup>1</sup> London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK e-mail [e.steers@londonmet.ac.uk](mailto:e.steers@londonmet.ac.uk)

<sup>2</sup> now at Evans Analytical Group SAS 94, chemin de la Peyrette, Tournefeuille, France 31170. e-mail [vweinstein@eaglabs.com](mailto:vweinstein@eaglabs.com)

<sup>3</sup> Evans Analytical Group, 6707 Brooklawn Parkway, New York 13211 Syracuse, e-mail [gchurchill@eaglabs.com](mailto:gchurchill@eaglabs.com)

A survey has been made using the Thermo Element GD on the effects which the addition of small quantities (0-1%) of molecular gases have on the observed ion signals. Three typical sample materials were used – copper, iron and titanium. To obtain discharge conditions as near as possible to the OES conditions used for the majority of such investigations (700 V, 20 mA, 4 mm anode tube diam.) the constant voltage, constant current mode (700 V, 80 mA, 8 mm anode tube diam.) was used for most of the investigations.

The largest changes are obtained with hydrogen. The Ar<sup>+</sup> signal falls dramatically, by ~ four orders of magnitude, while the ArH<sup>+</sup> and Ar<sup>++</sup> signals rise by similar amounts. At 1% hydrogen, the ArH<sup>+</sup> signal exceeds the Ar<sup>+</sup> signal by two orders of magnitude, with the Ar<sup>++</sup> is higher by a further order. The ArH<sup>+</sup> and H<sub>3</sub><sup>+</sup> signals become very high compared with the H<sup>+</sup> and H<sub>2</sub><sup>+</sup> signals. The Cu<sup>+</sup> and Ti<sup>+</sup> signals increase by an order of magnitude, whilst the Fe<sup>+</sup> signal initially rises but then falls again to its initial value. With added oxygen, the changes are much smaller, the majority being less than an order of magnitude. The sample signal drops in all cases, the fall being significantly larger than that of the sputtering rate. With nitrogen, the effects are similar, with the changes in the sample signals again greater than the fall in the sputtering rate.

Some experiments were carried out with an iron sample for added hydrogen using typical analytical conditions – constant current (43 mA) constant pressure (1.13 mbar), voltage (870 - 1100 V, rising with increasing hydrogen concentration). The general trends were similar. But in this case the ArH<sup>+</sup> and Ar<sup>++</sup> signals became of similar magnitude at ~ 1% hydrogen, exceeding the Ar<sup>+</sup> signal by two orders of magnitude. Despite the very large change in the matrix signal, the signals from minor and trace constituents, normalised to the matrix signal, changed **only** by factors ~ 1-3, the significant changes for all constituents except sulphur being limited to hydrogen concentrations < 0.2%.

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## Study of Ar/He mixed plasmas to probe the excitation and ionization processes in Grimm-type glow discharges

Sohail Mushtaq<sup>1</sup>, Edward B.M. Steers<sup>1</sup> and Juliet C Pickering<sup>2</sup>

<sup>1</sup>London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK, e-mail: [s.mushtaq@londonmet.ac.uk](mailto:s.mushtaq@londonmet.ac.uk), [e.steers@londonmet.ac.uk](mailto:e.steers@londonmet.ac.uk)

<sup>2</sup>Blackett Laboratory, Imperial College London, London SW7 2BW, UK

In low pressure analytical glow discharges (GD) such as Grimm-type sources, the plasma gas plays a vital role in the excitation/ionization processes in discharge. To identify unusual excitation processes affecting particular lines in GD, helium was added up to 60 % v/v in argon plasma. It is noted that the additional gas can cause drastically influence to emission intensities of the main plasma gas and sputtered analyte. Selective excitation processes which are mainly dependant of nature of plasma gas and analyte material are also observed.

In this presentation, we report results of investigation on the effect of Ar/He mixed plasmas on the emission intensities of samples (Cu & Fe) and plasma gas, electrical parameters, pressure and sputter rate. A detailed study of spectral lines profiles has been carried out; as the helium concentration is increased, Ar I lines in the 600 - 900 nm region (transitions to the 4s levels) show increasing amounts of self- absorption and self reversal suggesting an increase in the population of these levels. A significant increase in the number density of argon metastable atoms would cause major changes in the excitation processes for argon atomic lines. Argon ionic lines with total excitation energy 35-36 eV are excited 'selectively' by Penning *excitation* of ground state argon *ions* by of helium metastable atoms. The intensity of Ar II lines from this energy group in particular increases with the increase of helium concentration in the mixed gas plasma.

It also appears that a group of Fe II lines, upper energy near to 19 eV, are excited by non-selective Penning *ionization* by helium metastable atoms of ground state iron atoms. This ionization/excitation process may have significant effects on analytical applications of mass spectrometry. With a copper cathode, a large number of Cu II lines within 460-580 nm range are observable in Ar-He plasma. It is suggested that these lines are predominately excited by asymmetric charge transfer between helium ions and ground state copper atoms (He-ACT). Several intense Cu II lines with upper energies in the range 16.2 – 16.5 eV also appeared in Ar-He mixtures. It is suggested that these intense Cu II lines maybe the result of a cascade effect. The increase in the population of highly excited levels of Cu II lines by He-ACT strongly affects the intensity of lines from lower levels.

## Glow Discharge Techniques in the Chemical Analysis of Photovoltaic Materials

S. W. Schmitt<sup>1,3</sup>, C. Venzago<sup>2</sup>, G. Gamez<sup>3</sup>, B. Hoffmann<sup>4</sup>, V. Sivakov<sup>4</sup>, T. Hofmann<sup>2</sup>, S. Christiansen<sup>1,4</sup> and J. Michler<sup>3</sup>

1) Max Planck Institute for the Science of Light, Erlangen, Germany

2) AQura GmbH, Hanau, Germany

3) EMPA, Thun, Switzerland

4) IPHT, Jena, Germany

Fast, sensitive and quantitative chemical analyses of photovoltaic (PV) materials are still challenging and of particular interest in the support of a PV development or production process. Three glow discharge (GD) analytical techniques, mass spectrometry (GD-MS), time of flight MS (GD-TOF-MS) and optical emission spectrometry (GD-OES) exist that permit this type of analyses. All based on GD ionising sources, which sputter craters with nano-scale depth resolution in the material of interest. GD ionising sources require no sample preparation and work in low vacuum (10-2mbar), in contrast to x-ray photoelectron spectroscopy (XPS) or secondary ion MS (SIMS). Furthermore, GD methods have the capability to carry out quantitative multi-elemental analysis with a high elemental differentiation. GD methods are straight forward to be applied to the analysis of industrial feedstock materials and they are even applicable for the chemical analysis of thin films due to the high depth resolution. Of course GD methods permit to study materials even in devices, at all stages of PV development and production.

## Laser – Hollow Cathode Discharge Emission Spectroscopy for Direct Analyses

V. Steflekova<sup>1</sup>, S. Karatodorov<sup>1</sup>, P. Zahariev<sup>1</sup>, V. Mihailov<sup>1</sup>, D. Mihailova<sup>2</sup>, J. van Dijk<sup>2</sup> and M. Grozeva<sup>1</sup>

<sup>1</sup> *Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria, e-mail: [vasilka@issp.bas.bg](mailto:vasilka@issp.bas.bg)*

<sup>2</sup> *Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*

We present a comparative novel analytical scheme - laser ablation-hollow cathode glow discharge source (LA-HCD) for elemental analysis. The basic idea of this research is to gain knowledge on the processes in HCD plasma at laser ablation in order the sensitivity and selectivity of the spectral measurement to be improved - important requirement in quantitative spectral analysis of objects.

A major advantage of the suggested combination LA-HCD is the possibility of direct analysis (without special sample preparation), which will allow preservation of the integrity of the object (as sample archeological objects).

Our discharge source is a laboratory-made conventional hollow cathode discharge lamp. The cathode is a hollow cylinder in which the discharge is confined. The laser beam enters the hollow cathode (HC) through one of the open ends and is focused at the opposite end where the sample is placed. The sample is ablated by the laser beam and the ablated material is excited in the discharge zone. In our experiments the sample is a copper disc which acts also as an anode. The novelty of the registration scheme is the detection of the axial side-emission from the discharge through an on-axis slit (< 1 mm width) cut along the hollow cathode cylinder. Such registration scheme allows axial resolution of different ablated species, as well as investigation of their temporal evolution. This is very important when multi-component samples are analyzed. Moreover, this registration scheme enables decoupling of the ablating laser beam and the analytical signals. In this report we present initial studies of the novel LA-HCD set-up with a modified HC.

The performance of the hollow cathode discharge (HCD) as an excitation medium is optimized by varying the input parameters: gas pressure and input voltage. The efficiency of the LA-HCD as a tool for elemental analysis is tested at various conditions: type and pressure of the ambient gas, discharge voltage, current and laser pulse parameters.

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## 4 List of Attendees

The list below is sorted into Alphabetical order by surname.

|                    |                                 |  |
|--------------------|---------------------------------|--|
| Michael Analytis   | Spectruma, Germany              | <a href="mailto:manalytis@spectruma.de">manalytis@spectruma.de</a>   |
| DeAnn Barnhart     | EAG Labs, USA                   | <a href="mailto:dbarnhart@eaglabs.com">dbarnhart@eaglabs.com</a>   |
| Marcel Baak        | ALPS, Switzerland               | <a href="mailto:marcel.baak@bfh.ch">marcel.baak@bfh.ch</a>   |
| Arne Bengtson      | Swerea KIMAB, Sweden            | <a href="mailto:arne.bengtson@swerea.com">arne.bengtson@swerea.com</a>                                     |
| Nerea Bordel       | Univ of Oviedo, Spain           | <a href="mailto:bordel@uniovi.es">bordel@uniovi.es</a>   |
| Juergen Brozek     | Univ Jena, Germany              | <a href="mailto:Juergen.brozek@ini-jena.de">Juergen.brozek@ini-jena.de</a>                                 |
| Andy Burrows       | Nu Instruments, UK              | <a href="mailto:andyb@nu-ins.com">andyb@nu-ins.com</a>   |
| Carine Bazille     | EAG Labs, France                | <a href="mailto:cbazille@eaglabs.com">cbazille@eaglabs.com</a>   |
| John Cantle        | JCS, UK                         | <a href="mailto:johncantle@btconnect.com">johncantle@btconnect.com</a>                                     |
| Partick Chapon     | Horiba Jobin Yvon, France       | <a href="mailto:Patrick.chapon@horiba.com">Patrick.chapon@horiba.com</a>                                   |
| Glyn Churchill     | EAG Labs, USA                   | <a href="mailto:gchurchill@eaglabs.com">gchurchill@eaglabs.com</a>   |
| Udo Collisi        | Hydro Alum Hi Purity, Germany   | <a href="mailto:udo.collisi@hydro.com">udo.collisi@hydro.com</a>   |
| Jennifer Day       | Firth Rixson, UK                | <a href="mailto:jday@firthrixson.com">jday@firthrixson.com</a>   |
| Zoltan Donko       | Wigner Research Centre, Hungary | <a href="mailto:Donko.zoltan@wigner.mta.hu">Donko.zoltan@wigner.mta.hu</a>                                 |
| Varvara Efimova    | IFW Dresden, Germany            | <a href="mailto:v.efimova@ifw-dresden.de">v.efimova@ifw-dresden.de</a>                                     |
| Rolf Grundkowsky   | Hydro Alum Hi Purity, Germany   | <a href="mailto:rolf.grundkowsky@hydro.com">rolf.grundkowsky@hydro.com</a>                                 |
| Philippe Guillot   | Albi Univ, France               | <a href="mailto:philippe.guillot@univ-jfc.fr">philippe.guillot@univ-jfc.fr</a>                             |
| Steve Guilfoyle    | Nu Instruments, UK              | <a href="mailto:steveg@nu-ins.com">steveg@nu-ins.com</a>   |
| Keir Hague         | LECO, UK                        | <a href="mailto:keir.hague@lecouk.com">keir.hague@lecouk.com</a>   |
| Joachim Hinrichs   | ThermoFisher, Germany           | <a href="mailto:joachim.hinrichs@thermofisher.com">joachim.hinrichs@thermofisher.com</a>                   |
| Volker Hoffmann    | IFW Dresden, Germany            | <a href="mailto:v.hoffmann@ifw-dresden.de">v.hoffmann@ifw-dresden.de</a>                                   |
| Thomas Hofmann     | AQura GmbH, Germany             | <a href="mailto:thomas.hofmann@aqura.de">thomas.hofmann@aqura.de</a>                                       |
| Martin Kasik       | EAG Labs, USA                   | <a href="mailto:mkasik@eaglabs.com">mkasik@eaglabs.com</a>   |
| Sabine Kuemmel     | Continental, Germany            | <a href="mailto:sabine.kuemmel@continental-corporation.com">sabine.kuemmel@continental-corporation.com</a> |
| Florence Liggins   | Imperial College, UK            | <a href="mailto:f.liggins11@imperial.ac.uk">f.liggins11@imperial.ac.uk</a>                                 |
| Jeffery Machold    | Special Metals, USA             | <a href="mailto:jmachold@specialmetals.com">jmachold@specialmetals.com</a>                                 |
| Kim Marshall       | LECO, USA                       | <a href="mailto:kim_marshall@lecotc.com">kim_marshall@lecotc.com</a>                                       |
| Sylke Meyer        | Fraunhofer, Germany             | <a href="mailto:sylke.meyer@csp.fraunhofer.de">sylke.meyer@csp.fraunhofer.de</a>                           |
| Cyril Michellon    | EAG Labs, France                | <a href="mailto:cmichellon@eaglabs.com">cmichellon@eaglabs.com</a>   |
| Chiara Modanese    | NTNU, Norway                    | <a href="mailto:chiara@material.ntnu.no">chiara@material.ntnu.no</a>                                       |
| Sohail Mushtaq     | London Metrop. Univ, UK         | <a href="mailto:s.mushtaq@londonmet.ac.uk">s.mushtaq@londonmet.ac.uk</a>                                   |
| Thomas Nelis       | ALPS, Switzerland               | <a href="mailto:Thomas.nelis@bfh.ch">Thomas.nelis@bfh.ch</a>   |
| Ekbal Patel        | MSI, UK                         | <a href="mailto:Ekbal@massint.co.uk">Ekbal@massint.co.uk</a>   |
| Jorge Pisonero     | Univ of Oviedo, Spain           | <a href="mailto:pisonerojorge@uniovi.es">pisonerojorge@uniovi.es</a>                                       |
| Karol Putyera      | EAG Labs, USA                   | <a href="mailto:kputyera@eaglabs.com">kputyera@eaglabs.com</a>   |
| Peter Robinson     | MassCare Ltd, UK                | <a href="mailto:pete@masscare.co.uk">pete@masscare.co.uk</a>   |
| Qian Rong          | Shanghai Ceramics, China        | <a href="mailto:qianrong@mail.sic.ac.cn">qianrong@mail.sic.ac.cn</a>                                       |
| Sergey Ryabov      | Nu Instruments, UK              | <a href="mailto:sergey.ryabov@nu-ins.com">sergey.ryabov@nu-ins.com</a>                                     |
| Marisa Di Sabatino | NTNU, Norway                    | <a href="mailto:mariisa.di.sabatino@material.ntnu.no">mariisa.di.sabatino@material.ntnu.no</a>             |
| Greg Schilling     | LECO, USA                       | <a href="mailto:greg_schilling@lecotc.com">greg_schilling@lecotc.com</a>                                   |
| Peter Siegmund     | Univ Jena, Germany              | <a href="mailto:peter.siegmund@uni-jena.de">peter.siegmund@uni-jena.de</a>                                 |
| Mykola Skulskyi    | Pure Materials, Ukraine         | <a href="mailto:nskul86@gmail.com">nskul86@gmail.com</a>   |
| Petr Smid          | AQura GmbH, Germany             | <a href="mailto:petr.smid@aqura.de">petr.smid@aqura.de</a>   |
| Edward Steers      | London Metrop. Univ, UK         | <a href="mailto:e.steers@londonmet.ac.uk">e.steers@londonmet.ac.uk</a>                                     |
| Vasilka Steflekova | ISSP-BAS, Bulgaria              | <a href="mailto:vasilka@issp.bas.bg">vasilka@issp.bas.bg</a>   |
| Jan Sunderkoetter  | HC Starck GmbH, Germany         | <a href="mailto:jan.sunderkoetter@hcstarck.com">jan.sunderkoetter@hcstarck.com</a>                         |
| Sebastian Timmel   | Fraunhofer, Germany             | <a href="mailto:Sebastian.timmel@csp.fraunhofer.de">Sebastian.timmel@csp.fraunhofer.de</a>                 |
| Rebeca Valledor    | Univ of Oviedo, Spain           | <a href="mailto:rebeca_val@hotmail.com">rebeca_val@hotmail.com</a>   |
| Lene Valvik        | Vigeland Metal Refinery, Norway | <a href="mailto:lene.valvik@vmr.no">lene.valvik@vmr.no</a>   |
| Paola Vega         | Univ of Oviedo, Spain           | <a href="mailto:vegapaola.uo@gmail.com">vegapaola.uo@gmail.com</a>   |
| Cornel Venzago     | AQura GmbH, Germany             | <a href="mailto:cornel.venzago@aqura.de">cornel.venzago@aqura.de</a>                                       |
| Maxim Voronov      | IFW Dresden, Germany            | <a href="mailto:VoronovMV@mail.ru">VoronovMV@mail.ru</a>   |
| Zdenek Weiss       | LECO, Czech Republic            | <a href="mailto:weissz@leco.cz">weissz@leco.cz</a>   |
| James Whitby       | EMPA, Switzerland               | <a href="mailto:james.whitby@empa.ch">james.whitby@empa.ch</a>   |