

Organised by the European Working Group for Glow Discharge Spectroscopy

3rd International Glow Discharge Spectroscopy Symposium



**Hard Days Night Hotel
Central Buildings
North John Street
Liverpool
United Kingdom**

18th – 20th April 2016

Meeting Organisation Committee

Peter Robinson (MassCare Ltd, UK. Chair of EW-GDS)
Arne Bengtson (Swerea KIMAB AB, Sweden)
Petr Smid (Evonik Technology and Infrastructure GmbH, Germany)

Acknowledgements

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Nu Instruments, Wrexham, UK
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Thermo Fisher Scientific GmbH, Bremen, Germany

Also Evans Analytical Group of Syracuse, USA

We also acknowledge the generous extra support from Nu Instruments for the symposium dinner, Thermo Fisher Scientific for the welcome buffet and Mass Spectrometry Instruments for the name badges.

This sponsorship allows us to stage these events at suitable venues without having to set a registration fee that would be prohibitive for some small businesses or research groups, so again we pass on our thanks.



Introduction

We, the Organising Committee, wish to welcome you to the 3rd International Glow Discharge Spectroscopy Symposium (IGDSS2016) taking place in the Hard Days Night Hotel in Liverpool, United Kingdom, from 18th to 20th April 2016. With more than 80 people attending from nearly 20 different countries you can see that the Symposium has a truly international flavour. And with 23 oral presentations and 16 posters the scientific content is exciting with great opportunities for all to see and discuss the work of others.

The topics included in the Symposium will cover all aspects of GDS, with oral and poster presentations given by internationally recognised experts and early stage researchers. While the focus of the Symposium is the analysis of solids by optical emission and mass spectrometry, there will be a wide spread of topics including Fundamentals (GD Processes), Instrumentation, Bulk as well as Thin Film Analysis, Solution Analysis and Application Methodology. This shows that GDS is a field in which very exciting progress is being made all the time.

IGDSS2016 is being organised and driven by the European Working Group for Glow Discharge Spectrometry (EW-GDS), a group that 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 second meeting as a post-symposium following the 1993 York Colloquium Spectroscopicum Internationale (CSI), and its scope was then widened to include bulk analysis, Glow Discharge 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.

Another application for a further Innovative Training Network is currently under consideration and we are hopeful that it will be approved shortly after this meeting.

Following the close of the Symposium activities there will be a meeting of EW-GDS to discuss the plans for work over the next year or so, including the very early planning for the 4th International Glow Discharge Spectroscopy Symposium. All will be welcome to attend, so please feel free to discuss your interest with Dr Peter Robinson, the Chair of EW-GDS, or any of the Organising Committee during the Symposium.

At each EW-GDS meeting we present a prize to the most impressive presentation (oral or poster) from the Symposium, with preference being given to younger scientists. This is kindly sponsored by the manufacturers of all Glow Discharge instruments, both optical and mass, and is known as the Payling Prize in recognition of Richard Payling who died in a tragic mountaineering accident in February 2004 after a career that contributed significantly to the world of GDS. This will be presented at the end of the Symposium, on the morning of Wednesday 20th April.

Again can we welcome you to IGDSS2016 and hope that you have a scientifically rewarding Symposium as well as a good time in the wonderful city of Liverpool, European City of Culture in 2008.

3rd International Glow Discharge Spectroscopy Symposium

Liverpool, UK

18th to 20th April 2016

Programme of Events

Key

- Inv x Invited Lecture
O x Oral Presentation
P x Poster

Sunday 17th April 2016

- 15:00 Registration Opens
19:00 Welcome Buffet Sponsored by Thermo Fisher Scientific
21:00 Close

Monday 18th April 2016

- 09:00 Welcome and Opening Comments from Chair of EW-GDS

Session Chair: Volker Hoffmann

- 09:10 Inv 1 Challenges in GD-TOFMS for Direct Analysis of Innovative Materials. *Jorge Pisonero, Oviedo University, Spain.*
10:00 O 1 Investigation of GD-OES Spectra in the First Fraction of a Second – Ways to Improve Extreme Thin Film Analysis. *Arne Bengtson, Swerea KIMAB AB, Sweden.*

- 10:25 Coffee

Session Chair: Rosario Pereiro

- 10:55 O 2 Role of the Triplet Metastable Levels in Ionization/Excitation of Palladium Atom in Glow Discharge Plasmas Using Several Plasma Gases. *Kazuaki Wagatsuma, Inst for Materials Reseach, Japan*
11:20 O 3 Considerations on Accuracy in GD-OES and the Use of the Standard Model. *Zdenek Weiss, LECO Instruments, Czech Republic.*
11:45 O 4 Applications of Microsecond Pulsed Glow Discharge for OES Analysis. *Maxim Voronov, Univ of Munster, Germany.*

- 12:10 Lunch

Session Chairman: Peter Robinson

- 13:30 O 5 Overview of the Latest Improvements to the Nu Astrum High Resolution GDMS. *Glyn Churchill, Nu Instruments, UK*
13:55 O 6 Is Automation a Reality in HR-GDMS? *Ekbal Patel, Mass Spectrometry Instruments Ltd, UK*
14:20 O 7 Applications of Microsecond Pulsed Fast Flow Glow Discharge Mass Spectrometry (μ s-FF-GD-MS). *Joachim Hinrichs, ThermoFisher Scientific, Germany*

- 14:45 Coffee

Session Chair: Petr Smid

- 15:15 O 8 An Unordinary Application of GDMS: Impurities and Isotope Ratios of "Avogadro" Silicon. *Angela Kaltenbach, Physikalisch-Technische Bundesanstalt, Germany*
- 15:40 O 9 Use of GDMS for Purity Statements of High Purity Materials Serving as Primary Standards. *Silke Richter, BAM, Germany.*
- 16:05 O 10 Novel Glow Discharge Mass Spectrometry Techniques: Zoom-TOFMS and Distance-of -Flight Mass Spectrometry. *Steven Ray, State University of New York at Buffalo, USA*
- 16:30 Close Meeting for the Day
- 18:00 User Meetings, Invitation Only
- 20:00 User Meetings Close

Tuesday 19th April 2016

09:00 Welcome and Daily Notices from Chair

Session Chair: Arne Bengtson

- 09:10 Inv 2 Ultra High Throughput Surface Elemental Mapping Via Glow Discharge Optical Emission Spectroscopy. *Gerado Gamez, Texas Tech University, USA*
- 10:00 O 11 Surface Modification of Co-Cr-Mo Alloy Using a Hollow Cathode Type Oxygen Glow Discharge Plasma and the Characterization by Optical Emission and X-Ray Photoelectron Measurements. *Kosue Satoh, Inst of Materials Research, Japan*
- 10:25 Coffee

Session Chair: Silke Richter

- 10:55 O12 Investigations Towards Matrix Independent Calibrations in Glow Discharge Mass Spectrometry. *Petr Smid, Evonik Technology and Infrastructure GmbH, Germany*
- 11:20 O 13 Further Studies of the Role of Asymmetric Charge Transfer and Other Ionisation Processes in Glow Discharge Mass Spectrometry. *Sohail Mushtaq, London Metropolitan University, UK*
- 11:45 O 14 Comparison of the Effects of Small Amounts of Molecular Gases in Argon and Neon Plasmas Using the Element GD Glow Discgarge Mass Spectrometer. *Edward B. M. Steers, London Metropolitan University, UK.*
- 12:10 Lunch

Session Chair: Steven Ray

- 13:30 O 15 Renewable Energy: How GDOES Can Assist in Development of Thin Film Solar Cells, Li Batteries (LTO) and Wind Power. *Rudiger Meihnsner, Spectruma Analytik GmbH, Germany*
- 13:55 O 16 Real Time Measurement of Layer Thickness, Erosion Rates and Crater Depth in Glow Discharge Optical Emission Spectrometry. *Sofia Gaiaschi, Horiba Scientific, France.*
- 14:20 O 17 Application of XYZ Manipulator in Glow Discharge Mass Spectrometer for Depth Profile Analysis. *Maciej Misnik, Inst of Tele and Radio Technology, Poland.*
- 14:45 Coffee
- 15:15 Poster Session. Authors Will Attend Posters for Discussion
- 16:45 Close Meeting for the Day
- 19:30 Symposium Dinner Sponsored by Nu Instruments

Wednesday 20th April 2016

09:00 Welcome and Daily Notices

Session Chair: Jorge Pisonero

09:10 Inv 3 A General Overview of the Application and the Experiences on GD-MS. *Yutaka Hayashibe, Mitsubishi Metals Corporation, Japan*

10:00 O 18 Application of GD-MS for Purity Assessment in NIM, China. *Tao Zhou, National Inst of Metrology, China*

10:25 Coffee

Session Chair: Zdenek Weiss

10:55 O 19 2D Analysis in GDMS: Application of In Situ Translation of Sample. *Piotr Konarski, Inst of Tele and Radio Technology, Poland*

11:20 O 20 Evaluation of PP-TOFMS for Depth Profile Analysis. *Rosario Pereiro, Oviedo University, Spain.*

11:45 Presentation of the Payling Prize

12:15 Symposium Close

12:15 Lunch

13:30 EW-GDS Meeting

15:00 Close Meeting

Posters

- P1 A Time Resolved Study of Thin Coated and MultiLayered Composite Materials Using the Astrum GDMS. *DeAnn Barnhart, Nu Instruments, UK.*
- P2 Trace Analysis of Gas Phase Elements in Metals by Fast-Flow GD-MS. *Joachim Hinrichs, Thermo Fisher Scientific, Germany*
- P3 Round Robin -- Quantification of N in Nitrided Steels. *Marcel Baak, Bern University, Switzerland*
- P4 Effects of H₂, O₂ and N₂ on Excitation of Cu⁺ ions in a Cu/Ne Glow Discharge: Transition Rate Ratio Diagrams. *Zdenek Weiss, LECO Instrumente, Czech Republic*
- P5 Preliminary Analytical Results from a DBD Neon Plasma Jet at Atmospheric Pressure Coupled to a TOF-MS. *Philippe Guillot, University of Toulouse, France.*
- P6 Spatiotemporal Distribution of Neon Gas and Air Species from a DBD Plasma Jet at Atmospheric Pressure. *Laurent Therese, University of Toulouse, France*
- P7 Does asymmetric charge transfer play an important role as the ionization mode in low power-low pressure GD-MS? *Sohail Mushtaq, London Metropolitan University, UK*
- P8 Determination of 13 Matrix-Dependent RSFs for Nickel Matrix using Doped Pressed Powder Samples as Needed for Fast Flow Glow Discharge Mass Spectrometry. *Jens Pfeifer, BAM, Germany.*
- P9 Concentric APGD Ionisation Source for Mass Spectrometry: Operation Regime Characterisation. *Jonaton Fandino, University of Oviedo, Spain*
- P10 Analysis of Silicon by Radio Frequency Glow Discharge Mass Spectroscopy. *JaeYeol Yang, KBSI, Korea*
- P11 Analysis of Low Melting Point such as Gallium by Low Discharge Mass Spectrometry. *JaeSik Yoon, KBSI, Korea.*
- P12 Surface Sample Preparation for EMPA using GDOES. *Sergey Khromov, NTNU, Norway*
- P13 Procedures Used for Control of XYZ Manipulator in GD-MS Analysis. *Aleksander Zawada, Institute of Tele and Radio Technology, Poland*
- P14 Analysis of Alumina Powder According to Target Design by Glow Discharge Mass Spectrometry. *HangYoul Ryu, KBSI, Korea*
- P15 Optical Spectrometric Spatial Filtering by Digital Micromirror Arrays: Prospectus for Atomic Spectrometry. *Steven Ray, State University of New York, USA*
- P16 Characterization of DLC-Layers. *Christin Schubert, Continental Automotive GmbH, Germany*

Abstracts

The following pages contain the abstracts for all the presentations to be given during the Symposium. They are grouped into four sections:

In1 to In3 are the three invited talks.

O1 to O20 are the scientific oral presentations

P1 to P16 are the posters that will be on display throughout the Symposium

CHALLENGES IN GD-TOFMS FOR DIRECT ANALYSIS OF INNOVATIVE MATERIALS.

Jorge Pisonero¹, Cristina González¹, Jonatan Fandiño¹, Alfredo Sanz-Medel² and Nerea Bordel¹

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Manufacturing industry requires the development and characterization of challenging materials (e.g. photovoltaic cells, production of high wear-resistant coatings, hard-disks, Ni and Co super-alloys, etc.). In this context, the ability to accurately analyse and characterise bulk and layered materials is essential for the development of new products and processes.

Atomic spectrometry techniques have long been used for direct chemical characterization of materials. In particular, for the analysis of layers and coatings, a range of techniques is available, including Secondary Ion Mass Spectrometry (SIMS), Secondary Neutral Mass Spectrometry (SNMS), Auger Electron Spectroscopy (AES) or X-Ray Photoelectron Spectroscopy (XPS). These techniques provide very valuable information about the chemical composition of the surfaces/coatings; however they also have some major drawbacks, such as high operating costs, complex sample pre-treatment and handling, low sample throughput and/or severe matrix effects that result in difficult quantification procedures. In order to overcome some of these drawbacks Glow Discharge Spectroscopy, and in particular Glow Discharge Time-of-Flight Mass Spectrometry (GD-TOFMS), is proposed as a complementary methodology that provides an ideal solution for fast and accurate bulk and layer analyses [1,2].

In this work, we critically evaluate the analytical capabilities and limitations of GD-TOFMS for the analysis of challenging materials. In particular, this GD ion source is operated in pulsed radiofrequency mode, allowing the analysis of conducting and non-conducting materials with high depth resolution and moderate sensitivity.

[1] C. Venzago, J. Pisonero; "Glow discharge mass spectrometry", Sector Field Mass Spectrometry for Elemental and Isotopic Analysis (editors T. Prohaska, J. Irrgeher, A. Zitek and N. Jakubowski), Series of New Developments in Mass Spectrometry, Volume 2015-January, Issue 3, 2015, Pages 319-380; DOI: 10.1039/9781849735407; ISBN: 978-1-84973-392-2.

[2] J. Pisonero, N. Bordel, C. Gonzalez de Vega, B. Fernández, R. Pereiro, A. Sanz-Medel, "Critical evaluation of the potential of radiofrequency pulsed glow discharge time of flight mass spectrometry for depth profile analysis of innovative materials", Analytical and Bioanalytical Chemistry, 2013, 405(17), 5655-5662. DOI 10.1007/s00216-013-6914-1.

ULTRA-HIGH THROUGHPUT SURFACE ELEMENTAL MAPPING VIA GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY

Gerardo Gamez, John Usala, Trevor Adesso.

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Traditionally, glow discharge optical emission spectroscopy (GDOES) has been employed for solid sample bulk analysis through spectrally resolved detection. Next, temporally resolved detection pushed the development of GDOES as a depth profiling technique. Recently, coupling of GDOES with spectral imaging systems, as well as operating the GD in pulsed mode and under higher pressures, has allowed access to two more dimensions of information within the sputtered crater, thus expanding the capabilities to three dimensional surface elemental mapping.

The potential impact of the new GDOES capability becomes apparent when one recognizes the following: a) traditional elemental mapping techniques based on pixel-to-pixel rastering are throughput limited, such that large diameter surfaces require many hours for measuring an elemental map with enough pixel density; b) GDOES elemental mapping does not require pixel-to-pixel rastering. Thus, GDOES elemental mapping has shown it can yield chemical composition landscapes with several orders of magnitude faster acquisition times compared to traditional techniques. As a result, elemental mapping of large diameter surface samples has the possibility of being implemented in routine analysis and diagnostics, as opposed to being limited to a few fundamental studies.

Recent advances in GDOES elemental mapping to be presented include: novel lamp geometries to implement GDOES elemental mapping on large diameter surfaces, novel spectral imaging techniques to allow wider accessibility of the technique, and development of applications enabled by GDOES elemental mapping.

A GENERAL OVERVIEW OF THE APPLICATION AND THE EXPERIENCES ON GD-MS

Yutaka Hayashibe, Takahiro Abe

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Among the several mass spectrometry techniques for elemental analysis, Glow Discharge Mass Spectrometry (GD-MS) has an excellent potential for direct solid sample analysis. The application of GD-MS is increasing because they offer several important advantages, such as multi-element capabilities (almost all metals and non-metals can be determined), simple and easy to use, low matrix effects, high sensitivity and low limits of detection in various matrix (in the range of ppb levels and even sub ppb), and wide applicability for conductive and semi conductive materials with minor sample pretreatment. It is believed that the accurate elemental analysis with GDMS can easily be realized by utilizing Relative Sensitivity Factor (RSF).

Mitsubishi Materials Group is the largest smelter and refinery company in Japan, which has been producing base metals and precious metals. Furthermore, we also produce the electronic materials and components, which are advanced materials and tools, chemical products, electronic components and polycrystalline silicon. GD-MS is the most important elemental analysis of solid sample to support the official analytical method (JIS or ISO) and to qualify our original products as the in-house method.

We have introduced the first GD-MS (VG Elemental, VG-9000) in 1989, and the second one (Nu Instrument, Astrum) in 2012. Usually, for the quantitative elemental analysis using GD-MS, establishment of RSF and also maintaining the stability of GD-MS are the very first requirement for accurate analysis. It is very important to understand the mechanism of the variation range of the RSF value for different elements. In general, RSFs are influenced by several factors. I will introduce some of our experimental results of RSF related to those influencing factors. In this presentation, I also will introduce some of the practical applications of GD-MS obtained in our laboratory [1, 2], including its applications to the proficiency testing exercise of gold fire assayer in LBMA [3]. Finally, I would like to propose and suggestions for the future improvement in instrument and offering requests to the GD-MS manufacturer, from our technical standpoint and being a heavy user of GDMS.

[1] Y. Nakamura et.al, Bunseki Kagaku, 40(1991) T209.

[2] ASTM F2405-0004, Standard Test Method for Trace Metallic Impurities in High Purity Copper by High-Mass-Resolution Glow Discharge Mass Spectrometer.

[3] <http://www.lbma.org.uk/proactive-monitoring-programme>

INVESTIGATION OF GD-OES SPECTRA IN THE FIRST FRACTION OF A SECOND – WAYS TO IMPROVE EXTREME THIN FILM ANALYSIS

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In GD-OES depth profiling of very thin films, it is common to observe surface peaks of “unexpected” elements given the material analysed. Previous research has shown that several of these signals are in fact false, due to emission from short-lived molecular species. In addition, it has been shown that a broad continuum emission from dissociating hydrogen molecules causes a decaying, elevated background level through a large segment of the optical spectrum. For improved accuracy and “trueness” in thin film analysis, these effects must be taken into account in the interpretation and quantification of the data.

In this work, spectra from the initial stage of the glow discharge has been recorded at high acquisition rate (100 Hz) using a state-of-the-art CCD spectrometer of high sensitivity. The spectra allow a more detailed study of the initial molecular and background emission than previously possible. However, they also show that several elements (in addition to C, H, and O) indeed “contaminate” almost any sample, which means that some of the “unexpected” surface peaks are in fact true.

One further issue in extreme thin film analysis is the inevitable variation in the plasma conditions before stabilisation. This has an impact on the emission intensities and thereby the emission yields, which form the basis for quantification of the signals. The information in complete spectra provides more detailed information also on these effects.

Suggestions on how to improve the accuracy in extreme thin film analysis by making use of the added information available in complete spectra will be presented and discussed.

ROLE OF THE TRIPLET METASTABLE LEVELS IN IONIZATION/EXCITATION OF PALLADIUM ATOM IN GLOW DISCHARGE PLASMAS USING SEVERAL PLASMA GASES

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Glow discharge optical emission spectrometry (GD-OES) is extensively employed for the direct analysis of solid samples, because the excitation source has several benefits for the analytical application: rapid sampling through cathode sputtering, minimal sample pretreatment, and wide concentration range. In addition, GD-OES would provide more accurate analytical results under high signal-to-background-ratio conditions compared with other plasma sources, because of the low background continuum. The characteristics of the GD plasma are largely varied by several discharge parameters, such as voltage, current, plasma gas composition and the pressure. It has been reported in the GD plasma that the kind of the plasma gas principally determines the spectrum pattern: different kinds of spectral lines are excited depending on the kind of the plasma gas employed^{1,2}. Whereas argon is usually used in conventional GD-OES, various plasma gases and their mixtures have been thus investigated as alternative plasma gases^{1,2}. Their observed spectrum patterns were different from each other, in which the difference is not only in their relative intensities but in the kind of emission lines that can be excited. This effect could be explained by selective excitation to a particular excited level of analyte atom through asymmetric charge-transfer collision, which was first discussed in the copper spectrum by Steers³

In the case of palladium, the GD spectrum patterns are drastically changed when different plasma gases, such as argon, krypton, neon, and helium, are employed. It was observed that particular emission lines of singly-ionized palladium were much more intense in the argon plasma than the other gas plasmas. For instance, Pd II 248.652 nm ($4d^85p\ ^4G_{9/2}$, 8.344 eV) and Pd II 244.617 nm ($4d^85p\ ^4D_{5/2}$, 8.426 eV), having higher emission intensities, are emitted from the argon plasma; however, the excitation to their upper energy levels cannot be explained by a charge-transfer collision between the ground state of palladium atom ($4d^{10}\ ^1S_0$) and argon ion ($3p^5\ ^2P_{3/2,1/2}$), due to lack of the total excitation energy. We should notice that there are metastable triplet levels of palladium atom ($4d^95s\ ^3D_{3,2,1}$) about 1 eV above the singlet ground state level, where optical transitions between them are strictly forbidden due to the same parity. It can be suggested that the excitation of the intense Pd II lines would be attributed to charge-transfer collision with the triplet metastables of palladium atom, because of good matching in the total excitation energy as well as in the spin conservation. Other Pd II lines resulting from the similar excitation mechanism were observed in the GD plasmas with neon or helium gas.

[1] K. Wagatsuma and H. Honda, *Spectrochim. Acta Part B*, 60 (2005) 1538.

[2] K. Wagatsuma, *Anal. Bioanal. Chem.*, 393 (2009) 2067.

[3] E.B.M. Steers, R.J. Fielding: *J. Anal. Atom. Spectrom.*, 2 (1987) 239.

CONSIDERATIONS ON ACCURACY IN GD-OES AND THE USE OF THE STANDARD MODEL

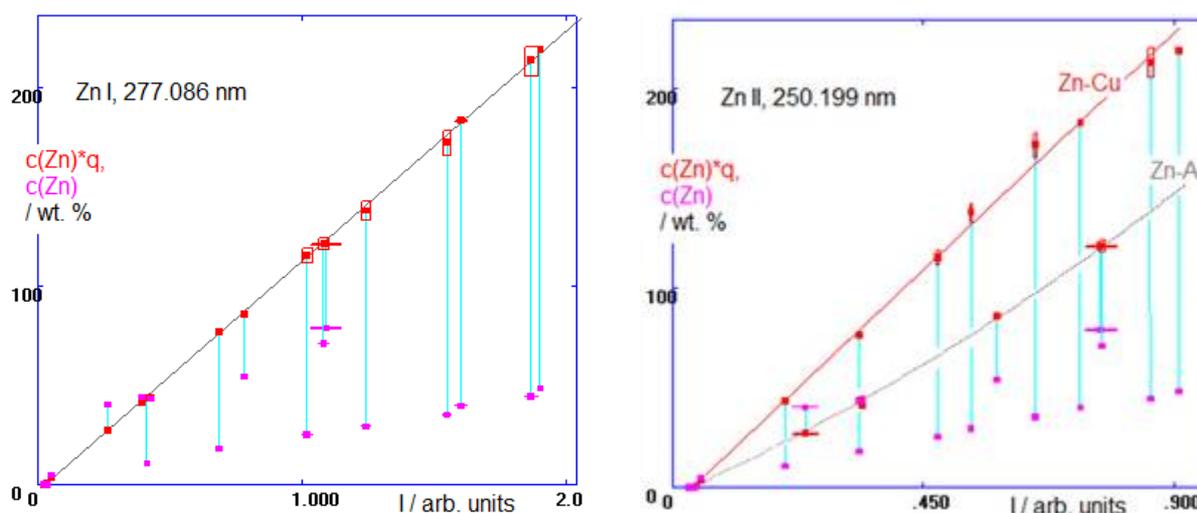
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The success of GD-OES is largely associated with the 'standard' calibration model, the basis of all existing calibration/quantification schemes, aimed at an accurate elemental analysis of wide ranges of materials (matrices). In this model, the basic relation between the composition of the sample and the recorded intensities of emission lines of the elements present is

$$I_{\lambda(E),M} = R_{\lambda(E)} c_{E,M} q_M \quad (1)$$

where $I_{\lambda(E),M}$ is the intensity of certain emission line $\lambda(E)$ of an element E , $c_{E,M}$ is the concentration of this element in a material M analyzed, q_M is the sputter factor of the material M and the proportionality constant $R_{\lambda(E)}$ is the emission yield of line $\lambda(E)$. The standard model holds with a stunning accuracy for certain class of emission lines of many elements. There are, however, exceptions to this rule, usually called the *matrix effects*. Despite a lot of effort that was put into this topic, it is still not understood well why exactly the standard model holds and why some matrix effects occur. This area is still largely in an empirical domain. A clue to why the standard model holds may be found in the classical treatment by Ferreira and Human [1] of transport processes in the GD source and by a small extension thereof.



As an example, an excitation-related matrix effect occurring in the analysis of zinc in various alloys is shown in the two plots above: whilst the Zn I line at 277.086 nm clearly follows the standard model for the samples used (and other zinc atomic lines also), the calibration function of zinc, based on the Zn II line at 250.199 nm, is split into two separate curves, one for Cu-Zn alloys and another for Al-Zn alloys. Other zinc ionic lines behave likewise. The data in both plots come from the same experiment and identical samples are shown: compare the distributions of ordinate values of the points [2]. Some consequences for the analytical practice of this kind of behavior can be found in the review [3].

In the presentation, the standard model will be discussed, some matrix effects will be mentioned and some thoughts about accuracy in GD-OES will be presented.

References

- [1] N.P. Ferreira and H.G.C. Human, *Spectrochim. Acta, Part B*, **36**, 1981, 215-229
- [2] Z. Weiss, E.B.M. Steers, P. Šmíd, *J. Anal. At. Spectrom.*, **20**, 2005, 839-846
- [3] Z. Weiss, *J. Anal. At. Spectrom.*, **30**, 2015, 1038-1049

APPLICATION OF MICROSECOND PULSED GLOW DISCHARGE FOR OES ANALYSIS

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The application of a microsecond Pulsed Glow Discharge (μ s-PGD) for routine OES analysis was investigated. Therefore, many spectral lines of different elements were detected using μ s-PGD in DC mode applied to a Spectrums GDA650 instrument with CCD detection and a Spectrums GDA750 instrument with polychromator and PMT detection. In comparison to continuous GD, an enhancement of the detected signals of 3-8 times was found for many spectral lines; few lines are enhanced by more than 10 times. Not surprisingly, it was found that those lines are stronger enhanced, which have a strong emission prepeak.

OVERVIEW OF THE LATEST IMPROVEMENTS TO THE NU ASTRUM HIGH RESOLUTION GD-MS.

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The ability to accurately and precisely quantify elemental composition from matrix to sub-ppb (parts per billion, ng/g) levels is virtually unique to GD-MS.

The Nu Astrum high resolution glow discharge mass spectrometer uses a low flow, low power, cryo-cooled discharge cell which allows a large range of solid materials to be analysed.

The first Astrum was commissioned in 2010, and there are now over 20 installed worldwide including the USA, Europe, Japan and China. The Astrum has a diverse customer base, ranging from refineries for high purity materials (including copper, indium and gallium) to manufacturers of metal alloys such as nickel and cobalt based superalloys. The Astrum is also being utilised in research and contract laboratories, which require the ability to analyse a wide range of materials on the same instrument. The continuing development of the Astrum has resulted in numerous improvements. These include automatic control of the discharge gas flow rate to enable the current and voltage to remain constant without user intervention, and the redesigning of the line of sight valves to virtually eliminate any gas leaks by the use of a bellows seal. This has the added benefit of increased lifetime.

Building upon the improvements to the cooling system and the addition of the option of supplying liquid nitrogen from an atmospheric dewar, the system software has been improved to allow cooling to be started automatically at a set time in the morning and switch off at the end of the last acquisition run. The improvements in the cooling and heating of the cell have also allowed for the time required to switch between alternative discharge gases to be optimised.

Examples of these and other improvements to the Astrum will be given in this talk as well as data obtained during the development processes.

IS AUTOMATION A REALITY IN HR-GDMS?

Ekbal Patel

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Most modern Instruments are fully automated in terms of their operation based on optimum operation and data processing. However, there can be issues with regards to the quality of data if for instance, there is contamination or the sample analysis is using standard RSF. Will automation address these issues? Will it also assist in cases where direct comparison is required or in a production line where a quality procedure is required or simply for observing deviations from known defined standards? The automation that is considered is based on using a new approach at the front end of the Instrument. The GD90 design is now enhanced with a dual chamber and an Autosampler capable of having several sizes of carousel. With this new approach, contamination can be minimised as the plasma chamber is removable with the sample. Multiple samples consisting of pin and flats can now be analysed unattended.

With the Autosampler, the ability to analyse any sample in similar conditions enables the determination of the RSF from a known sample in real time and then applying them to the unknown samples. Using this method, any variation in temperature, plasma condition or instrumentation will be compensated. In addition, using a known blank standard, cross contamination issues can be checked. The Autosampler also has a separate cooling and pre-sputter area within the Vacuum chamber and away from the MS Analysis area. This will save considerable time per analysis.

APPLICATIONS OF MISCROSECOND PULSED FAST FLOW GLOW DISCHARGE MASS SPECTROMETRY (μ s-FF-GD-MS)

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Sector field glow discharge mass spectrometry has gained renewed interest over the last years due to the significantly increased requirements for high purity metals, alloys, semiconductors and ceramics, especially by the aerospace, electronics and photovoltaic industries.

The Thermo Scientific ELEMENT GD PLUS GD-MS features a pulsed glow discharge (μ s-FF-GDMS) for improved performance and extending the application range. The main areas for elemental analysis of conductive and non-conductive solids by μ s-FF-GDMS are: (i) bulk metal analysis with improved stability, (ii) non-conductive materials trace metal analysis using a secondary electrode, and (iii) advanced semiquantitative depth profiling.

For the traditional GD-MS market of bulk metals analysis, the pulsed mode results in enhanced stability, minimizing calibration efforts. The source parameters are widely adjustable with minor influence on the elemental ratios analyzed. The more efficient ionization mechanism sputters less sample material at similar sensitivity, causing smaller amounts of re-deposits in the anode and thus less cleaning effort. It has been shown that in >2 hours sputter time elemental ratios vary only by 5-10%, equivalent to ~10 sample runs without any source cleaning.

For the analysis of non-conducting materials, e.g. alumina powder using a secondary electrode, pulsed GD-MS is approaching the stage of a routine technique for onsite production control. The commonly accepted semiquantitative calibration approach developed for bulk metal analysis is also applicable, opening up a method for quick full survey analyses that avoids issues with sample digestion. This is a true value-added alternative to the previously established GD-MS method in co-axial geometry discharge cells using secondary cathodes. The older approach usually requires one to two hours for full surveys, compared to typically 15 to 20 minutes for the ELEMENT GD PLUS.

Depth profiling on the ELEMENT GD PLUS shows a boost in performance, enabling quantification of major to trace elements from thin layers of several nanometers up to hundreds of micrometers. The crater profile shows a flat bottom, a prerequisite for layer detection, and the use of smaller anode diameters maintains the sensitivity per sputter area. The main advantage of GD-MS for depth profiling, compared to techniques like SIMS or GD-OES, is the ease of concentration calibration: using the semiquantitative calibration approach, the measured concentrations for every scan are typically within 30% of the true value without any further sample information necessary. At the same time, still typical detection capabilities of sub-ppm levels are maintained.

AN UNORDINARY APPLICATION OF GDMS: IMPURITIES AND ISOTOPE RATIOS OF “AVOGADRO”-SILICON.

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The “Avogadro“-project was initiated to redefine the SI base unit “kilogram”, made necessary due to increasing deviations of up to 50 ppb in a time frame of 100 years being found between the masses of the international prototype and the official copies used to define the unit. Consequently, the project is aimed at relating the unit “kilogram” to the fundamental Avogadro constant instead of a material artefact. In turn, this requires the re-determination of the Avogadro constant with a drastically reduced combined standard uncertainty of $u_{rel}(N_A) < 1.0 \times 10^{-8}$ instead of $u_{rel}(N_A) = 3.1 \times 10^{-7}$ [1].

For this purpose almost perfect silicon spheres, highly enriched in ^{28}Si , were produced to determine the number of atoms contained in them. A vital part of this undertaking is the verification of the isotopic composition and the corresponding mass of the silicon utilised. However, to calculate the accurate mass of the spheres it is crucial to identify any impurities altering either an isotopic ratio of silicon or the mass of the spheres themselves.

Glow Discharge Mass Spectrometry is an excellent technique to analyse impurities in a high purity solid (semi-)conductive material like the “Avogadro“-silicon over the mass of nearly the entire periodic table. Hence, utilising a Nu Instruments Nu Astrum GDMS, several pin-shaped samples from different parts of the zone-refined silicon monocrystals used to machine the spheres were analysed for their impurities. The results show the extremely high purity of the material but also variations in the quantity and composition of the impurities as well as they are supporting the silicon isotopic compositions of the material analysed by multi-collector ICPMS.

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USE OF GDMS FOR PURITY STATEMENTS OF HIGH PURITY MATERIALS SERVING AS PRIMARY STANDARDS

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The realisation and dissemination of primary standards is of fundamental importance for the comparability of measurement results through traceability in all fields of chemical analysis.

Primary standards are materials with known total purity and, therefore, appropriate to realise the link with the International System of Units (SI).

Materials of ideal purity do not exist in reality. Therefore the determination of the mass fraction of the main component using a direct or indirect approach is necessary. The direct determination is limited by the lack of element specific detection methods with an adequate precision. In order to achieve a sufficiently small uncertainty (i.e. < 0.01%) of the total mass fraction of the matrix element it is necessary to determine all possible impurity contributions and to subtract their sum from the ideal purity of 100 %.

GD-MS has the potential to significantly reduce the effort for purity determination, because it is a fast, sensitive multi-element analysis without extensive sample preparation. For many analytes this technique has very low limits of quantification, a dynamic range over several orders of magnitude and the additional benefit that contaminations and losses through dissolution are avoided.

In this presentation the use of different calibration strategies are compared and their potential and limitations are highlighted. It is shown that the concept of Relative Sensitivity Factors (RSFs) provides good approximations especially for high purity materials. However, it only works with large uncertainties on the results.

Furthermore, the preparation of synthetic pressed powder samples doped with liquids or used for the determination of both metallic and non-metallic impurities are described. With this approach an efficient determination of metallic impurities by GD-MS measurements with a significantly reduced target uncertainty of 20 % could be achieved. The determination of impurities has been evaluated by independent analytical methods such as HR-ICP-MS, Electrothermal Atomic Absorption Spectroscopy (ETAAS); Carrier Gas Hot Extraction (CGHE) and combustion analysis.

NOVEL GLOW DISCHARGE MASS SPECTROMETRY TECHNIQUES: ZOOM-TOFMS AND DISTANCE-OF-FLIGHT MASS SPECTROMETRY.

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Several new types of velocity-based mass spectrometry techniques have been recently developed which will provide enhanced analytical capability for glow discharge mass spectrometric determinations.

Distance-of-Flight mass spectrometry (DOFMS) is a close analog to the more conventional Time-of-Flight Mass Spectrometry (TOFMS) used in GD-MS, but differs in the important point that it spatially separates ions of different mass-to-charge ratio (m/z). As a consequence, the DOFMS approach can be used with solid state array-based mass spectrometry detectors, which possess many advantages over conventional detectors for MS.

In GD applications, these advantages are principally the very wide dynamic range simultaneously available to each m/z being investigated ($>10^9$), and the fact that each individual m/z is detected by an independent channel of the detection system which can be tailored to the flux of that m/z to optimize S/N.

In a second example, a new approach to TOFMS is described which permits the resolution and S/N of an analysis to be increased over a small portion of the atomic mass range. The Zoom-TOFMS strategy uses a new constant-momentum acceleration technique to increase the mass resolving power of the mass spectrometric analysis, but only over a window of the mass spectrum. In GD-MS techniques, this approach may permit isobaric overlaps to be overcome by simple manipulations of electrostatic pulses and fields. More importantly, Zoom-TOFMS can be implemented in conventional TOFMS instruments quite readily, and can be 'switched' between a conventional TOFMS mode and a 'Zoom' mode of operation on-the-fly. The current capabilities and future outlook for these strategies will be examined.

SURFACE MODIFICATION OF Co-Cr-Mo ALLOY USING A HOLLOW CATHODE TYPE OXYGEN GLOW DISCHARGE PLASMA AND THE CHARACTERIZATION BY OPTICAL EMISSION AND X-RAY PHOTOELECTRON MEASUREMENTS

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Cobalt-based alloys, as well as Ti alloys, have been used for biomaterials such as artificial hip and knee joints due to their excellent corrosion and wear resistances [1]; however, it has also reported that several alloying elements such as Ni may cause allergies and cancer in living organisms [2]. Thus, there has been a strong demand to suppress an elution of the toxic elements from the alloys into a human body for obtaining biomaterials with long lifetimes. An oxide layer needs to be formed on the alloys as a barrier layer between body fluid and the alloy substrate by using surface treatment. In our previous study, we first presented an application of an oxidation technique using a parallel plate type d.c. glow discharge plasma with pure oxygen gas on a biomedical Ti-6Al-4V alloy to suppress an elution of the toxic Al and V in the alloy into a physiological environment [3]. In this study, the surface treatment of a Co-Cr-Mo alloy was carried out by using a hollow-cathode type d.c. glow discharge plasma with pure oxygen gas or He-O₂ mixed gas. It is expected that the hollow-cathode plasma could produce more reactive conditions for any reactions between excited oxygen species and the sample surface than a conventional planar-cathode plasma, because it would have higher electron number density. In order to understand the fundamental process regarding surface reactions occurring in the plasma, the plasma characteristics were closely evaluated by optical emission spectrometry.

Co-28Cr-6Mo alloy was used as a sample for surface treatment. Self-produced surface treatment equipment with an emission spectrometer was employed. A cathode electrode was made of stainless steel. A d.c. power supply was operated in a constant current mode, and helium gas containing small amounts of oxygen gas was used as a plasma gas. The emission spectrum was observed from the axis direction of the hollow cathode to identify excited states of the plasma. The chemical state, the elemental distribution in a depth direction, and the thickness of the oxide layers were evaluated by X-ray photoelectron spectroscopy (XPS).

Helium atomic lines, atomic and ionic lines of oxygen atom, and molecular bands of oxygen molecule ion were observed in the emission spectra. These intensities drastically changed depending on the mixing ratio of He-O₂ mixed gas; particularly, the emission intensity of the O₂⁺ molecular bands was largely enhanced in the He-O₂ plasma compared to the pure O₂ plasma. These band spectra are assigned to an electronic transition from the ⁴Σ_g⁻ to ⁴Π_u⁻ states of oxygen molecule ion, whose excitation energies are 18–19 eV from the ground state of oxygen molecule. It can be thus suggested that a Penning-type ionization process with metastables of helium atom (1s2s ¹S₀ and ³S₁, c.a. 20 eV) is an excitation mechanism to increase the number density of the corresponding excited state in the He-O₂ plasma. This enhancement of the O₂⁺ species in the plasma would also exert an influence on the resultant oxide layer, such as the chemical composition and the layer thickness. XPS analysis reveals that the oxide layer which was predominantly comprised of Fe and Cr oxides was formed by the surface treatment. The thickness of the oxide layer varied with the mixing ratio of He-O₂; on the other hand, there was no significant difference in the composition of the layer.

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INVESTIGATIONS TOWARDS MATRIX INDEPENDENT CALIBRATIONS IN GLOW DISCHARGE MASS SPECTROMETRY

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Mass spectrometry (MS) utilizing analytical glow discharges (GD) as an atomization and ionization source has proved to be a very sensitive, fast and reliable analytical technique for direct solid state trace and ultra-trace elemental analysis with small requirements on sample preparation (GD-MS). The quantification approach applied traditionally in GD-MS is based on the concept of standard relative sensitivity factors (StdRSF). This approach compensates the lack of matrix-specific reference materials for various elements in trace concentration range and provides fairly accurate analytical results; the uncertainty associated with this quantification concept amounts up to a factor of 2 depending on the element analyzed [2]. Matrix and plasma parameter dependence of the StdRSF when using the so called 'static flow' cryo-cooled GD source used in the GD-MS instruments since 80s was found to be relatively small in comparison to the 'fast-flow' GD sources implemented in the commercial GD-MS systems later on. The main advantage of the fast-flow concept is the high sample throughput compared to the earlier GD-MS concept of the 'static-flow' GD.

The lack of knowledge on matrix and plasma parameter dependence of the StdRSF was the main motivation for the recent investigations carried out within the European Metrology Research Project (EMRP) SIB09 ELEMENTS with the objective to improve the overall measurement uncertainty of GD-MS with the fast-flow GD sources. Relevant reference materials with Al, Cu and Zn matrices containing defined traces of metallic elements were investigated. A special attention was paid to the effect of voltage, current and gas flow. Suitable working parameters were selected for calibration and extensive experimental work including sputter rate measurements was undertaken. A suitable model for matrix independent calibration was achieved when normalizing the measured signals to Fe. The determination of non-metals (such as H, C, N and O) is also of great importance since the presence of small amounts of these elements affects significantly the properties of the materials. However, the lack of matrix matched calibration materials with certified amounts of the non-metallic elements is especially noticeable. In this context, the possibility of a multi-matrix calibration of oxygen in GD-MS was investigated. For this purpose, a set of new conductive samples containing oxygen in the percent range of concentration in three different matrixes (Al, Mg and Cu) were produced by a sintering process. For sample preparation, pure metallic and oxide powders were mixed in a defined mass fraction and then sintered. Discharge parameters were optimized for the generation of reproducible background and signal intensities of non-metals. Under these conditions matrix specific RSFs were generated and limits of detection were determined. After the introduction of the sputtering rate correction matrix independent calibration were obtained for oxygen. These investigations were undertaken using two GD-MS source concepts – fast flow (ELEMENT GD) and low gas flow (VG 9000).

This work was conducted within the EMRP project SIB09 ELEMENTS. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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FURTHER STUDIES ON THE ROLE OF ASYMMETRIC CHARGE TRANSFER AND OTHER IONISATION PROCESSES IN GLOW DISCHARGE MASS SPECTROMETRY

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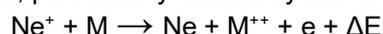
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We have recently compared the “mass spectra” of a titanium reference sample recorded with argon and krypton as the plasma gases, using a Nu Instruments Astrum Glow Discharge Mass Spectrometer, and have shown that Asymmetric Charge Transfer (ACT) plays a significant role as an ionisation process [1] under these low power conditions, contrary to the accepted view that the only important process normally is Penning Ionisation. Whilst an understanding of the fundamental processes in glow discharge plasmas is not a pre-requisite for the use of Glow Discharge Spectroscopy (GDS) as an analytical tool, it can help to explain anomalous results and calibration problems. It can also explain why the use of an alternative plasma gas can significantly improve limits of detection in certain cases.

We have now extended this study to iron reference samples and to the use of neon as the plasma gas, and will show that, for some minor constituents, the effect of the plasma gas is dependent on the matrix in which these elements are present. This effect is mainly due to the role of ACT in the production of ion signals in GD-MS (e.g. for oxygen and tungsten with krypton and iron and vanadium with argon), and occurs even under the low power/low pressure discharge conditions (~3 W and ~1 hPa) used in the Nu Instruments Astrum GD mass spectrometer. We will also show that when using neon as the plasma gas, significant ion signals can be obtained for doubly ionised species (M⁺⁺) of certain metallic elements, presumably excited by the “charge transfer and ionisation” process [2], viz.:



The presence of a significant population of doubly ionised species when using neon has been reported previously for the matrix element – e.g. using neon with a titanium matrix, the Ti⁺⁺ ion signal is about half that of Ti⁺, whereas using argon the ratio is less than 10⁻³ [3]. The Astrum data will be supplemented by data obtained under higher power/higher pressure conditions using the Thermo Fisher ELEMENT GD mass spectrometer at BAM, Berlin. GD-OES spectra recorded under high and low power conditions using the Spectrumba GDA650 at IFW Dresden will be used to provide additional evidence where appropriate.

The interpretation of these results will demonstrate the great importance of the critical energies (ionisation energies and energies of metastable states) of all the species involved in the discharge, gases, matrix elements and constituent elements.

We wish to thank Dr Karol Putyera, Evans Analytical Group, for access to an Astrum at EAG. NY 13088, USA.

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COMPARISON OF THE EFFECTS OF SMALL AMOUNTS OF MOLECULAR GASES IN ARGON AND NEON PLASMAS USING THE ELEMENT GD GLOW DISCHARGE MASS SPECTROMETER

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Using a ThermoFisher Scientific ELEMENT GD glow discharge mass spectrometer at EAG Labs, NY, USA, Weinstein [1] compared the effect on the ion signals when molecular gases (hydrogen, nitrogen and oxygen) in the concentration range 0 - 2% v/v were added to the argon plasma gas. The Element GD produces an 8 mm diam. crater, so to obtain conditions similar to the “standard” conditions used in Glow Discharge Optical Emission Spectrometry, Weinstein used constant voltage, constant current conditions, 700 V, 80 mA. Hodoroaba [2] and others had previously shown that the presence of small amounts of hydrogen (<2% v/v) reduced the $^{40}\text{Ar}^+$ signal by several orders of magnitude, with the main reduction occurring in the range 0 - 0.5% v/v. Weinstein confirmed this, and also showed that whilst nitrogen did not significantly affect the $^{40}\text{Ar}^+$ signal, oxygen caused a steady decrease in the $^{40}\text{Ar}^+$ signal, falling by about one order of magnitude with the addition of 2% v/v oxygen. Weinstein also reported the totally unexpected result that with added hydrogen, the $^{40}\text{Ar}^{++}$ signal, about three orders of magnitude less than the $^{40}\text{Ar}^+$ signal in pure argon, initially fell by about an order of magnitude for a concentration of about 0.35% v/v, but then rose sharply so that, at 1% v/v hydrogen, the $^{40}\text{Ar}^{++}$ signal had risen by two orders of magnitude compared with its original value and was at least 2 orders *greater* than the $^{40}\text{Ar}^+$ signal. On the other hand, with increases in the nitrogen or oxygen content, the $^{40}\text{Ar}^{++}$ signal decreased by a factor of about three.

We have now used the ELEMENT GD at BAM to repeat some of Weinstein’s work with argon/ hydrogen gas mixtures, and in particular have confirmed the behaviour of the $^{40}\text{Ar}^{++}$ signal. The concentration at which the minimum value of this signal occurs depends on the discharge current and is lower at 40 mA than at 80 mA. In general, the behaviour of the ion signals is similar at the lower current, and we therefore used 40 mA for the majority of the new experiments, to reduce the crater depths and the heating of the sample.

We hoped to make direct comparison with the effects of adding hydrogen and nitrogen to a neon discharge and connected a gas mixing system to the ELEMENT GD additional gas line, to mix pure neon with pre-mixed 2% Ne/H₂ and Ne/N₂. However, the pressure required for a given voltage and current is significantly higher when neon is used compared with the pressure for argon, and we could not achieve more than about 17 mA at 700V or 20 mA at about 900V. We will present the preliminary measurements made with these conditions. With added hydrogen and a copper cathode, the $^{20}\text{Ne}^+$ and $^{63}\text{Cu}^+$ signals increase steadily by a factor of about five for 0.6% v/v added hydrogen, whilst the $^{20}\text{Ne}^{++}$ and $^{63}\text{Cu}^{++}$ signals fall rapidly initially (with about 0.1% v/v H₂) and then stabilise. At 2% v/v H₂, the H₂⁺ signal is about 1% of the $^{63}\text{Cu}^+$ signal, whereas in an argon discharge at 40 mA, the H₂⁺ signal is 10⁻⁶ times the magnitude of the $^{63}\text{Cu}^+$ signal.

We have now modified the pumping line to the source, so that the flow can be restricted when required by about one third, so enabling a higher pressure to be achieved in the source for a given gas flow. This will enable higher currents to be achieved at 700 V with neon as the discharge gas, and further experiments will be then be made on the effect of added molecular gases.

Acknowledgements: We wish to thank Joachim Hinrichs (ThermoFisher Scientific) for advice on recording H⁺, H₂⁺ and H₃⁺ signals using the ELEMENT GD.

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RENEWABLE ENERGY: HOW GDOES CAN ASSIST IN DEVELOPMENT OF THIN FILM SOLAR CELLS, LI BATTERIES (LTO) AND WIND POWER.

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Our sources for oil and coal run short. On the other hand the energy consumption increases. Projects like ITER and Tokamak (fusion reactor) are the focus of intensive research, but it will take at least ten years (still) until they can contribute to the energy supply. GDOES is involved in fusion research because of its excellent capabilities of determining deuterium (D).



In this situation the main focus is on development of new, clean but first of all renewable energy. The amount of Power plants which convert the energy of sun, wind and water has risen, but there is still room for improvement. The greatest endeavor is to increase the efficiency of these methods.

The presentation shall demonstrate how GDOES can assist this development. Our customers use the GDOES for thin film solar cells like CIGS (copper-indium-gallium(di)selenide).

Others develop material for the generators of wind power (Fe-Nd alloys) or for turbines (super alloys).

And last but not the least our customers work on storage systems like batteries (Lithium ion batteries).

In all cases the Spectruma GDOES instruments are involved. The instruments are located in the Research & Development department as well as the production line. The advantages of GDOES compared with other applications can be found in presentation by D. Abou-Ras [1]. Especially the complex layers can be analysed with all elements including the light elements like C, N, O and H. By the use of multi matrix calibrations many possibilities are available.

Thick layers, mostly used for batteries, can be analysed as well as thin layers like cadmium sulphide of less than 50 nm, which are used for thin film solar cells.

In this presentation the excellent capability for compositional depth profile analysis and the reliability of GDOES in the field of research and development are illustrated at the example of Li-ion-batteries and thin-film solar cells. Some of the latest advances Spectruma developed according to the customers' requests like for contamination on batteries are highlighted as well.

[1] "Comprehensive Comparison of Various Techniques for the Analysis of Elemental Distributions in Thin Films" by D. Abou-Ras (*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*) et al.

REAL TIME MEASUREMENT OF LAYER THICKNESS, EROSION RATES AND CRATER DEPTH IN GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY

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Pulsed Radio Frequency Glow Discharge Optical Emission Spectrometry provides Ultra Fast Elemental Depth Profile of thin and thick films. The technique relies on the sputtering of a representative area of the material of interest by a plasma which also excites the sputtered species. The quantitative information on the elements present in the film can be achieved through the real time analysis of the light emitted from the de-excitation of the excited elements.

A new function giving the capability to measure, in real time, the depth of the sputtered crater is being introduced. Such measurement, based on differential interferometry with nanometer sensitivity, is able to provide direct information about the thickness of the layers and their erosion rates. This is crucially important, notably when the investigated materials are non transparent, as in this case an alternative technique such as ellipsometry cannot be used.

Several examples of applications of this new development - on both non transparent and transparent layers - will be presented.

APPLICATION OF XYZ MANIPULATOR IN GLOW DISCHARGE MASS SPECTROMETER FOR DEPTH PROFILE ANALYSIS

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We present application of XYZ vacuum manipulator in glow discharge mass spectrometer SMJW-01 [1]. The use of the manipulator in depth profile analysis allows to reduce crater edge effects. This solution also allows to detect ions emitted from different parts of the crater. Choosing of translation rate parameter of the sample makes possible to control sputtering rate of the analysed sample.

The scan range of the sample can be adjusted from 0 mm to 5 mm in both directions. In experiments we use several intermediate cathodes with various diaphragms. Some results of the depth profile analysis of layered structures obtained with and without use of the manipulator are presented.

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APPLICATION OF GD-MS FOR PURITY ASSESSMENT IN NIM CHINA

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As a powerful tool for purity analysis, glow discharge mass spectrometry (GD-MS) can be used to analyze more than 70 elemental impurities, except for gas elements and radioactive elements.

In order to check the characteristic of GD-MS, measurement repeatability and series certified reference materials with different metallic matrix were researched in detail [1]. The measurement repeatability was a range of 1-5% for the impurities which the contents were over than 1mg/kg in iron matrix.

The series of certified reference materials of steel and copper from National Institute of Standards and technology (NIST, USA) were measured and the results were compared. It was found that the same correction factors could be used by measurement of impurities with similar matrix in wide range of contents under the same measurement conditions. But there were obvious matrix effects during measuring different matrix. The standard relative sensitivity factors (RSFs) of different elements were not suitable for the quantitative analysis. But it is enough for semi-quantitative analysis because the general differences were no more than double of the RSFs.

In the purity analysis of high pure metal which is the basic material of certified reference material and standard calibration solution, screening analysis and homogeneity testing could be used GD-MS. If small uncertainty of purity was needed, the impurities with high contents would be measured by ICP-MS or ID-MS method again. The measurement results of main impurities in high copper and high silver with different methods were compared [2].

We participated in the international comparison CCQM-K72 (Purity of Zinc with respect to six defined metallic analytes) and measured the six elements in zinc with different method. The results were consistent with that of international laboratories. It is indicated that purity analysis by using GD-MS method was very convenient and effective.

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2D ANALYSIS IN GDMS: APPLICATION OF IN-SITU TRANSLATION OF SAMPLE

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We show results of in-situ translation of samples during GDMS analysis. The results are obtained on a DC-glow discharge quadrupole mass spectrometer [1]. The glow discharge voltage of 0.8 to 2.5kV DC and discharge current of 0.5 to 5mA are used. The add-on 'xyz' manipulator system uses a membrane bellows and allows for 10mm x 10mm sample translation above a stationary glow discharge cell.

We discuss possible benefits of using such a manipulator and show some examples of sample mapping. We also describe the possibility of using a pre-sputtering protocol prior to the analysis of selected areas of the sample. Advantages and limitations of the use of this manipulator are discussed.

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EVALUATION OF PP-TOFMS FOR DEPTH PROFILE ANALYSIS.

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The coupling of a pulsed glow discharge (PGD) source to a time-of-flight mass spectrometer (TOFMS) offers interesting features, such as^{1,2}: (i) high acquisition rates (thus making this instrumentation ideal for fast transient signals measurement); (ii) sensitivity and mass resolution is independent of the number of selected isotopes; (iii) the temporal distribution of the applied power enables to obtain not only elemental but also molecular information. In fact, it is possible to differentiate three different time regimes along the GD pulse duration: prepeak, plateau and afterglow, each of them characterized by different predominant ionization processes.

A PGD-TOFMS instrument is now commercially available, the PP-TOFMS. Interesting features of this equipment also include: (i) possibility to blank up to four isotopes along the mass spectrum (this allows to eliminate most intense ions and so to achieve higher sensitivity for the rest of the ions acquired in the spectra) and (ii) to detect negative ions.

In this presentation, optimization of instrumental operating conditions for the PP-TOFMS is presented both in positive and negative detection modes, including the effect of blanking. Also, evaluation of plasma gas mixtures (Ar+ oxygen and Ar+He) on analytical sensitivity and depth profile resolution will be shown.

Analytical examples will include the identification of polymers (brominated flame retardants and PTFE), the depth profile analysis of thin film solar cells and coated ceramics, among others.

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A TIME RESOLVED STUDY OF THIN COATED AND MULTI-LAYERED COMPOSITE MATERIALS USING THE ASTRUM GDMS

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High-resolution direct-current glow discharge mass spectrometry (HR-dc-GDMS) is a mature, versatile technique for the direct determination of trace and ultra-trace elements in bulk materials. By means of a flat geometry GD source configuration, it is also a proven technique for high sensitivity depth dependent distribution analysis of trace elements in coatings and other multi-layered advanced materials. The Astrum, the latest generation in HR-dc-GDMS technology from Nu Instruments, is a perfect candidate for such time resolved analysis. Due to the low-flow GD source of the instrument, the Astrum at normal analytical conditions (1kV,2mA) has a sputter rate which can range from 1 μm / 2 minutes for copper to 1 μm / 6 minutes for ceramics. If operational conditions are lowered, the sputter rate can be slowed by a least 5x. This low sputter rate translates into ample time to acquire meaningful and reproducible data for thin and even ultrathin films, layers and coatings. The low sputter rate also allows for time resolved analysis of coated powders as well as bulk composite materials, while obtaining information about the contaminants in each matrix layer. The Astrum offers some significant advantages over other instrumentation frequently used for depth profile work. For example, as the Astrum does not rely on matrix matched standards, the time needed and possible errors generated for this matrix dependent step are eliminated. Secondly, as the RSF values are matrix independent, the same standard relative sensitivity factor (StdRSF) data set [1] can be used throughout each time dependent study to achieve semi-quantitative results directly. Thirdly, as the Astrum offers both low power and cryo-cooling, temperature sensitive materials can be readily analysed and interferences from high gas backgrounds are significantly reduced. Lastly, as the Astrum is capable of analysing all types of materials, composite samples containing layers of both conducting and non-conducting material can be evaluated. The study presented here takes a closer look at the depth profiling capabilities of the Astrum by evaluating the thin coating of a powder sample and the layers of a computer hard disk platter. The matrix independent RSFs, the low sputter rate and the cryo-cooling of the source are among some of the many features which serve to make the Astrum a powerful and versatile technique in the evaluation of the layers in conductive, semi-conductive and non-conductive composition materials.

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TRACE ANALYSIS OF GAS PHASE ELEMENTS IN METALS BY FAST-FLOW GD-MS

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Current studies have been carried out to improve the detection capabilities of the ELEMENT GD PLUS GD-MS for trace amounts of gas phase analytes. This high-resolution glow-discharge mass spectrometer features a fast-flow source enabling a much higher sample turn-around than the previously used static high-vacuum sources that required intense cooling with liquid nitrogen. While the fast-flow concept is generally superior in sensitivity, speed, analytical performance and formation rate of polyatomic interferences, it generally suffered from elevated backgrounds of the gas phase elements Carbon, Nitrogen, and Oxygen.

In this presentation the results of several high purity Copper samples and reference materials will be shown. The samples have been selected to cover the low ppm level for gas phase analyte concentrations. Several contributing factors to elevated levels of gas phase analytes have been identified.

Detection limits of <1ppm Carbon are achieved with a modified design of the fast-flow glow discharge source. Large improvements are also achieved for Nitrogen and Oxygen, although for these elements the calibration factors will need to be verified. Preliminary results indicate detection limits in the range 1 – 10 ppm. As an outlook, several options for even further increased performance of the ELEMENT GD PLUS for low-level gas phase analyses will be discussed.

ROUND ROBIN – QUANTIFICATION OF N IN NITRIDED STEELS

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Eleven laboratories participated in a Round Robin test to quantify the amount of N and C by GDOES in two different nitrided steels. The quantification of these two elements was done by measuring depth profiles. On the one hand, the repeatability of the measurements of each laboratory was satisfying. However on the other hand, the comparison of all results showed a surprisingly large scattering, with a relative standard deviation of about 30%. Measuring the exact amount of N in higher amounts seems still to be quite a challenge.

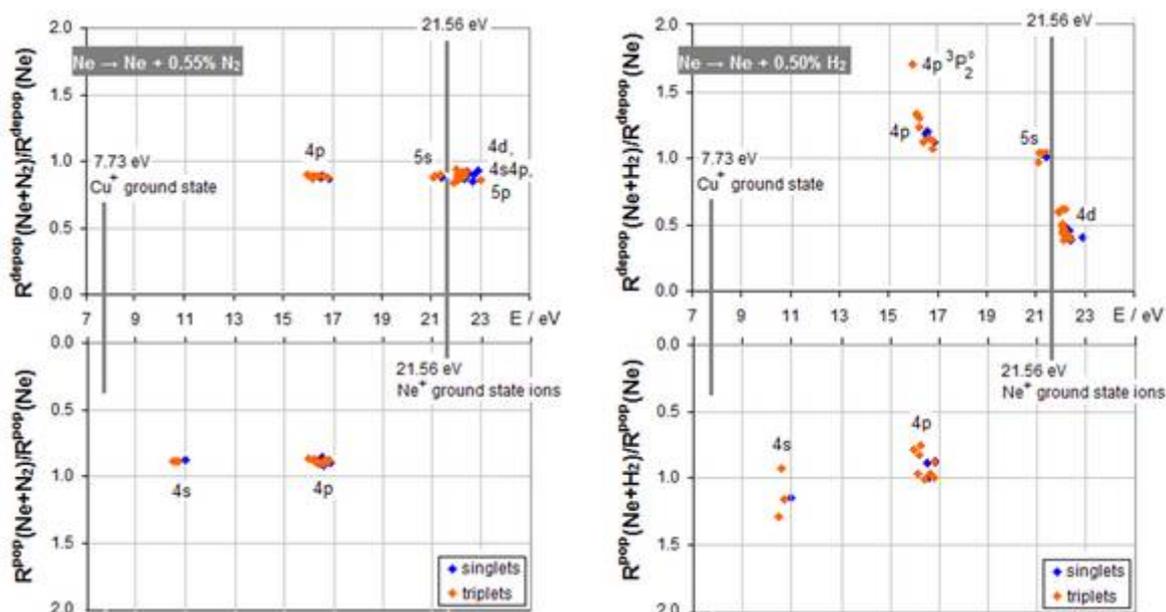
EFFECTS OF H₂, O₂ AND N₂ ON EXCITATION OF Cu⁺ IONS IN A Cu/Ne GLOW DISCHARGE: TRANSITION RATE RATIO DIAGRAMS

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Excitation processes in a glow discharge can be studied by considering *radiative transition rates* (TRs) between different states of an atom or ion. TRs can be presented in a TR diagram, in which radiative population- and depopulation rates of different states of an atom or ion are depicted as functions of their energy [1, 2]. TR diagrams can be established from intensity-calibrated emission spectra. To study *changing excitation conditions*, e.g., the changes caused by adding into the discharge gas a small amount of another gas, the *ratios* of TRs can be considered, i.e., the TR measured under altered plasma conditions divided by the TR of the same state under the original, unperturbed conditions. These ratios can be presented in a *transition rate ratio* (TRR) diagram. This approach was used to study the changes in the excitation of Cu⁺ ions in a Ne discharge, caused by small admixtures of O₂, N₂ and H₂ [3]. The Cu⁺ TRR diagrams reflecting small additions of N₂ and H₂ are shown below.



N₂ addition does not selectively affect excitation of Cu⁺ ions (the plot on the left), whilst additions of H₂ (the plot on the right) and O₂ do [3]. With TRR diagrams, it is possible to distinguish between changes in the emission spectrum caused by cascade excitation (radiative decay of higher excited states) and changes due to the direct collisional excitation of the states under study.

A better understanding of the effects of light elements on glow discharge plasmas is the key factor in the development of quantitative analysis by GD-OES of anodic- and thermally grown oxide layers, layers containing hydrogen such as galvanic coatings, CVD-deposited diamond-like carbon (DLC), amorphous Si:H layers, nitrided steels, nitride coatings, diffusion- and ion implantation profiles, etc. Corrections in the GD-OES quantification algorithms reflecting the presence of light elements must be line-specific and are in most cases nonlinear functions of the amount of the light element present.

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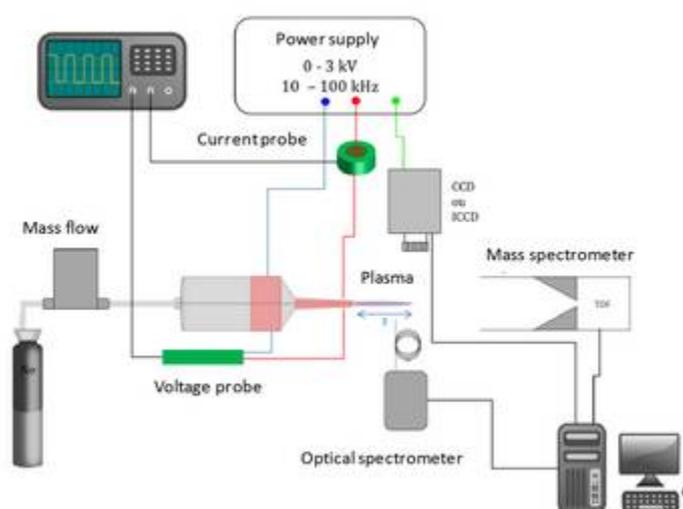
PRELIMINARY ANALYTICAL RESULTS FROM A DBD NEON PLASMA JET AT ATMOSPHERIC PRESSURE COUPLED TO A TOF-MS.

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In direct sample analysis domain, atmospheric pressure sources are widely investigated for ambient desorption/ionization mass spectrometry and atmospheric-pressure ionization mass spectrometry. Dielectric barrier discharge (DBD) can be used to generate low temperature plasmas at atmospheric pressure and create soft ionization. Coupled to mass spectrometry detection, high selectivity and sensitivity can be obtained but its efficiency is influenced by the plasma properties.

A dielectric barrier discharge source has been developed with a future aim of source coupling with a Time Of Flight Mass Spectrometer (TOF-MS, CTOF-Tofwerk AG, Thun, Switzerland) and analytical investigations. This source is composed of a large cylindrical dielectric chamber with a capillary termination. The different electrodes cover both the cylindrical chamber and the capillary tube. The plasma is created in the cylinder and a plasma jet is generated out of the capillary tube. The source is operated in flowing Neon and is powered by a square alternating voltage (20 kHz).



The aim of this study was to characterize the discharge in open air by mass spectrometry in positive and negative mode. The different mass spectra will be presented and commented. Then the number of ions/extraction for some m/q of interest will be presented as a function of the distance between the plasma source and the mass spectrometer. Finally the sources capacity to generate specific m/q ratios for known analytical samples such as ethanol, toluene and caffeine will be evaluated and presented.

SPATIOTEMPORAL DISTRIBUTION OF NEON GAS AND AIR SPECIES FROM A DBD PLASMA JET AT ATMOSPHERIC PRESSURE.

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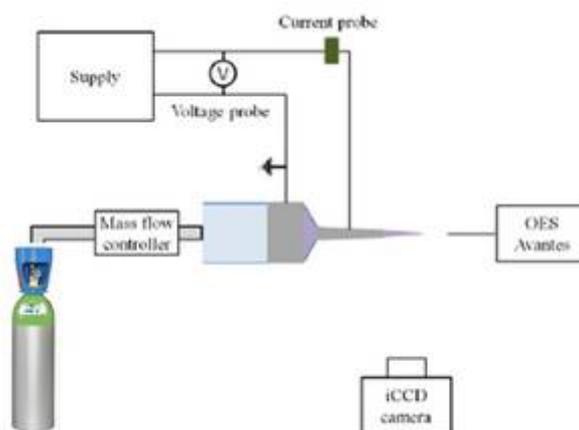
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The source developed in our laboratory is based on DBD (Dielectric Barrier Discharge) in such a configuration that no conductive electrode is needed inside the source. It allows the formation of a plasma jet in open air that can be directed toward the surface to be analyzed.

The experimental set-up consists of a dielectric cylinder ending by a dielectric cone with a smaller diameter. Electrodes surround each part of the device. The originality of this source is its asymmetric geometry.

The source is fed with high purity neon introduced into the source through a gas inlet connected to the back of the source. The source is powered with a symmetric square alternative voltage. The frequency delivered by the supply can vary from 10 to 100 kHz, and the maximum amplitude is 3 kV (6 kV peak to peak voltage) with a rising/falling time of 100 ns.

Optical measurements were performed with an optical spectrometer (Avantes 2048-2) placed in front of the source exit and an iCCD camera (Princeton PIMAX-2K-RB) placed on the side of the plasma jet. Optical filters with different central wavelength (band pass region of 10 nm for each) can be added.



In this work, emission spectra of the discharge were used to characterize the emission lines of interest corresponding to the buffer gas and to the ambient air species - i.e. O, H, OH, N₂ and N₂⁺. In the same time, the spatiotemporal evolution of the jet during the positive and the negative half periods of the signal were observed with the iCCD camera. The optical filters coupled with the iCCD camera are used in order to study spatial distributions of neon gas and air species present within the jet during the period (Ne, 703 nm and 584 nm, N₂, 380 nm, N₂⁺, 390 nm and O, 777 nm). These distributions will be presented and commented.

DOES ASYMMETRIC CHARGE TRANSFER PLAY AN IMPORTANT ROLE AS THE IONIZATION MODE IN LOW POWER-LOW PRESSURE GD-MS?

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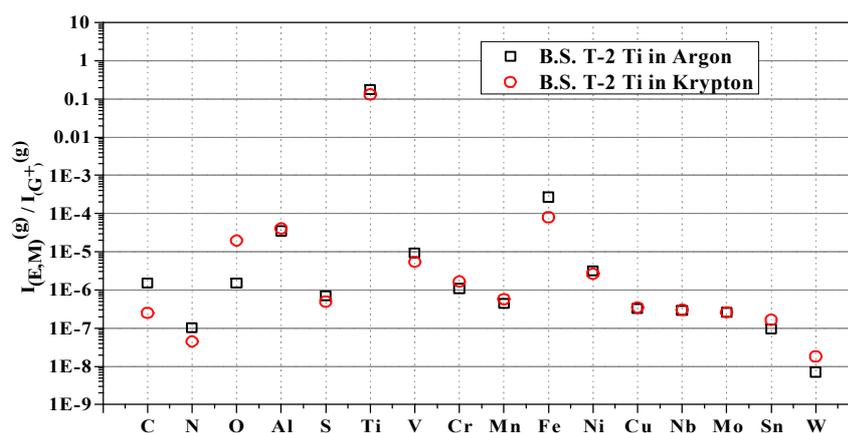
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It has been suggested that in low power (~ 5W) analytical glow discharges (such as VG9000 type sources) running in low pressure noble gases ~1 hPa, electron impact ionization and Penning ionization (PI) are the main ionization pathways for the sputtered atoms [1], and that although asymmetric charge transfer (ACT) may occur in such sources, there is only minor contribution from this process [2]. On the other hand, it has been shown that departures from a regular pattern of relative sensitivity factors (RSF) can be attributed to ACT [3]. In the current work, the ion signals of the constituent elements in various standard reference materials have been compared with various plasma gases (Ar, Kr and Ne), using the Nu Instruments Astrum high resolution glow discharge mass spectrometer (~1 kV & ~3 mA.)



The figure shows the ion signals of the constituent elements relative to that of the plasma gas. The order of magnitude higher value of this ratio for oxygen when krypton is used is due to ACT by Kr. It will be shown that other differences in the ratios similar to those shown above are linked to the arrangement of atomic energy levels of the elements concerned and the resulting relative importance of ACT and PI [4].

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DETERMINATION OF 13 MATRIX-DEPENDENT RSFs FOR NICKEL MATRIX USING DOPED PRESSED POWDER SAMPLES AS NEEDED FOR FAST FLOW GLOW DISCHARGE MASS SPECTROMETRY

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Direct current (DC) fast flow glow discharge mass spectrometry is an important and versatile tool for multielemental trace analysis of conductive solid materials down to the $\mu\text{g}/\text{kg}$ level. Special benefits are minimum demands on sample preparation, avoiding losses and contamination, and only short analysis time.

For fast flow GD sources, the quantification strategy based on relative standard sensitivity factors (standard RSFs) which are independent of matrix is not sufficiently satisfying regarding accuracy for each matrix and element [1]. Therefore matrix-matched calibration samples (MMCS) are required to achieve reliable quantification. In fact, the list of existing certified reference materials (CRM) appropriate for calibration in trace analysis is rather short.

Convenient synthesis of homogeneous MMCS, as e.g. easily obtained in liquid sampling spectrometry, can facilitate the application of fast flow GD-MS for quantification of impurities in a variety of matrices.

Pressing of metal powders for the preparation of MMCS for GD-MS was suggested earlier [2], the method was further modified by use of analyte solutions for doping of rather pure metal powders such as Cu and Zn [3], but has not yet been applied Ni matrix.

In the present work we describe the determination of matrix-dependent relative sensitivity factors (RSFs) for Mg, Al, Cr, Mn, Fe, Co, Cu, Zn, Ag, Cd, Tl, Pb and Bi in pure Ni by using the liquid doping approach for the preparation of synthetic pressed Ni-powder samples. A four point-calibration was used applying the fast flow glow discharge mass spectrometer, Element GD (Thermo Fisher). The determined RSF were verified against suitable CRM and compared with the standard RSF given by the supplier of the instrument.

The obtained results demonstrate a satisfying agreement with the certified values of the CRM and a significant improvement for the quantification of most of the determined elements in comparison with standard RSF.

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CONCENTRIC APGD IONIZATION SOURCE FOR MASS SPECTROMETRY: OPERATION REGIME CHARACTERIZATION.

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Electric discharge plasmas generated at atmospheric pressure have acquired great interest for analytical applications since their initial development. These plasma devices are often used as excitation/ionization sources for Optical Emission Spectrometry (OES) and/or Mass Spectrometry (MS). In particular, the development of appropriate inlet interfaces removed the limitations that these atmospheric pressure ionization (API) sources used to have when getting coupled to mass analysers that typically work at low pressure conditions (10^{-4} - 10^{-7} Pa).

The development of different API sources has resulted in a new group of MS-based analytical methodologies, englobed in a field called *Ambient Desorption/Ionization Mass Spectrometry* (ADI-MS) [1]. This methodologies try to remove (or, at least, lessen) pre-treatment processes by means of incorporating sampling, desorption and ionization into one step at standard laboratory conditions. When the ADI source faces the sample, molecules present in the sample are first desorbed and then ionized (through different processes, depending on the particular source design). These ions are detected by a mass spectrometer, allowing the identification of the sample components thanks to the measurement of the mass-to-charge ratio of the so-formed molecular ions.

There is a great number of ADI sources based in electrical discharges at atmospheric pressure [2]. These desorption/ionization sources typically use helium as discharge gas due to the great energy of his metastable states, the long half-life of these species and the high gas thermal conductivity. This last parameter is very important for the effectivity of desorption, which is essentially based on thermal processes. He excited/ionic species generated in the discharge react with the atmospheric constituents leading to the formation of several reagent ions: N_2^+ , O_2^+ , NO^+ , H_2O^+ , and protonated water clusters $[(H_2O)_n + H]^+$, which are involved in the protonation of molecular species [3]. Also noteworthy is the presence of reactive negatively charged reagent ions (eg. OH^- , O_2^- or NO_3^-) that can produce negative ionization processes.

In the last years, our laboratory has developed an experimental set-up for ADI analysis using a quadrupole mass spectrometer. The ADI source is based in a concentric electrode geometry atmospheric pressure glow discharge (APGD). To get a trusted experimental system, fundamental characterization of the discharge is essential. This study presents an electric characterization of the discharge regimen depending on the discharge parameters (helium flow rates and electrode dimensions). In addition, this characterization is complemented by the acquisition of total emission images at different discharge regimes. These discharge regimes are then correlated with the mass spectrum of reagent ions generated by the device.

Acknowledgements

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ANALYSIS OF SILICON BY RADIO FREQUENCY GLOW DISCHARGE MASS SPECTROSCOPY

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Analysis of trace element in solid sample such as metal, semi-conductor, insulator without chemical pre-treatment is possible by Glow Discharge Mass Spectroscopy (GDMS). However, insulator or semi-conductor is not flowing the current. So, In that samples need physical pre-treatment such as press on high purity metal (Indium, Tantalum, etc.) But, pre-treatment using high purity indium plate, indium concentration is not correct.

In this study, direct analysis trace element in Solar grade silicon without any pre-treatment using radio frequency GDMS(RF-GDMS). Internal standard sample is metallurgical silicon with sub hundred ppm or sub thousand ppm contained impurities. Standard concentration analyzed by Inductively Coupled Plasma optical emission spectroscopy (ICP-OES) using standard calibration curve. Relative sensitivity factor (RSF) of ion beam ratio(IBR) in GDMS is calculated using standard concentration. And trace element in SoG Si quantified using RSF.

$$RSFs = C_x * IBR_x \text{ (eq. 1)}$$

$$IBR = I_m/I_x \text{ (eq. 2)}$$

ANALYSIS OF LOW MELTING POINT MATERIALS SUCH AS GALLIUM BY GLOW DISCHARGE MASS SPECTROMETRY.

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Recently, the market demand for high-purity metal is increased and purification method of the gallium high productivity is required. Gallium has low melting point (29.76 °C) and super cooling properties and that property was not applied to zone refining method of the ordinary. Therefore, we produced zone refining system for low melting metal by using Direct Cooling and Indirect heating. Purification of 4N gallium was carried out zone refining process. Depending on the refining process up to 5pass, the trace metal impurities such as B, Al, S, Cr, Fe, Ni and Si decrease 4N to 6N. We adopted GD90(MSI, UK) to the measurement of impurities in high purity Gallium metal for prevent gallium melt. GDMS, especially GD 90 is a powerful analytical method capable of analyzing solid samples without chemical decomposition step and analyzing a low-melting metal by adopting liquid nitrogen cooling and slow sputter method.

SURFACE SAMPLE PREPARATION FOR EPMA USING GDOES

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Al-Si cast alloys are in high demand for automotive applications and there is an indication that additions of Ni to these alloys can significantly improve their high temperature mechanical properties. Accurate quantification of Ni concentrations is therefore important to assess the influence of Ni on the microstructure and mechanical properties of the resulting alloy.

In this work we present a study of three Al-Si cast alloy samples with varying Ni concentrations, namely 0.5, 1, and 2 wt.%. Glow discharge optical emission spectroscopy (GDOES) was used to measure the chemical composition while electron probe microanalysis (EPMA) was used to make elemental mappings and reveal the microstructure. Samples for EPMA were prepared by mechanical polishing with SiC and diamond papers down to 1 μm . We also studied the possibility of using GDOES at various analytical conditions (power and pressure) as a final polishing step for EPMA.

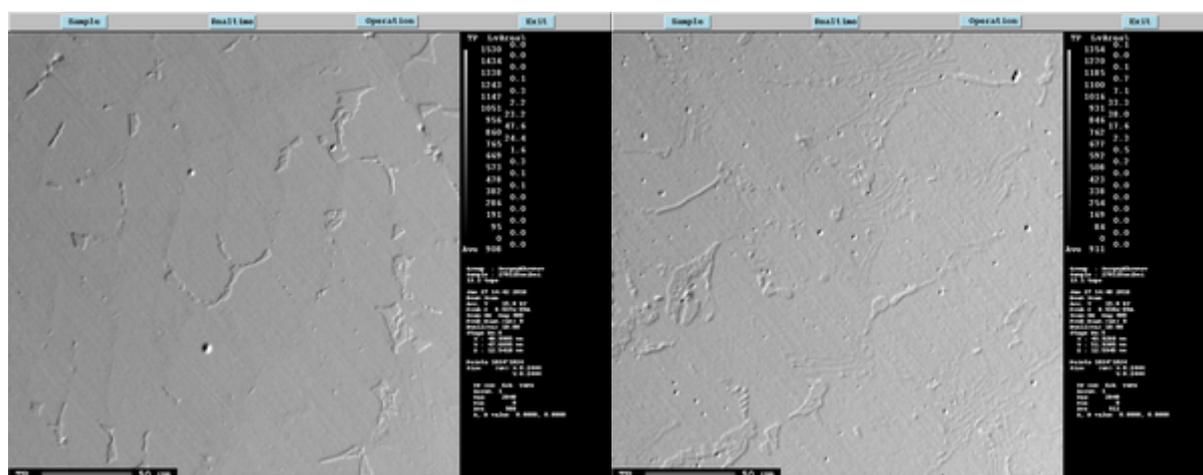


Figure 1. SE micrographs of the sample (1% Ni) surface outside (left) and inside (right) the GDOES crater.

The results of the GDOES analysis confirm the target levels of Ni for all the three samples investigated. EPMA analyses were conducted both outside and inside the areas of the crater made by GDOES sputtering. The results seem to indicate that GDOES cannot be used as a final polishing step for EPMA and that the presence of Ni can significantly change the sputtering rate during GDOES analysis, thus affecting the GDOES quantification.

PROCEDURES USED FOR CONTROL OF XYZ MANIPULATOR IN GD-MS ANALYSIS

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We present control procedures of 'xyz' manipulator allowing for *in-situ* translation of sample during GDMS analysis. We discuss possible trajectories and their effect on topography of eroded craters.

We also discuss how such parameters as translation rate of sample and distance between neighbouring scan lines affect crater bottom topography. Another procedure allowing to choose separate parts of the sample for analysis is described.

Also we describe 2D mapping procedures. The results: several examples of GDMS maps are presented.

ANALYSIS OF ALUMINA POWDER ACCORDING TO TARGET DESIGN BY GLOW DISCHARGE MASS SPECTROSCOPY

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Glow discharge mass spectrometry (GDMS) is a powerful tool for trace elements in solid state materials not only conductive metal but also nonconductor ceramic. The alumina powder was analyzed by using a GDMS so that the specimens were mounted by using a conductive indium plate. For a fine aluminum powder, even if mounted on the indium plate current was not stable. So, carbon type and grooved indium plate were used to ensure electric conductivity. Few elements were not analyzed to use carbon type. Thin grooves were made on indium plate that filled grooves by using alumina powder. Good sensitivity and stability may only be improved to use grooved indium plate.

OPTICAL SPECTROMETRIC SPACIAL FILTERING BY DIGITAL MICROMIRROR ARRAYS: PROSPECTUS FOR ATOMIC SPECTROSCOPY.

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Over the last several years, consumer electronics have developed a sophisticated set of light manipulation tools based on microelectromechanical (MEMS) devices. Perhaps the most successful of these is the digital micromirror array (DMMA): a set of micron-sized mirrors that can be manipulated very rapidly under computer control. While these devices currently are most popular for optical projection technologies, they can also be used as a spatial light manipulator in spectroscopic systems. Here, we examine the utility of current and future DMMA technology for atomic spectrometry, and in particular for Glow Discharge Optical Emission Spectrometry.