

Organised by the European Working Group for Glow Discharge Spectroscopy

# 2<sup>nd</sup> International Glow Discharge Spectroscopy Symposium

**Czech Technical University  
Masarykova kolej  
Thakurova 1  
160 41 Praha 6  
Czech Republic**

**7<sup>th</sup> – 9<sup>th</sup> April 2014.**



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### Meeting Organising Committee:

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### **Acknowledgements:**

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- 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.

# 1 Introduction

The Organising Committee wishes to welcome you to the 2<sup>nd</sup> International Glow Discharge Spectroscopy Symposium (IGDSS2014) taking place in the Czech Technical University in Prague, Czech Republic, from 7<sup>th</sup> to 9<sup>th</sup> April 2014. With more than 80 people attending from around 20 different countries you can see that the Symposium has a truly international flavour. And with over 30 oral presentations the scientific content is exciting with great opportunities for all to see 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.

IGDSS2014 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.

There will be other opportunities to coordinate a further Innovative Training Network going forward, and the feasibility of submitting a further proposal will be discussed in a meeting of the EW-GDS that is scheduled to take place on Wednesday 9<sup>th</sup> April, 2014 following the close of the Symposium activities. 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 9<sup>th</sup> April.

Again can we welcome you to IGDSS2014 and hope that you have a scientifically rewarding Symposium as well as a good time in the beautiful and historic city of Prague.

### 3 Programme of Talks and Events

Key:

Inx Invited Lecture  
Oxx Oral Presentation  
Mx Manufacturer's Presentation  
Pxx Poster

#### Sunday 6<sup>th</sup> April, 2014

16:00 Registration Opens  
17:30 Welcome Buffet Starts  
21:00 Close

#### Monday 7<sup>th</sup> April 2014

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

##### Session Chair: Volker Hoffmann

09:10 In1 GDOES That Changed My Life. *Ken Shimizu, Keio University, Japan.*  
10:10 O1 Use of a Pure Copper Anode in the GDL for Reduced Hydrogen  
Background – The Impact on Molecular Emission. *Arne Bengtson.*  
10:30 O2 Towards Exploitation of “Complete” GD-OES Spectra in Analytical  
Applications and Fundamental Studies. *Zdenek Weiss*

10:50 Coffee

##### Session Chair: Myriam Madani

11:10 O3 Leakage Effects on Glow Discharge Depth Profiling and Their  
Minimization. *Michael Koester.*  
11:30 O4 Depth Profiling Characterisation of Nanostructured Materials by  
Plasma Profiling Time of Flight Mass Spectrometry. *Agnes Tempez.*  
11:50 Brief Introduction to Posters

12:10 Lunch

##### Session Chair: Petr Smid

13:30 M1 Introduction of a New High End Performance Desktop GD-OES  
Instrument. *Michael Analytis.*  
13:50 M2 Applying  $\mu$ s-FF-GD-MS to Non-Conductive Sample Analysis. *Joachim  
Hinrichs.*  
14:10 M3 Overview of the Latest Improvements to the Nu Astrum High  
Resolution GD-MS. *Glyn Churchill.*

14:30 Coffee

##### Session Chair: Silke Richter

15:00 O5 Investigations of Matrix and Plasma Parameter Dependence  
of RSF in GD-MS. *Cristina Gonzalez-Gago.*  
15:20 O6 A Comparative Study to Explore and Evaluate the Performance of  
the VG9000 RSF Data Set as Applied to Nu Astrum Flat Cell and  
Pin Cell Data. *DeAnn Barnhart.*  
15:40 O7 Direct Current Glow Discharge Mass Spectrometric Analysis of  
Non-Conducting Materials Using a Surface Coating Method. *Qian  
Rong.*  
16:00 O8 Sputter Rates in GDMS. *Martin Kasik.*

16:20 Close Meeting for the Day.  
16:20 Thermo Fisher User Group Meeting (Invitation Only)  
20:00 Close.

## Tuesday 8<sup>th</sup> April 2014

08:30 Welcome and Daily Notices

### Session Chair: Jorge Pisonero

- 08:40 In2 Diagnostics of Pulsed Glow Discharges by Optical Emission Spectroscopy. *Rebeca Valledor, Bern University, Switzerland.*
- 9:40 O9 Non-LTE Behaviour of Argon and Krypton Glow Discharge Plasmas Estimated from the Intensity Analysis of Nickel Atomic Lines. *Kasuaki Wagatsuma.*
- 10:00 O10 Formation of the Plasma Radiation Prepeak in Microsecond Pulsed Glow Discharge with a Grimm Type Source. *Maxim Voronov.*

10:20 Coffee

### Session Chair: Arne Bengtson

- 10:50 O11 Effect of Small Quantities of Oxygen in a Neon GD. *Sohail Mushtaq.*
- 11:10 O12 GD-OES Applications in Steel Research. *Myriam Madani*
- 11:20 O13 Analysis of Small Cylindrical DLC Coated Parts with a Modified Unit for the GDA 750. *Sabine Kummel,*
- 11:50 O14 Using Krypton as a Discharge Gas to Help in Assessing the Relative Importance of GD Excitation Processes. *Edward Steers.*

12:10 Lunch

### Session Chair: Nerea Bordel

- 13:30 M4 A Comparison of CCD Array Detector vs PMT Signals During Thin Layer Compositional Depth Profile Analysis. *Kim Marshall.*
- 13:50 M5 Advances in GDMS. *Ekbal Patel.*
- 14:10 O15 Combined Hollow Cathode and Grimm Cell: A Comparison of the Analytical Capabilities. *Alexander Ganeev.*
- 14:30 O16 Sample Preparation and Depth Profiling Analysis of Innovative Materials by Pulsed Glow Discharge Mass Spectrometry. *Jorge Pisonero.*

14:50 Coffee

### Session Chair: Steven Ray

- 15:20 O17 Depth Profile Analyses by Glow Discharge Mass Spectrometry and Ion Implantation. *Marisa Di Sabatino.*
- 15:40 O18 Comparison of GDMS and SIMS Depth Profile Analysis Results of Several Layered Systems Like CIGS, TiN/Fe and (TiVZrNbHf)N/Fe *Piotr Konarski.*
- 16:00 O19 Measurement of Copper Diffusivity in Silicon by Glow Discharge Mass Spectrometry. *Chiara Modanese.*
- 16:20 O20 Calibration Strategies for Full Survey Chemical Analysis of Superalloys and Coatings by Fast Flow Glow Discharge Mass Spectrometry. *Karol Putyera.*
- 16:40 O21 Compact Electron Beam Welding Device Based on Glow Discharge in Low Pressure Argon. *Aleksander Zawada.*

17:00 Close Meeting for the Day.

19:00 Conference Dinner Sponsored by Nu Instruments.

**Wednesday 9<sup>th</sup> April, 2014.**

08:30 Welcome and Daily Notices

**Session Chair: Juliet Pickering**

08:40 In3 New Instrumental Capabilities for Glow Discharge Spectroscopy.  
*Steven Ray, Indiana University, USA.*

09:40 O22 Trace Metal Element Determination by Atmospheric Pressure  
Solution Cathode Glow Discharge and Atomic Emission  
Spectrometry. *Zheng Wang.*

10:00 O23 Studies on the Reagent Ions and Ionisation Processes of Flowing  
Atmospheric Pressure Afterglow (FAPA)-APGD. *Jaime Orejas.*

10:20 Coffee

**Session Chair: Philippe Guillot**

10:50 O24 Optical Emission Spectroscopy Characterization of a DBD  
Atmospheric Pressure Plasma Source for Mass Spectrometry  
Analysis. *Laura Chauvet.*

11:10 O25 New Accurate Atomic Data and Applications in GDS. *Juliet Pickering.*

11:30 Payling Prize Presentation

11:50 Close of Meeting

12:00 Lunch

13:30 EW-GDS Meeting

17:00 Close

## Posters

- P1 Determination of Trace Elements in High Purity Aluminium Oxide By GDMS.  
*Mykola Skulskyi*
- P2 Spacio-Temporal Study of a DBD Atmospheric Pressure Plasma Source for Analytical Applications.  
*Phiiippe Guillot.*
- P3 Analysis of Powdered Geological Samples Using Isotope Dilution Analysis and Radio frequency Pulsed Glow Discharge - Time of Flight Mass Spectrometry.  
*Rosario Pereiro.*
- P4 Depth Profile Characterisation of Photovoltaic Devices by Pulsed Glow Discharge - Time of Flight Mass Spectrometry.  
*Rosario Pereiro.*
- P5 Analytical Potential of RF-PGD-TOFMS to Evaluate Oxidation in Reverse Osmosis Membranes.  
*Nerea Bordel.*
- P6 Full Survey and Depth Specific Analysis of High Purity Graphites, Carbon/Carbon Composites and Silicon Carbide Based Materials and Coatings.  
*Cyril Michellon.*
- P7 Enhanced Excitation of Various Analyte Atomic Lines in Analytical Glow Discharges in the Presence of Molecular Gases.  
*Sohail Mushtaq.*
- P8 An Exploration of Sample Preparations and Detection Limits for Conductive, Semi-conductive and Non-conductive Materials as Pertaining to the Nu Astrum HR-GDMS.  
*DeAnn Barnhart.*
- P9 RF-GD-OES Analyses of Optical Multilayers.  
*Olaf Zywitzki.*
- P10 Application of Glow Discharge Mass Spectrometry for the Analysis of High Purity Magnesium Using Pressed Powder Samples with Different Dopant Types.  
*Jens Pfeifer.*
- P11 ArI and NeI Spectral Line Shapes in Cathode Fall Region of Grimm-Type Glow Discharge.  
*Nikola Sisovic.*
- P12 Study of Quantitative Depth Profile Analysis of Nanometer Scale Film on Steel by Glow Discharge Optical Emission Spectroscopy. *Yi Zhang*

## **4 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 O25 are the scientific oral presentations

M1 to M5 are the presentations that will be given by the manufactures and will refer to their specific instrumentation

P1 to P11 are the posters that will be on display throughout the Symposium.



## GDOES THAT CHANGED MY LIFE

K.Shimizu,

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***“Everything flows, nothing stays stationary”***

and

***“Not know what is around the corner”***

are the two main rules of our lives.

My happy encounter with GDOES took place in 1998 just by a chance, not by choice. On the 28<sup>th</sup> March, I was at the spring meeting of the Surface Finishing Society of Japan which was held at Keio University. During the lunch break, I was looking around the booths of instrument manufactures. When I passed by the booth of Atago Bussan which was an exclusive distributor of Jobin Yvon instruments in Japan, a salesperson kept eye on me and was walking toward me with a big smile. He was Mr Yohinobu Uchida, a sales manager, who was responsible for the sales of GDOES. He took me to the booth and tried to convince me that GDOES is a powerful tool for depth profiling analysis of various surface coatings. Unfortunately, however, the examples displayed were mostly for thick films, over tens micron thick, like galvanized steels. I was not so impressed, since I was working on depth profiling analysis of thin surface films on metals, a few to hundreds nm thick, using SIMS. Watching my reaction, he was apparently discouraged, but did not forget to add “Professor Shimizu, please do come to see our instrument with your specimens”.

A week later, and on the 3<sup>rd</sup> April, the entrance ceremony was held at the university auditorium, which was only 50 meters away from my office, and the university campus was full of new students and their parents. It was a sunny good day and tens of cherry trees around the auditorium were all coming to full bloom, celebrating new students who had been working very hard for many years to pass the entrance examination to Keio. It was a happy moment when their hard efforts were fully rewarded. The entrance ceremony was over at noon and I went back to my office. When I turned the knob of the door of my office to open, I had a telephone call from Mr.Uchida who said “let’s fix the date of your visit”. Then I realized he was serious and I replied back to him “OK, but please give me a couple of days to prepare specimens with known distribution of impurities”. The specimen which immediately came to my mind was anodic oxide films on aluminium, ~360 nm thick, with fine distribution W species. Through cross-sectional transmission electron microscopy, it has been shown that a thin W-doped layer, only ~10 nm thick, is located at a depth of 90 nm from the oxide surface and runs parallel to the flat metal/oxide interface. Further, the oxide is amorphous so that the surface roughening associated with anisotropic sputtering, often found for crystalline solids, does not exist here, making the sample ideal for the assessment of depth profiling capability of GDOES.

On the 8<sup>th</sup> April, I visited the demo-lab. of Atago bussan; Mr.Uchida was waiting for me with the Jobin Yvon RF 50 GDOES instrument ready. Everything that happened in 10 min after the arrival was unbelievable and very different for me who had been familiar with SIMS. Firstly, I was surprized that the instrument looked so simple; it was just a box painted yellow colour and not so impressive like SIMS and Auger instruments. Analysis was also done in an amazingly simple way and in a very short time, less than 2 min. Mr.Uchida picked up a sample from the sample box by fingers, without wearing a plastic glove to avoid contamination, and attached to the cathode where I could see only a tiny hole, ~4 mm diameter. Then, he pumped down, closed sample chamber and pressed “measure”. The discharge cell was replaced by an ultra-high purity Ar gas in 30 s and analysis got started. It took only 15 seconds to get through the 360 nm thick oxide film and analysis was completed to generate a fine depth profile never seen before. This was the moment that changed the direction my research and my life drastically and in a way never imagined before.

So let me start my talk to tell you “I’ve had a wonderful life with GDOES”.

## DIAGNOSTICS OF PULSED GLOW DISCHARGES BY OPTICAL EMISSION SPECTROSCOPY

Rebeca Valledor<sup>1</sup>, Paola Vega<sup>2</sup>, Jorge Pisonero<sup>2</sup>, Nerea Bordel<sup>2</sup>, Thomas Nelis<sup>1</sup>.

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The development of pulsed radiofrequency Glow Discharges (pulsed rf-GD) has opened new possibilities for the GD analytical community, since they produce less thermal heating of the sample, and they present different temporal regions where specific excitation and ionization mechanisms take place [1]. However, their behaviour is not completely understood yet. Optical emission spectroscopy (OES) can provide very interesting information when characterizing the fundamental processes in glow discharge plasmas. In commercial rf-GD-OES instruments, the average emission intensity of the whole plasma is acquired; therefore, fundamental studies can be useful, but give limited information about the plasma.

In this work, an in-house experimental set-up provided with a hollow anode source was developed to perform spatially resolved measurements of the glow discharge emission. Side-on as well as end-on observation of the plasma plume can be carried out. The spectrograph is equipped with an intensified charge coupled device (iCCD), which is synchronized with the rf-generator allowing, in addition, time resolved data acquisition. The emission coming from different spatial positions along the plasma plume axis is focused with a system of lenses, at distances where the sampler cone can be found when coupling the GD to a mass spectrometer (GD-MS).

The spatial and temporal distribution of the excited species in pulsed rf-GD has been investigated in order to characterize the ionization/excitation processes that take place within the plasma. Emission intensities were 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 was evaluated during prepeak and afterglow temporal domains, at different rf pulse frequencies. Transport phenomena involved in the formation of both emission maxima have been investigated. These results aim at better understanding the GD plasma dynamics and, thus at improving the performance of the GD instruments in which mass transport plays an essential role.

[1] P. Belenguer, M. Ganciu, P. Guillot and Th. Nelis, *Spectrochimica Acta Part B*, 64 (2009) 623-641.

## NEW INSTRUMENTAL CAPABILITIES FOR GLOW DISCHARGE SPECTROSCOPY.

Steven J. Ray<sup>1</sup>, Andrew Schwartz<sup>1</sup>, Andrew Storey<sup>1</sup>, Kevin Pfeuffer<sup>1</sup>, Volker Hoffman<sup>2</sup>, Maxim Voronov<sup>2</sup>, Carsten Englehard<sup>3</sup>, Wolfgang Buscher<sup>4</sup>, and Gary M. Hieftje<sup>1</sup>.

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The analytical glow discharge (GD) is, without doubt, the most versatile source used in atomic spectroscopy. While the GD has been most widely used in its classic role for the direct analysis of solid samples by atomic emission spectroscopy (AES), it has also been successfully applied in a wide range of atomic spectroscopy applications in the analysis of solids, liquids, and gases by atomic absorption, emission, and fluorescence, as an ionization source for both atomic and molecular mass spectrometry, and in alliance with chromatographic separations.

This presentation will explore several new adaptations of the multitalented GD for analytical spectroscopy. In one example, further development of a novel liquid-sampling GD known as a solution-cathode glow discharge (SCGD) will be examined.

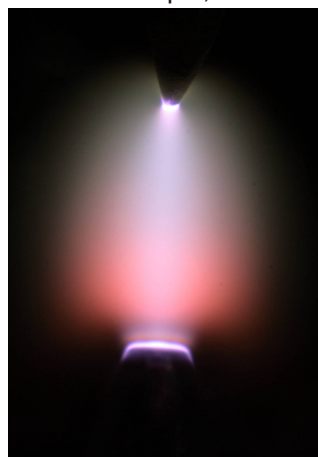


Figure 1: The SCGD in operation, pin anode (top) and solution cathode (bottom).

The SCGD shown in Figure 1 is an atmospheric-pressure glow discharge that is sustained in the open atmosphere between an anode pin and a sample solution, which acts as the discharge cathode. The plasma lies directly atop the surface of the analyte solution, and liquid sampling occurs by a mechanism akin to sputtering that ejects sample material into the SCGD plasma. There, analyte species are desolvated, atomized, and excited, and the constituent atoms observed by atomic emission spectroscopy. The SCGD-AES technique offers a number of significant advantages over conventional plasma emission techniques. Introduction of the analyte solution into the plasma occurs by a direct introduction mechanism, which promises high efficiency and rapid response. Further, because the surface of the flowing solution cathode is self-renewing, memory effects are minimized. The SCGD also operates in open atmosphere, employs a very simple experimental setup, requires no compressed gases, and uses only 70W of power. Thus, it well suited for portable instrumentation, and its simple construction and glow discharge structure make it amenable to miniaturization. The experimental construction of the SCGD, its operating mechanisms, spectroscopic characteristics, and analytical figures of merit of this SCGD-AES instrument will be presented, and the use of the SCGD in several applications examined.

A second discussion will examine a novel pulsed GD arrangement that permits lateral spatial information about a solid sample surface to be collected by GD-AES. In a typical GD-AES experiment, the cathode sputtering action liberates atoms from the sample surface. These atoms then diffuse into the GD plasma where they are excited and emit, and thus there is little correlation between the origin of each atom along the sample surface and the point within the discharge where it is finally observed in the AES experiment. However, when the GD is pulsed on the microsecond timescale, the atoms liberated from the sample surface do not have sufficient time to diffuse far from their origin before being excited to emission. When optical detection is gated to these pulsed GD events, the relationship between the observed atomic emission and the origin of the atom along the surface can be maintained, and it becomes possible to achieve lateral spatial resolution along the sample surface using GD-AES. Further, by taking advantage of the high depth resolution of GD techniques, it is possible that 3-D spatial characterization could be achieved. A theoretical discussion of the pulsed GD-AES and experimental details of instrument construction, as well as several novel applications of the instrumental approach will be detailed.

## USE OF A PURE COPPER ANODE IN THE GDL FOR REDUCED HYDROGEN BACKGROUND – THE IMPACT ON MOLECULAR EMISSION

Arne Bengtson<sup>1</sup>, Mats Randelius<sup>1</sup>

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A number of well-known artefacts in Glow Discharge Optical Emission Spectroscopy (GD-OES) are due to outgassing of adsorbed volatile compounds in the early stage of the discharge, lasting up to several seconds. This results in background signals from gaseous and other light elements, as well as transient emission from several molecular species. The molecular emission in turn interferes with several elemental emission lines. In addition, the excitation mechanisms of the glow discharge are influenced by primarily hydrogen [1], but possibly also by other light elements. Substantial work has been done in order to compensate for these unwanted effects in the data evaluation algorithms, but in order to improve analytical accuracy the best approach is to reduce both the adsorption and the outgassing of volatile compounds to the highest possible extent.

In previous work, a number of techniques have been explored to “clean” the discharge, with rather limited success. These techniques include pulsing of the source, a chemical filter on the argon supply line and pre-heating of the anode. More recently, it has been shown that the use of a pure copper anode leads to a dramatic reduction of the hydrogen background signal in the initial stage of the discharge. The mechanisms behind this positive effect are not understood. The high heat conductivity of pure copper may be partly responsible by reducing the surface temperature of the anode and thereby reducing the outgassing of volatile compounds. However, there may be more complex “catalytic” phenomena involved leading to a reduction of the dissociation rate of molecular hydrogen. In this work, the emission of the molecular species OH, NH, CH and CO has been studied. It has been shown that there is also a reduction in the emission intensity of these species when using a pure copper anode. The correlation between the emission intensities of light elements and the molecular species will be presented and discussed.

[1] Hodoroba, V.-D., Hoffmann, V., Steers, E. B. M., Wetzig, K.; Investigations of the effect of hydrogen in an argon glow discharge, *J.Anal.At.Spectrom.*, 15 (2000) 1075 - 1080.

## TOWARDS EXPLOITATION OF 'COMPLETE' GD-OES SPECTRA IN ANALYTICAL APPLICATIONS AND FUNDAMENTAL STUDIES.

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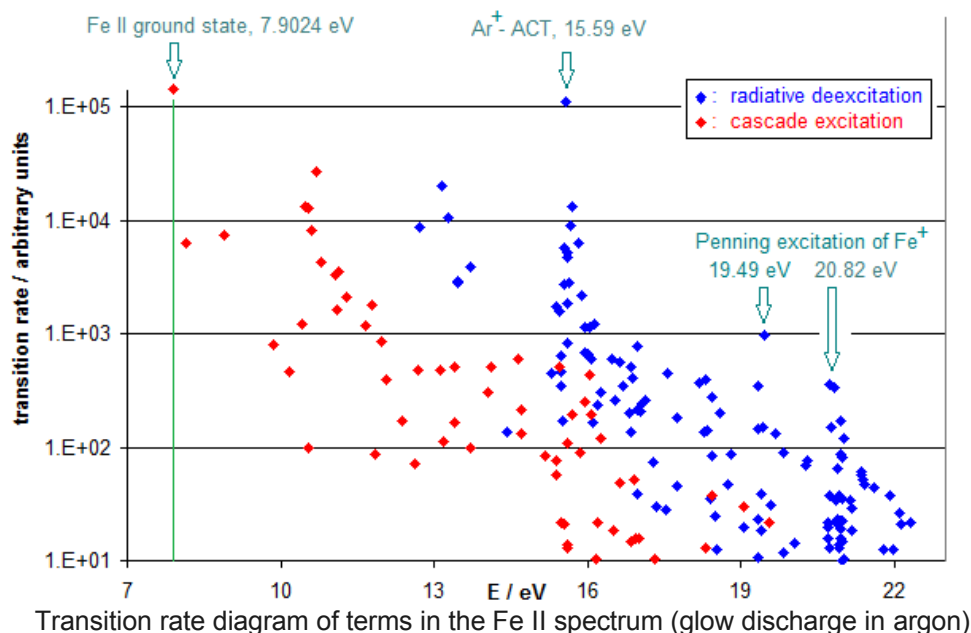
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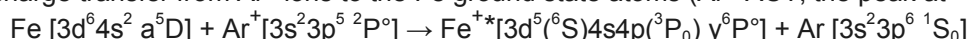
Progress in GD-OES instrumentation, in particular advanced detectors and data handling systems, makes it possible to collect routinely GD spectra spanning over wide wavelength ranges and save them in electronic form. This opens up ways unheard of in the past to utilize the information existing in raw data, both in analytical applications and fundamental studies. Examples are given of ways to improve the analytical performance of GD-OES by selecting suitable lines for a given application and by using several lines for a particular element to improve accuracy and precision.

Also, the recently proposed formalism of transition rate (TR) diagrams [1], utilizing many lines of an element, will be mentioned. The rate of a radiative transition is proportional to the product ( $I\lambda$ ) of the intensity  $I$  of the emission line associated with the transition and its wavelength  $\lambda$ . A TR diagram is a plot of the rates of observed radiative transitions from (blue points) and into (red points) different levels or terms of atoms or ions of an element as a function of their energy. In the TR diagram of Fe II below a logarithmic ordinate scale is used instead of the linear scale in Ref [1] and the rates of radiative (cascade) excitation are plotted as positive values instead of the negative values in Ref. [1].

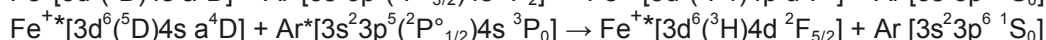
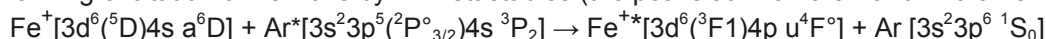


The 'blue' peaks that are not balanced by 'red' peaks at the same energy (cascade excitation) indicate selective excitation by collisional processes: in this case it is

- charge transfer from  $\text{Ar}^+$  ions to the Fe ground state atoms ( $\text{Ar}^+$ -ACT, the peak at  $\sim 15.59$  eV)



- Penning excitation of  $\text{Fe}^+$  ions by Ar metastables (the peaks at  $\sim 19.49$  eV and  $\sim 20.82$  eV):



- [1] Z.Weiss, E.B.M.Steers, J.Pickering and S.Mushtaq, Transition rate diagrams - A new approach to the study of selective excitation processes: The spectrum of manganese in a Grimm-type glow discharge, Spectrochim. Acta Part B 92C (2014), pp. 70-83

## LEAKAGE EFFECTS ON GLOW DISCHARGE DEPTH PROFILING AND THEIR MINIMIZATION

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Light elements are a major challenge in analytics, because they appear not only inside the samples, but also in higher concentration in the ambient atmosphere and in trace amounts in the flushing gases, protective gases or plasma gases used. This is particularly true for the GDOES where the plasma cleanliness suffer from substances emitted from surrounding surfaces of the measuring system or by a lack of sealing of the sample. So, a number of compounds can reach the plasma, preventing the correct determination of the corresponding elements and interfere with the analytic as a whole. In addition, the hydrogen content of a sample can be changed by implantation of external hydrogen from the plasma and subsequent diffusion. A noticeably change may appear already in the initial phase of a depth profile measurement. It is therefore of great importance to keep foreign substances such as oxygen or nitrogen molecules, water, carbon dioxide, hydrocarbon, water or other volatile compounds out of the plasma region. Starting points for this provides the structural design of the respective glow discharge source. I would like to give an introduction to this interesting subject by giving a background story and provide you with an overview of the most useful measures and their effects on analytical bias.

## DEPTH PROFILING CHARACTERISATION OF NANOSTRUCTURED MATERIALS BY PLASMA PROFILING TIME OF FLIGHT MASS SPECTROMETRY

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Plasma Profiling Time of Flight Mass Spectrometry (PP-TOFMS) provides direct measurement of the elemental composition of materials as a function of depth, with nanometre resolution and the capability to measure both thin and thick layers [1].

It consists in a pulsed radio frequency glow discharge plasma source fed with pure Ar and created under a pulsed RF potential coupled to a time of flight mass spectrometer (TOFMS). There is a perfect fit between the fast erosion rate of the high density and low energy plasma and the ultra-fast detection and quasi-simultaneous acquisition of all mass ions of the TOFMS. Furthermore the separation between sputtering and ionisation processes makes this technique much less matrix dependent compared to SIMS.

In addition, the orthogonal TOFMS configuration allows for temporal monitoring of the transient signals generated in the pulsed plasma. This is all the more important as signals are largely enhanced in the plasma extinction phase (once RF is turned off) in the so-called afterglow region. Ion signals are then generated through Penning Ionisation by Ar metastables.

Various examples in microelectronics and nanotechnology will be presented. It will be shown that PP-TOFMS allows for determining composition, detecting contamination, measuring doping level, and characterising diffusion mechanisms. Results will be compared to other techniques and aspects of analytical performance with regards to sensitivity, quantification, repeatability and sample throughput will be discussed.

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DOI: 10.1007/s00216-009-3382-8.

## INVESTIGATIONS OF MATRIX AND PLASMA PARAMETER DEPENDENCE OF RSF IN GD-MS

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The knowledge of the chemical composition of materials is an indispensable prerequisite for their use in Metrology in Chemistry. Therefore rational measurement methods for the determination of metallic and non-metallic elemental impurities are necessary to contribute to overcoming the current lack of these primary elemental standards [1].

Solid sampling techniques such as Glow Discharge Optical Emission Spectrometry (GD-OES) and Glow Discharge Mass Spectrometry (GD-MS) are very attractive for industry and research since they allow fast and sensitive multi-element analysis and do not require laborious sample treatment [2]. As other solid sampling techniques glow discharge based techniques require calibrations to link the measured signal and the concentration. Without calibration, only semi-quantitative analysis is possible. The availability of SI traceable calibration material is an essential prerequisite for the reliable determination of the chemical composition of solid material by GD-OES and GD-MS [2]. However, suitable calibration materials are missing in many cases. The lack of calibration samples is especially noticeable for light elements such as H, C, N and O. The determination of light elements is of great importance for the characterisation of primary materials in metrology since the presence of small amounts of these elements affects significantly the properties of the material.

The application of the concept of matrix independent relative sensitivity factors (RSF) in GD-MS provides useful approximations especially for pure substances but it is not appropriate for metrological applications. The sensitivity of GD-MS depends on the discharge conditions voltage, current and pressure/flow. Therefore, investigations into the effect of the discharge parameters on RSFs will help to improve the robustness of this quantification procedure, if no matrix specific calibration is possible.

This contribution reports preliminary results carried out during the fundamental studies about the robustness of the RSF. A special attention was paid to the effect of the discharge conditions (voltage, current, discharge gas pressure/flow) on the RSFs in the fast flow GD-MS source. Three matrices were chosen for this investigation – Al, Cu and Zn – and relevant reference materials were analysed. Furthermore, results related to the possibility of a multi-matrix calibration of oxygen in GD-MS will be presented. For this purpose, a set of new conductive samples containing oxygen concentration in the percent range 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. Matrix specific RSFs are generated and limits of detection are determined. All 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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[2] Volker Hoffmann, Martin Kasik, Peter K. Robinson, Cornel Venzago, Anal. Bioanal. Chem., Issue 381 (2005) 173-188



## A COMPARATIVE STUDY TO EXPLORE AND EVALUATE THE PERFORMANCE OF THE VG9000 RSF DATA SET AS APPLIED TO NU ASTRUM FLAT CELL AND PIN CELL DATA

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Relative Sensitivity Factors (RSF) are a set of correction factors that are applied to the instrument output to achieve quantitative analysis. These values are calculated from the analysis of various types of certified reference materials. Historically for glow discharge mass spectrometry (GDMS), the RSF values were based on the 1991 publication of Vieth and Huneke [1] which established a RSF data set for use with the VG9000, the first commercially available double focusing instrument used for elemental analysis [2]. As the VG9000 is still the industry standard for the direct analysis of high purity solid materials, this instrument was used as a model in the development of the next generation of high resolution direct current glow discharge mass spectrometer, the Astrum from Nu Instruments. The globally recognized and accepted performance and functional benefits of the traditional VG9000 system were combined with the latest advances in software, sample cell geometries, electronics and vacuum technology to produce a high performance new instrument designed specifically for ultra-trace analysis of impurities. Like the VG9000, the Astrum is able to analyse samples using both pin cell and flat cell geometries. While the flat cell method is used to analyse the surface of a sample, the pin cell approach lends itself more to the analysis of bulk material. As the Astrum was designed to analyse the same types and sizes of samples as the VG9000, the expectation was that the Astrum would also be able to utilize the same RSF data set as the VG9000. To explore this possibility, several reference materials, *i.e.*, Nickel IARM 69D, Copper ERM EB385, Aluminium CRM 166/02, and Silicon Nitride NMIJ CRM 8004a and 8005a, were analysed by both pin and flat cell techniques using the Astrum. The nickel, copper and aluminium standards consisted of lower purity solid pieces while the silicon nitrides were higher purity powders. For the analysis, the solid pieces were cut into pins and flat samples of ~2 x 2 x 22mm and ~20 x 20 x 2mm in dimension, respectively. As the silicon nitride powders are non-conductive, these materials were pressed onto a conductive indium binder having both pin (~2 x 2 x 22mm) and flat sample (~15mm Ø) configurations. The nickel, copper and silicon nitride standards were each analysed one time by pin cell and one time by flat cell method, while the aluminium standard was analysed three times by pin cell and twice by flat cell method. The same RSF data set adapted from the publication of Vieth and Huneke was applied to all data. The results from the Aluminum CRM 122/06 were typical in that the resulting average concentrations were within 30% of the certified values with no significant difference between pin cell and flat cell data. For all other standards, the resulting values achieved by pin cell analysis were in good agreement with those obtained from the flat cell method, and both results from the reference materials showed good agreement with the certified values. The findings from this RSF study showed that the same RSF data set developed for the VG9000 was able to be applied successfully to both Astrum pin and flat cell data for nickel, copper, aluminium and silicon nitride reference materials to within the accepted ±30% for GDMS data.

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## Direct Current Glow Discharge Mass Spectrometric Analysis of Non-conducting Materials Using a Surface Coating Method

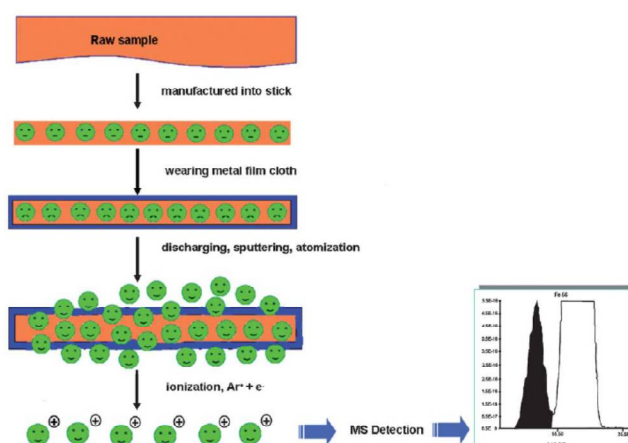
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A surface coating method was developed to analyze some non-conducting materials using the pin cell of a direct current glow discharge mass spectrometer (dc-GD-MS). As the materials were non-conducting there were many problems associated with sustaining a dc glow discharge, and this could be overcome by coating the surface with a very thin layer of conducting material. During the sample preparation process the melted indium was coated manually onto the surface of the sample, thus supporting the sputter process and causing the sample to be sputtered and ionized for analysis. After optimization of the plasma conditions, the prepared samples could be analyzed directly by dc-GD-MS with satisfactory detection limits, stability and reproducibility. Two NIST standard reference materials were used to validate the precision, accuracy and reproducibility of this method. The results showed that this method could avoid grinding, sustain the relatively stable discharge and enhance the stability of signals compared to the method of using a cathode made from indium pin rolled in the sample powder [1].



Scheme. Schematic representation of the surface coating method.

[1] Rong Qian, Shangjun Zhuo, Zheng Wang, Peter Kenneth Robinson, J. Anal. At. Spectrom., 2013, 28, 1061–1067.

## Sputter Rates in GDMS

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

Sputter rates are results of interaction between glow discharge and sample. Some relationship between sputter rates and glow discharge parameters and sample properties are discussed and demonstrated including Bouman equation.

## NON-LTE BEHAVIOR OF ARGON AND KRYPTON GLOW DISCHARGE PLASMAS ESTIMATED FROM THE INTENSITY ANALYSIS OF NICKEL ATOMIC LINES.

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Glow discharge produces a plasma state not being in local thermodynamic equilibrium (non-LTE), which means that particles in the gaseous body, such as electrons, ions, and neutral atoms, do not have the same distribution in the kinetic energy. The non-LTE characteristics result from the fact that collisions with energetic electrons, which are first accelerated by the electric field, occur insufficiently enough to cause the energy transfer to gas species, because the glow discharge is generated under reduced pressures and thus large parts of the accelerated electrons pass through the gaseous body with weak interactions.[1] Accordingly, there is a large difference in the average kinetic energy between the gas particles and the electrons in the glow discharge plasma. In an LTE plasma, a unique temperature can be determined to represent the spectrochemical properties of the plasma, which can predict a spectrum pattern from the Boltzmann distribution among the corresponding excited energy levels.[2] However, glow discharge plasmas are in non-LTE conditions, yielding lower gas temperature than the electron temperature, and therefore, the excitation/ionization phenomena in GD-OES cannot be explained from the Boltzmann distribution.

Our previous papers have indicated that high-lying excited energy levels of iron atom are largely overpopulated from normal Boltzmann distribution, when Boltzmann plots for many iron atomic lines having excitation energies of 3.3 - 6.9 eV were investigated in argon or neon glow discharge plasmas.[3,4] The plots did not follow a linear relationship over a wide range of the excitation energy, but showed that the emission lines having higher excitation energies largely deviated from the normal Boltzmann distribution whereas those having low excitation energies (3.3 - 4.3 eV) were on a straight line. This result would be derived from an overpopulation among the corresponding energy levels. A probable reason for this is that excitations for the high-lying excited levels would be caused predominantly through a Penning-type collision with the metastable atom of argon or neon, followed by recombination with an electron and then stepwise de-excitations which can populate the excited energy levels just below the ionization limit of iron atom.[3]

In this study, a series of nickel atomic lines, having excitation energies of 3.84 - 7.68 eV in the wavelength range of 300 - 338 nm, was observed so as to investigate the non-LTE behavior occurring in the glow discharge plasma in more detail. Also in the nickel system, a large over-population of the excited levels having the excitation energy of more than 5 eV was clearly recognized in the Boltzmann plot. The enhancement factor, which was defined as a ratio of the observed intensity to the value expected from the normal Boltzmann distribution, was estimated for several emission lines of nickel atom, indicating that the factor exceeded 1000 in the Ni I 322.127 nm line (7.68 eV). This result implies that the excited energy level would be populated through de-excitation channels from singly-ionized nickel.

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## FORMATION OF THE PLASMA RADIATION PREPEAK IN MICROSECOND PULSED GLOW DISCHARGE WITH GRIMM TYPE SOURCE

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The prepeak in the emission of plasma radiation in microsecond pulsed glow discharge ( $\mu\text{s}$  PGD) is reported in many different works [1-7]. In [4] a systematic investigation of the prepeak in the pulsed rf discharge is carried out for different lines. However in rf-PGD the evolution of the dc bias voltage in the leading edge of the pulse interferes with the radiation prepeak. This makes the interpretation of the results difficult.

The origin of the prepeak is still not clear. Sometimes the prepeak is attributed to self-absorption [3,4]. On the other hand there is also a prepeak in the electrical current in PGD [8,9]. In [10] a good correlation between the electrical current and plasma emission is measured. Therefore it is natural to suggest that the radiation prepeak is caused by the current.

To clarify the radiation prepeak nature, systematic investigation of the emission prepeak in  $\mu\text{s}$  dc-PGD was carried out. The first results of the investigation were already reported [11]. At a high power discharge, the prepeak is found in all plasma emission lines, including atomic and ionic lines of the discharge gas (Ar) and the cathode material. There is a certain similarity between the electrical and emission prepeak; a threshold voltage for formation of the prepeaks exists and the prepeak durations are similar. This points to the electric prepeak as a reason for the emission prepeak.

However, the form of the radiation prepeak differs for different emission lines. The present work is focused on explanation of the prepeak forms. Additional factors influencing the emission prepeak formation are discussed; self-absorption and recombination. Comparison with rf-PGD is given.

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## EFFECT OF SMALL QUANTITIES OF OXYGEN IN A NEON GD

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Many studies have already been carried out on the effect of small quantities of molecular gases (oxygen, hydrogen and nitrogen) in argon analytical glow discharges (GD). We report here the first multi-line study using small amounts of oxygen in a neon GD plasma with various pure metallic samples. Whilst neon is too costly for normal use in analytical GD, such studies help the interpretation of the excitation and ionization processes taking place in the discharge. The experimental results were obtained using a Grimm-type GD source and the Imperial College visible-vuv Fourier transform spectrometer, as described previously. The experimental results for neon/oxygen are compared with those for argon/oxygen and neon/hydrogen mixtures.

In all GD, Penning excitation (PE), Penning ionization (PI) and asymmetric charge transfer (ACT) have significant roles in populating excited ionized levels, so the higher energy of the neon metastable states and

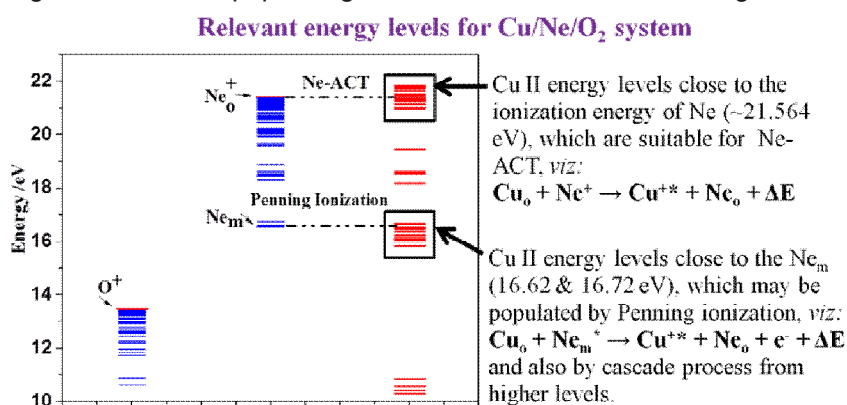


Fig. 1 Schematic representation of some energy levels of relevant elements (atomic in blue, ionic in red). Only the region of interest from 10 eV up to 22 eV is shown.

In a neon GD, lines with upper levels with total excitation energy (TEE) ~ 21.5 eV are populated by ACT. Those with TEE ~ 16.7 eV are populated by PI, but also by radiative transitions from higher levels. Moreover, emission yields of Cu II lines excited by Ne-ACT fall when oxygen is added, probably due to a fall in the  $\text{Ne}^+$  population; lines excited by PI exhibit a smaller fall. On the other hand, for elements with suitable lines with TEE ~13.5 eV, e.g. iron and titanium, excitation of these lines by O-ACT is possible, which becomes more pronounced for higher oxygen concentrations.

A significant intensity decrease in the majority of Ne II lines is observed at low oxygen concentrations. However, at higher concentrations, lines from doublet levels are enhanced whilst those from quartet levels show a further intensity fall.

Examples of all these effects will be presented for various cathode materials.

the higher ionization energy compared to argon have a major effect on the appearance of the spectrum. Relevant energy levels for Cu/Ne/O<sub>2</sub> are shown in Fig 1. The presence of small quantities of oxygen in the GD affects the populations of neon metastable levels and ions and so changes the observed spectrum. Some typical changes are shown in Fig. 2. The ratios of emission yields of analyte lines are used as the presence of oxygen in neon or argon plasmas reduces the sputter rate.

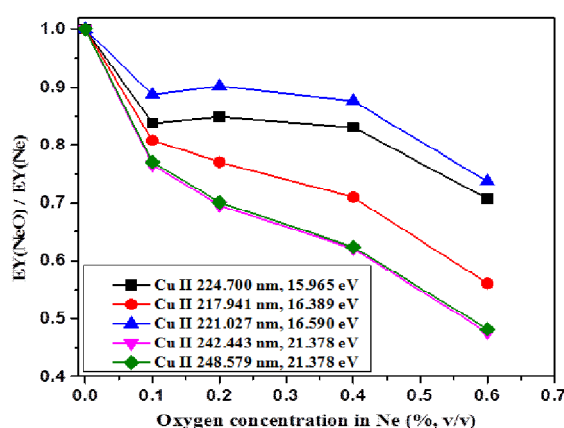


Fig. 2 Emission yield ratios against various oxygen concentrations for selected Cu II lines for 700 V & 20 mA.

## GD-OES APPLICATIONS IN STEEL RESEARCH.

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OCAS is an advanced, market-oriented research centre for steel applications. Based in Belgium, it is a joint venture between the Flemish Region and steel group ArcelorMittal.

In our ArcelorMittal mission we offer support to production plants, both for quality control as for defectology on finished products. Another objective is to develop new products and solutions for steel applications.

Both in the development of new substrates, metallic coatings and environmentally friendly passivation layers, as in quality control of production processes and defectology GD-OES is a valuable tool.

GDOES is mainly applied for elemental depth profiling with a very high depth resolution (down to a few nm). The method is very versatile, as it can be used for bulk analysis as well. Conductive and non conductive samples as well as tube shaped samples can be analysed. The analysis is in principle qualitative, however when calibration panels are available or when sputter rates are known, quantitative information can be obtained.

In this presentation the specifications, advantages and drawbacks of GD-OES will be discussed. Its added value is illustrated based on some examples and case studies.

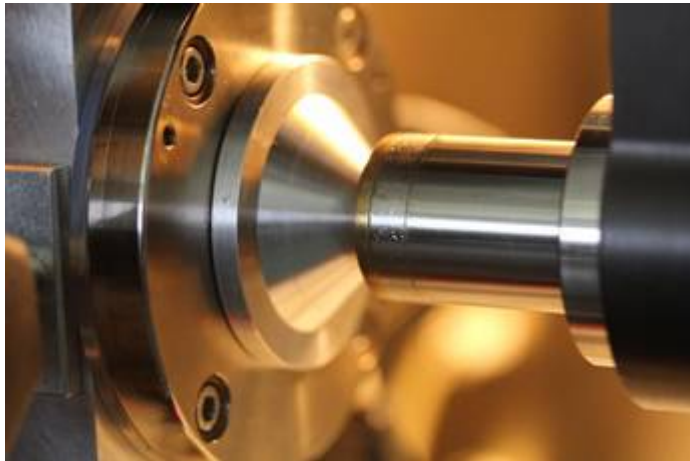
## ANALYSIS OF SMALL CYLINDRICAL DLC COATED PARTS WITH A MODIFIED UNIT FOR THE GDA 750.

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The demands for higher performing diesel injectors in the automotive sector are constantly rising. Parts in the injector become smaller and experience higher stresses in operation. These small, highly loaded components in the injector are coated with a conventional DLC-layer system.



With the commercially available universal sample unit (USU, by Spectruma) cylindrical samples can be measured in principle, but this has some disadvantages for industrial style measurements (e.g. incoming inspections). There is only one available sample adaptor which must be customised for every geometrical variation. Due to the size of the standard chamber, multiple intermediate flushings are applied increasing the total measurement time.

In order to measure small coated parts with complex geometries quickly and repeatedly, a master's thesis was undertaken at Continental, Limbach-Oberfrohna, which included the development of an improved sample unit. With this prototype unit, the time required for the measurement could be minimised. The sample geometry was taken into account for the accurate manufacturing of the sample holder. The layer composition of the DLC-coated components can be analysed. The evacuation is improved by the smaller sample unit size. The sample unit can be placed directly on the 2.5 mm cathode plate. Since the focal spot of a 2.5 mm anode is too large, the original 2.5 mm anode was modified to a smaller inner diameter.

Comparative measurements between flat and cylindrical samples have proved that the measuring unit is suitable for this type of analysis. The repeatability of these tests can also be demonstrated.



## USING KRYPTON AS A DISCHARGE GAS TO HELP IN ASSESSING THE RELATIVE IMPORTANCE OF GD EXCITATION PROCESSES

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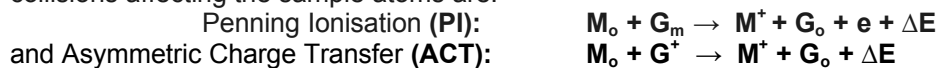
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In analytical glow discharges (GD), the two main ionisation/excitation processes apart from electronic collisions affecting the sample atoms are:



where  $M_o$  is a sample atom, usually in the ground state,  $M^+$  a sample ion, in ground or excited state,  $G_o$ ,  $G_m$  a plasma gas atom, in ground or metastable state respectively, and  $G^+$  a plasma gas ion.

ACT is only possible when  $\Delta E$ , the energy released, is small, so it is a highly selective process which only excites a limited number of levels and transitions from these levels, e.g. Cu II 224.7 nm and the Fe II 165 nm multiplet in argon discharges. Lines excited by ACT can easily be identified by comparing the spectra obtained with two different plasma gases. Argon is almost always used for routine analytical GD Optical Emission Spectrometry (GD-OES) in view of its low cost and the ready availability of high purity gas. Krypton is rarely used, even for studies of fundamental processes, although Steers [1] used it to investigate ACT in GD with iron and titanium cathodes and Wagatsuma [2] has used it to identify ACT excitation in nickel, cobalt and vanadium spectra. Compared with other noble gases, krypton has the advantages that in the constant voltage, constant current mode, the pressure required and the sputtering rate with krypton are similar to those in argon discharges.

PI is possible whenever the energy of the metastable state of the plasma gas is greater than the total excitation energy of the level to be populated. The electron produced allows energy and momentum conservation laws to be satisfied for much larger values of  $\Delta E$ , although PI is more likely when  $\Delta E$  is small. PI is a major factor in the production of sample ions in their ground state or low lying metastable states. There are relatively few elements where there are non-metastable ionic energy levels which can be excited by PI in an argon plasma, so that it is not easy to investigate PI using GD-OES. However, such levels exist for titanium, and they cannot be excited by PI in a krypton plasma, so a detailed study of PI can be made by comparing the intensities of appropriate lines in argon and krypton discharges. In Fig. 1, lines 1-4 have upper levels with energies above those of the krypton metastable states but below those of the argon metastable states and so can be excited by Ar-PI but not by Kr-PI and are more intense in argon; the upper energy of line 5 is too high for Ar-PI, but not high enough for Ar-ACT. Line 6 is a Ti I line and is more strongly excited in krypton.

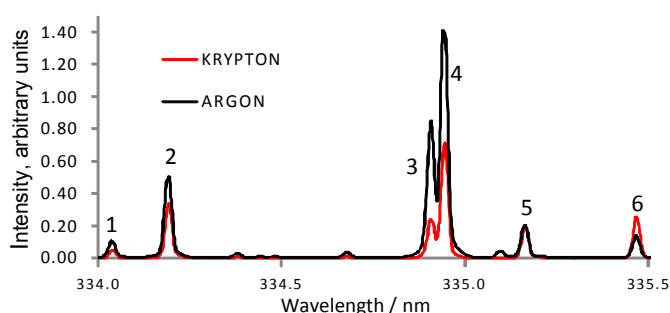


Fig 1. Comparison of titanium spectra using argon and krypton

Line	Wavelength /nm		Upper level. Total energy /eV
1	334.034	Ti II	10.651
2	334.187	Ti II	11.111
3	334.903	Ti II	11.136
4	334.940	Ti II	10.577
5	335.159	Ti II	14.589
6	335.464	Ti I	3.715

For such studies, it is necessary to observe a large number of spectral lines simultaneously under a range of discharge conditions; the current studies were carried out using the Spectra GDA650A Glow Discharge Analyser at IFW, Dresden. This instrument can record the average of 10 spectra over the range 120 – 600 nm, with a resolution of 30 pm in less than one minute with a dynamic range of about  $10^4$  and is therefore very suitable for this work.

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## COMBINED HOLLOW CATHODE AND GRIMM CELL: A COMPARISON OF THE ANALYTICAL CAPABILITIES

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The hollow cathode cell (HC) and the Grimm cell have been used as the most typical glow discharge (GD) cells for decades. The HC, being historically the first source for analytical GD, is almost totally replaced by the Grimm source nowadays. The latter proved itself to be very convenient and effective in use. However in recent years several works revealing the advantages of the HC system [1-3] were published and several different comparisons of the cells were made[2-4]. The present work includes a new approach for the comparison of analytical capabilities of the cells, based on consideration in equal power conditions. Particular accent was made on the effect of sample conductivity and differences in sputtering mechanisms.

Conductive (steel, copper), semiconductive (silicon, silicon carbide, gallium nitride) and nonconductive (quartz and alumina) samples were considered, with the main focus on the nonconductive ones. In this connection a combined hollow cathode (CHC) was used, which consists of a cylindrical cathode and a flat sample in the bottom of the cylinder. The comparison of the discharge cells was made by OES signal intensities of sample components at equal power and similar pressure conditions, applying continuous DC and RF and pulsed DC power supply modes.

The CHC source operated in continuous RF mode gives almost the same or higher intensities in comparison with the Grimm cell for both matrix components and impurities. The advantages of the CHC cell were shown to be realized with the reduction of electrical conductivity of the sample. For thick dielectrics even the use of continuous RF CHC discharge becomes considerably more favorable than the use of the Grimm construction. Such a distinguishing behavior was found to be related to the principal differences in the CHC sputtering mechanism. The latter was thoroughly investigated and proved to be connected with the formation of a conductive surface layer on the sample surface. The layer is generated as a result of two types of processes: the enrichment of sample surface by the less sputtered sample atoms and the deposition of cathode material. The thickness of the formed surface layer (few nm) was shown to be defined mainly by cathode and sample material and is quite independent of the conditions and time of sputtering.

Furthermore, when operating in pulsed DC mode, the CHC system produces up to several orders of magnitude higher intensities than the Grimm cell, especially for dielectric samples. The pulsed mode with hollow cathode has also shown good ratios of sample to the cathode material intensities compared both with the continuous mode and the secondary cathode systems.

However, the application of hollow cathodes is complicated by instability of the discharge and cathode material redeposition on the sample. The operating parameters of the cell were found to strongly depend on the cathode material. Due to the latter facts the operating parameters of the hollow cathode cell should be thoroughly selected for each cathode material. In the present work aluminum, copper, and tantalum cathodes were considered and compared. Tantalum was observed to be the most effective.

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## SAMPLE PREPARATION AND DEPTH PROFILING ANALYSIS OF INNOVATIVE MATERIALS BY PULSED GLOW DISCHARGE MASS SPECTROMETRY.

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The development and characterization of innovative materials, for instance those based on thin coatings, highly require the use of direct-solid analytical techniques able to provide excellent analytical performance, including high depth resolution, high spatial resolution and/or high sensitivity for the determination of trace elements [1]. In this sense, a group of well-established analytical techniques, including Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), have been extensively used for direct depth profiling of thin layers due to their excellent capabilities. However, these techniques are operated at ultrahigh vacuum conditions and might suffer from some limitations, such as relatively low sputtering rates.

In this work, we evaluate the advantages and limitations of complementary techniques for depth profiling analysis such as radiofrequency pulsed-glow discharge (rf-PGD) mass spectrometry [2]. Moreover, the fast and smooth sputtering process of the PGD source could be used as a sample preparation method for other techniques such as AES or scanning electron microscopy.

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## DEPTH PROFILE ANALYSES BY GLOW DISCHARGE MASS SPECTROMETRY AND ION IMPLANTATION.

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Glow discharge mass spectrometry (GD-MS) is a well-know technique for bulk concentrations analysis, while no generally accepted method of quantification of depth profiles has emerged for this technique. Currently, the GD-MS instruments are receiving increasing attention for the analyses of materials for photovoltaic (PV) applications. Accurate measurements of doping elements, such as B and P, as well as metallic impurities, such as Fe, Cu and Ti, play a key role for predicting the electrical properties of the device.

In this work we have developed a method to assess the capability of depth profile analysis by GD-MS for several impurities relevant for solar cell silicon. A fast-flow direct-current high resolution glow discharge mass spectrometer (GD-MS) has been used. Six multicrystalline p-type silicon samples with contamination of B, P, Fe, Cu and Ti have been investigated. Ion implantation has been used for impurity contamination with a target depth of 3  $\mu\text{m}$ . The acquisition time was approximately 30 seconds, giving a depth resolution of approximately 0.5  $\mu\text{m}$ .

The GD-MS concentration profiles of the samples contaminated with B and P agreed well with the levels implanted, while for Fe, Cu and Ti the concentration profiles did not show clear trends. This indicates that for transition metallic impurities, and especially for the fast diffuser Cu, different impurity distribution mechanisms are occurring (e.g. solid-state diffusion, microsegregation, etc).

## COMPARISON OF GDMS AND SIMS DEPTH PROFILE ANALYSIS RESULTS OF SEVERAL LAYERED SYSTEMS LIKE: CIGS, TiN/Fe AND (TiVZrNbHf)N/Fe

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Results of two techniques applied for depth profile analysis of several layered systems as: CIGS/Mo (copper indium gallium (di)selenide), TiN/Fe, (TiVZrNbHf)N/Fe are presented. The two techniques are: glow discharge mass spectrometry (GDMS) and secondary ion mass spectrometry (SIMS).

Both techniques apply argon ion sputtering for erosion of the analysed samples. However different are ionization phenomena in the two cases. In GDMS, the ionization occurs in low-pressure plasma, while in SIMS, ionization occurs at the bombarded surface and neighbouring atoms of the surface influence strongly this process due to so-called matrix effects [1, 2].

GDMS analyses were performed on SMWJ-01 analyzer [3, 4] with Grimm type discharge cell and with the use of 1.5 mm diaphragm in intermediate cathode made of tantalum. The analyzer is equipped with Bessel-box energy filter and 6 mm rods quadrupole mass analyzer SRS-300. Quadrupole analyser is vertically positioned below the discharge cell. Depth profile analyses are performed over 1.5 mm diameter spots eroded due to 1500-1800V, DC glow discharge in ~0.1 Torr argon. Sputtering rate is calculated after stylus profilometry measurements of the eroded craters. Tencor Alpha-step 100 profilometer is used.

SIMS depth profiles were obtained with 3 keV Ar<sup>+</sup> beam at incidence angle 45°. Ion beam scanning was performed over 1.8 mm x 1.3 mm area. Secondary ions were analyzed from the central 5% part of the crater. Base pressure in SIMS analytical chamber is 1·10<sup>-10</sup> Torr. SIMS analyzer SAJW-05 [5] is equipped with Physical Electronics ion gun and 16 mm rods quadrupole mass analyzer – QMA-410 Balzers.

We will compare the obtained results and discuss selection of m/z of ions for depth profile analysis in each technique. Also the effects of mass interference in both techniques will be discussed. Obtained analytical parameters as sputtering rate, depth profile resolution etc. will be compared.

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## MEASUREMENT OF COPPER DIFFUSIVITY IN SILICON BY GLOW DISCHARGE MASS SPECTROMETRY.

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Unintentional copper contamination occurs frequently in silicon for photovoltaic applications due to its very fast diffusion coupled with a low solid solubility, especially at room temperature.

The combination of these properties exerts a challenge on the direct analysis of Cu bulk concentration by sputtering techniques like glow discharge mass spectrometry (GD-MS).

In this work, several monocrystalline (Czochralski) silicon samples were intentionally contaminated with Cu after solidification, and consequently annealed at 900 °C to ensure a homogeneous distribution of Cu in the bulk of the samples. The samples were quenched after annealing to limit the extent of the diffusion to the surface prior to the GD-MS analyses, which were carried out within few minutes after cooling. The time intervals between analyses were kept as similar as possible among the various samples. Samples with different thicknesses were studied in order to evaluate the impact of the out-diffusion over different ranges. In order to evaluate the contribution from external contamination during the Cu contamination and diffusion process, a blank sample (i.e. no Cu contamination) from the same ingot was annealed and analyzed by GDMS.

The Cu profiles were measured by high resolution GD-MS operating in a continuous mode, where the depth resolution was set to approximately 0.5  $\mu\text{m}$ , over a total sputtered depth in the order of tens of  $\mu\text{m}$ . The temperature of the samples during the GD-MS analyses was also measured in order to evaluate the diffusion. The profiles show a strong impact of out-diffusion from the bulk, which takes place in a short time after the annealing.

The Cu concentration profiles were used to calculate Cu diffusivity in these materials.

## CALBRATION STRATEGIES FOR FULL SURVEY CHEMICAL ANALYSIS OF SUPERALLOYS AND COATINGS BY FAST FLOW GLOW DISCHARGE MASS SPECTROMETRY.

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Superalloys are precisely engineered metallic materials, which have been developed for very specific elevated temperature applications. Because their main characteristic is high temperature strength, toughness, and resistance to degradation in corrosive or oxidizing environments their foremost utilization is engineering of gas turbine engine components for power generation and aircraft propulsion. Since there are known synergetic effects between chemical compositions, microstructures and mechanical properties of these materials, there is essential that their elemental makeup is assessed fully, very accurately and exceptionally precisely.

Superalloys should be considered complex alloys because they commonly incorporate as many as ten major elements, and many others at various minor range levels. For instance, Ni based superalloys are composed of several solid solution strengthening elements (Co, Cr, Fe, Mo, Ta, W, Re),  $\gamma'$  formers (Al, Ti), grain boundary refiners (B, Zr, Hf) and intentionally added elements for improving hot corrosion resistance (Y, La, Ce). They may also contain up to a dozen of other elements at limited mass fractions. Furthermore, specific manufacturing processes, such as conventional casting, mechanical alloying, powder metallurgy, directional solidification or single crystal making could contribute with unwanted residual impurities, which need to be minimized and/or bordered. This complex nature of manufacturing makes the quality control of their production or the process control of engineering parts from superalloys by standard chemical analytical techniques quite difficult and complex. However, thanks to the superior analytical characteristics of the glow discharge mass spectrometry (GDMS), such as solid sampling, excellent sensitivity and linearity, exceptional precision, and reproducibility and last but not least the depth specific acquisition capability with acceptable depth resolution, GDMS became the most suitable option for full chemical characterizations of these materials. Yet, currently there are no standard test methods for quantitative analysis of superalloys by any of the commercially available GDMS instruments. The lack of recognized standard test procedures in addition to limited availability of Certified Reference Materials (CRM) are generally the two major contributing factors to the unintended discrepancies found between various laboratories using GDMS techniques for analyzing superalloys.

This contribution will define a calibration strategy for high precision trace element analysis of superalloys using glow discharge mass spectrometry based on fast flow GD source. Additionally, a modified GD source and related operating conditions will be described. The impact of the nominal discharge gas flow rates on the linearity of the ion beam ratios and validation of the calibration procedure is going to be demonstrated using single crystal reference materials. Other promising applications of the fast flow GDMS, such as highly efficient and accurate depth specific analysis of advanced conversion type coatings will be also demonstrated.

## COMPACT ELECTRON BEAM WELDING DEVICE BASED ON GLOW DISCHARGE IN LOW PRESSURE ARGON

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Electron beam welding device based on glow discharge phenomena is presented. This simple construction instrument can be used for welding of metals and its alloys, however can also be used for surface melting of glass and ceramics.

The glow discharge develops between the two electrodes, one of them being a work piece. The other electrode, positioned 30 mm from the work piece, is hollow cathode of 20 mm diameter. The cathode is assembled in a quartz glass tube casing. Applied voltage to the cathode is in the range 1 – 3 kV. The operating pressure of argon is between 0.001 and 0.5 Torr. The optimal pressure during welding process is ca. 0.3 Torr. Before the welding, during focusing of the beam, the pressure should be less than 0.25 Torr. Focusing of the electron beam is provided only by curvature and shape of the cathode surface and there is no external-guiding magnetic field applied to the drift space.

Thus, electron bombardment parameters differ from conventional electron beam welding machines, which use typically 6 – 100 keV, well focussed electron beams. Here we use low energy electron beam, which is focussed only to about 0.4 mm, so high precision welding is not possible. However, advantage of this construction is possibility to melt insulating materials. Namely, surface charge neutralization is possible due to the glow discharge, which occurs in argon used as a working gas.

Some applications of this simple electron (glow discharge) welder will be presented. Examples show several wire thermocouples and a few welds of small pieces up to 0.4 mm thick metal sheet of Al, Fe, Ni, Ag and alloys. Additionally, we will show results of different types of glasses (sodium borosilicate and quartz) and alumina ceramic bombarded with electron beam.

The developed device may also be used to encapsulate small objects, such as micro electro mechanical systems (MEMS). Encapsulated systems can be flat silicon-glass based structures, or other geometry systems. If the encapsulated object allows, it can be also baked by the electron beam.



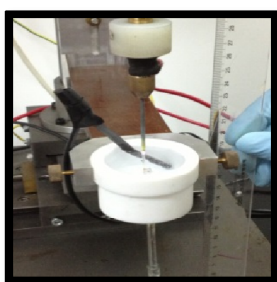
# TRACE METAL ELEMENT DETERMINATION BY ATMOSPHERIC PRESSURE SOLUTION CATHODE GLOW DISCHARGE AND ATOMIC EMISSION SPECTROSCOPY

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Atmospheric-pressure solution cathode glow discharge (SCGD) as an emerging testing tool has attracted more and more attention attributed in the advantages of the simpleness in sensor measurement and low-cost. Moreover, recent studies show that SCGD-AES can provide detection limits (DLs) for several metals, such as lithium, sodium, or potassium, at or below the tens of parts per billion ranges. However, SCGD systems provide heavy metals, such as Cd, Hg, Pb, and Cr, DLs higher than tens of parts per billion, which does not meet the requirements for quantifying heavy metals at very low levels, especially, in environmental and biological samples.



Here, we will introduce three our works on SCGD-AES. Firstly, trace impurities of sodium, lithium, magnesium, and potassium in colloidal silica were determined by SCGD. The applied voltage, solution flow rate, and distance between the metal anode and surface of the solution were optimized [1]. Emission from K (766.5 nm), Na (589.0 nm), Mg (285.2 nm) and Li (670.7 nm) demonstrated a linear range of nearly 4 orders of magnitude ( $R^2 \geq 0.998$ ) and steady-state sample introduction yielded limits of detection of 0.7, 0.4, 0.5 and 0.2  $\text{ng mL}^{-1}$ , respectively. For an integration time of 0.3 s, relative standard deviations (RSDs) from 1000  $\text{ng mL}^{-1}$  standard solutions introduced continuously were found to be better than 3% for all four elements. Transient sample introduction into the SCGD was also optimized and provided limits of detection for K, Na, Mg and Li of 3, 2, 2 and 0.8  $\text{ng mL}^{-1}$ ,

respectively, and RSDs for 1000  $\text{ng mL}^{-1}$  standard solutions of better than 3%. Determined concentrations of trace impurities in colloidal silica agreed satisfactorily (accuracy from 1.3 to 7.7% and precision from 4 to 14%) with those obtained from inductively coupled plasma atomic emission spectrometry.

Secondly, addition of the ionic surfactant CTAC to electrolyte solutions resulted in a decrease in dynamic surface tension, an increase in power density, and improvements in excitation efficiency, resulting in the enhanced sensitivity of SCGD-AES toward Cd, Hg, Pb, and Cr [2]. CTAC at 0.15% (mass percentage) showed maximum enhancement of emission signals. The net intensity of atomic emission lines of Cd, Hg, Pb, and Cr solutions with CTAC improved by 2.1-, 4.8-, 6.6-, and 2.6-fold, respectively, compared with solutions without CTAC. The DLs of Cd, Hg, Pb, and Cr were 1.0, 7.0, 2.0, and 42  $\text{ng mL}^{-1}$ , respectively.

Thirdly, a simple and sensitive analysis for  $\text{Hg}^{2+}$  has been investigated by combining a solution-cathode glow discharge atomic emission spectrometry (SCGD-AES) and flow injection (FI) based on on-line solid-phase extraction (SPE). A novel L-cysteine modified mesoporous silica (SH-SBA-15) packed in microcolumn for SPE was synthesized which had a good adsorption capacity and a short adsorption time. An enrichment factor of 42 was achieved under optimized experimental conditions at FI flow rate of 2.0  $\text{mL min}^{-1}$  and 10% thiourea in 0.2  $\text{mol L}^{-1}$   $\text{HNO}_3$  for  $\text{Hg}^{2+}$  elution. The detection limit of FI-SCGD-AES can be achieved 0.8  $\mu\text{g L}^{-1}$  and the precision of the 11 replicate  $\text{Hg}^{2+}$  measurements was 3.39 % at the 100  $\mu\text{g L}^{-1}$ . The proposed method has been validated by determining mercury in certified reference materials, human hair (GBW09101b) and stream sediment (GBW07310).

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## STUDIES ON THE REAGENT IONS AND IONIZATION PROCESSES OF FLOWING ATMOSPHERIC PRESSURE AFTERGLOW (FAPA)-APGD.

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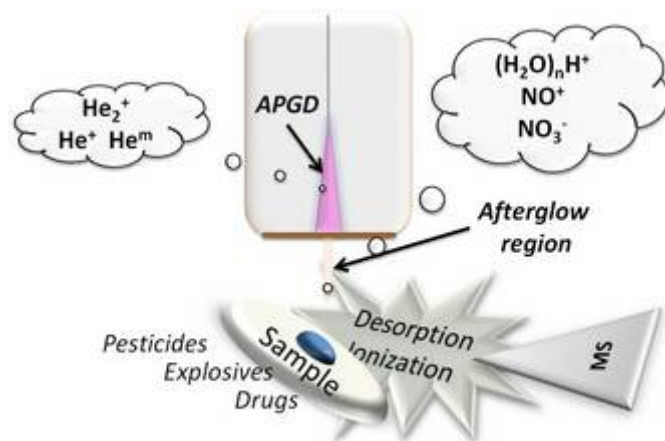
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Reduced-pressure glow discharges (GD) have long been used as ionization sources for Mass Spectrometry (MS). However, in the last decade, atmospheric-pressure glow discharges (APGD) have been explored as ionization and desorption sources for Ambient Desorption/Ionization Mass Spectrometry (ADI-MS). The field of ADI-MS was introduced in 2004 by Takáts *et al.* [1] with the design of the desorption electrospray ionization source (DESI), and since then it has been intensively investigated. For instance, during the last 10 years more than 40 ADI sources have been described [2].



The aim of ADI-MS is to analyze gaseous, liquid and solid samples in their natural form through MS, which provides outstanding selectivity and sensitivity. In this sense, atmospheric-pressure discharges are highly attractive due to their stability and low power requirements (normally tens of watts), versatility of electrode geometries and variety of plasma gases (e.g. He, Ar, Ne, N<sub>2</sub> or H<sub>2</sub>). The first such source was direct analysis in real time (DART), introduced in 2005 by Cody *et al.* [3] and based on a corona discharge. In 2008, a new design based on an APGD was published by Andrade *et al.* [4], and termed the flowing atmospheric pressure afterglow (FAPA). This source uses helium to generate the discharge in a sealed cell, using a pin-to-plate geometry for the electrodes. In the discharge,

reactive helium species are generated. These species exit the cell through a hole in the plate and subsequently react with atmospheric constituents. The generated species (mainly NO<sup>+</sup> and (H<sub>2</sub>O)<sub>n</sub>H<sup>+</sup>) are able to ionize samples, generating MH<sup>+</sup> and M<sup>+</sup> ions of the target analyte (M). The analyte is desorbed thanks to the high temperature generated in the afterglow.

This presentation describes the effect of the conditions under which the discharge is generated on the production of reactant ions and on the ionization processes (typically protonation and charge-transfer reactions). Moreover, since the discharge is generated in contact with the open atmosphere, the effect of the ambient humidity is also discussed.

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## OPTICAL EMISSION SPECTROSCOPY CHARACTERIZATION OF A DBD ATMOSPHERIC PRESSURE PLASMA SOURCE FOR MASS SPECTROMETRY ANALYSIS

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In direct sample analysis domain, atmospheric pressure sources are largely investigated for ambient surface analysis by mass spectrometry [1-2]. Many plasma sources have been studied including Dielectric barrier discharge (DBD). It is a mean to generate cold atmospheric plasma and create a soft ionization [3]. A DBD plasma jet allows the formation of plasma in open space [4]. The desorption and ionization capabilities of a plasma source coupled to mass spectrometry detection might achieve a high selectivity and sensibility according to the source efficiency.

In this study, a DBD source has been developed and is coupled to a time of flight mass spectrometer (TOFWERK TOF-MS) [5-6]. This source is composed by two parts, a cylindrical dielectric chamber ending by a slightly conic capillary tube. Each part is surrounded by an external conductive electrode. The source is operating in a flow of Helium and is powered by a square alternative voltage (tens of kHz). The plasma is ignited inside the dielectric chamber and a plasma jet is blown out of the capillary termination. The jet can be directed toward the surface to be analyzed. In our previous work a parametric study by optical emission spectroscopy has been performed, where the conditions for the longest and the most intense plasma jet were identified. The presence of  $N_2^+$  and excited species such as H $\alpha$ , OH, O,  $N_2$  was observed. In this work we will evaluate the capability of the DBD plasma source to ionize ambient air with TOF MS measurement; and the optimization of its efficiency will be also investigated with the TOF-MS.

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## NEW ACCURATE ATOMIC DATA AND APPLICATIONS IN GDS.

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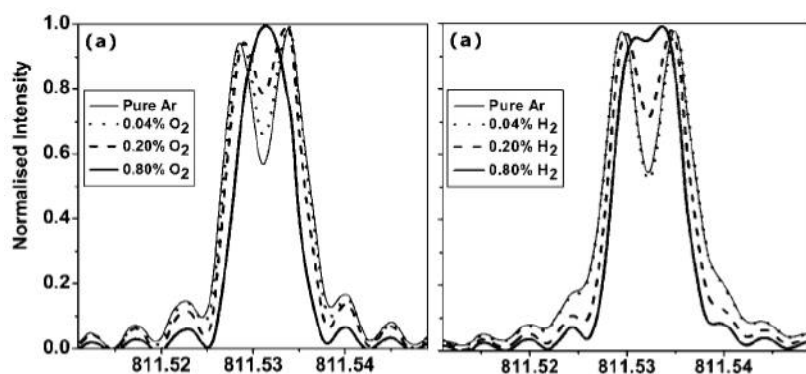
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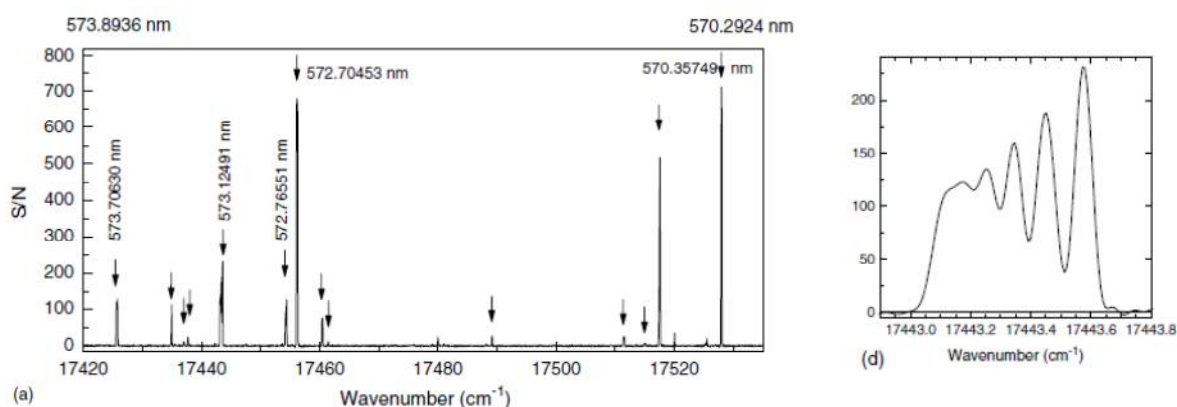
Modern instrumentation allows the observation of GD spectra covering wide spectral wavelength range, with the use of many lines of a particular species being possible. Large scale studies of individual element spectra by Fourier Transform Spectroscopy (FTS) under different GD conditions (for example in the presence of trace gases such as O<sub>2</sub> and H<sub>2</sub>, and different plasma gases such as argon and neon [1-5]) are giving new insights into the plasma processes. The high resolution of FTS allows observation of the true line profiles of lines, an important advantage over other techniques.

It is timely to consider the accuracy and completeness of the available atomic data to allow more reliable interpretation of GD spectra. Modern atomic data measurements using FTS, have seen order of magnitude improvements in the accuracy of line wavelengths and transition probabilities for a wide range of elements, for example, the 3d transition group, and heavier metals. Observations at high resolution from IR – VUV yield thousands of observed lines for a single 3d group element. Analyses of these spectra have led to new energy levels being found, many lines identified for the first time and many identifications corrected. However there are cases where significant numbers of lines remain unidentified in terms of the energy levels involved in the transitions, and these are often omitted from databases. Detailed knowledge of the spectra of interest is vital, for example, to avoid situations where a key line may be blended with another line, with potential detrimental impact for analytical GDS applications.



Left: example of normalised line profiles of the 811.531 nm Ar I line showing self-absorption (in some cases self-reversal) for various O<sub>2</sub> and H<sub>2</sub> concentrations. GD conditions: 700 V, 20 mA for a 4 mm anode tube diameter. [5]

Below: example 3nm section of vanadium spectrum recorded with FTS and hollow cathode source, with an example line profile [6].



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## INDRODUCTION OF A NEW HIGH END PERFORMANCE DESKTOP GD-OES INSTRUMENT

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New technologies let to the development of very powerful desktop GD-OES-instruments. This new generation of GD-OES instruments will not only have highest resolution and state of the art GD-Sources to accommodate for a broad range of applications but will also be highly affordable.

GD-OES has great reputation for its capabilities for depth profiling, but more than 40 years ago this technique was invented for the bulk analysis of precious metals. Bulk analysis since then became more and more a domain for arc/spark instruments and GD-OES had loosing ground, mainly because of a much higher price due to the more complex technology. Coming back to the roots and combining it with all the new technologies developed over the last decades, Spectruma will continue to promote the best analytical source available for spectrochemical analysis also for bulk analysis.

This presentation will show that it is possible to perform bulk analysis at the same level of high-end spark emission instruments and also use depth-profiling altogether in a highly affordable bench top instrument.

## APPLYING $\mu$ S-FF-GD-MS TO NON-CONDUCTIVE SAMPLE ANALYSIS

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New approaches for elemental analysis of non-conductive solids by pulsed fast flow glow discharge mass spectrometry ( $\mu$ s-FF-GD-MS) will be presented in this contribution. Special focus will be set on full survey analysis of high purity alumina samples. Other promising applications of this method, such as chemical analysis of rare earth oxide powders, will be also demonstrated.

Sector field glow discharge mass spectrometry has gained renewed interest over the last couple of years due to the significantly increased demands for high purity metals, alloys, semiconductors and ceramics, especially by the aerospace, electronics and photovoltaic industries. It will be demonstrated here that if the fast flow glow discharge source in the Element GD is driven with a pulsed supply in direct current mode, this provides outstanding atomization / ionization conditions for trace level determinations also in non-conductive samples. The analytical performance achieved by this approach is similar to the excellent capabilities when running conductive samples.

The pulsed fast flow mode in combination with a conductive working sampling electrode appears to be an exceptionally effective atomization and ionization medium for sensitive survey analysis of high purity non-conductive solids, including ceramic powders. This new approach is a true value-added alternative to the previously established method for direct analysis of non-conductive solids by GDMS in co-axial geometry discharge cells using conductive secondary cathodes. For instance, the older approach requires lengthy analysis times, usually between one to two hours for full surveys, and several elements with poor limits of detection due to increased interferences and contributions from the blank or the secondary cathode itself. This novel approach presented here gives a simpler way of preparing non-conductive samples for analysis, especially powders, faster analysis times, better matrix to secondary cathode ion ratios, and thus lower limits of detection for most of the elements in the periodic table. In addition, the flat geometry sampling allows larger area of samples to be atomized; hence the measurements are more representative. The sample preparation can be conducted with low risk of contamination, since it requires a simple pressing of the sample directly into a high-purity metal target electrode. This then acts as the secondary cathode for analysis. In this paper we are using a high purity tantalum plate and alumina reference sample for illustrating the method, but other high purity metal electrodes and non-conductive powders are currently under investigation.

## 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 10 installed worldwide including the US, UK, 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, both environments requiring the analysis of a wide range of materials on the same instrument.

The continuing development of the Astrum has resulted in numerous improvements, including a new liquid nitrogen cooling system. The new cooling system enables the use of non-pressurised dewars, increases cooling efficiency and reduces liquid nitrogen consumption. With the new cooling system cell alignment is also improved, and the use of boron nitride is completely eliminated from the instrument, thus eliminating the potential for accidental boron contamination of samples. Additional improvements include the cell exit slits, which are now laser cut to aperture sizes which have been individually optimised for flat and pin samples. The new cell exit slits improve sensitivity whilst (in tandem with the new cooling system) ensuring greater consistency between cells without causing a significant change to abundance sensitivity or molecular and multiple charged interferences.

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

## A COMPARISON OF CCD ARRAY DETECTOR vs. PMT SIGNALS DURING THIN LAYER COMPOSITIONAL DEPTH PROFILE ANALYSIS

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Glow discharge spectrometry (GDS) has proven to be a very capable "bulk" analysis technique. However, it is the analysis of surface layers, also known as compositional depth profiling (CDP), where GDS truly excels. Historically, CDP capable glow discharge instruments have utilized multichannel photomultiplier (PMT) based detection systems. Solid-state devices such as CCD detectors have been considered either too slow or too insensitive for these types of analyses. This is particularly true when such analyses involve so-called "thin layers", as for example, in the case of measuring the magnetic layers of a computer hard disk.

The required detection speeds for such analyses depend not only on the sample's structure but on the analysis conditions and, subsequently, the resulting material sputter rates. Previous work [1] has indicated that the data band-width requirements are less than 200Hz for even the most demanding thin layer applications. Fortunately these data acquisition rates are quite feasible with modern solid-state detectors. In addition, the dynamic range possible with modern spectroscopic CCD arrays is impressive. These two factors make it feasible to design a CDP capable system utilizing solid-state CCDs.

In the work presented here, the bandwidth requirements of various layered materials will be considered. The bandwidths and dynamic ranges observed utilizing both traditional PMT based instruments and CCD based detection systems, as well as other important attributes of these two approaches, will be compared and contrasted. Finally, the CDP analysis of thin layer materials such as the magnetic layers of hard drives will be presented and these results compared.

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## Advances in GDMS

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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.

## DETERMINATION OF TRACE ELEMENTS IN HIGH PURITY ALUMINUM OXIDE BY GD-MS

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Over the last 10 years, high purity aluminum oxide has become one of the leaders in the increase of the volume of production of high-tech materials. Mainly this increase is associated with an increased need for a single-crystal sapphire, which is known for its unique physical and chemical properties. For growing single crystals of sapphire optical quality, a important role has quality of the original Al<sub>2</sub>O<sub>3</sub> (charge), purity should be 99,99-99,999%.



**Fig.1** Samples of aluminum oxide: A- densified sinter as brick, B- fused aluminum oxide as rods, C- Verneuil sapphire, D- nanopowder

This paper is devoted to the problem of determining trace elements in samples of high purity aluminum oxide by glow discharge mass spectrometry.

Analysis was carried out on a glow discharge mass spectrometer VG9000 (Thermo elemental, UK). It was double-focusing spectrometer, which provides a resolution of about 5000. Construction of the instrument make it possible measuring low and high intensity of the ion beam in one scan using Daly and Faraday detectors accordingly.

We elaborated modernized methodic described previously [1] that includes flat cell, with insulating rings made of high purity sapphire. As secondary cathode was used tantalum of purity 5N, configured as a square plate (15x15 mm and a thickness of 2 mm). Samples were applied as thin layer on tantalum plate using tools made of high purity sapphire. Preliminarily compacted  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was milled to powder with a particle size of  $\leq 100$  microns. Before to analysis, the surface of the tantalum plate was pre-cleared by a mixture of ultrapure acids (HF + HNO<sub>3</sub>), after that tantalum was subjected purification by argon ions in the glow discharge during 10-15 min.

The determination of trace elements in aluminum oxide was carried out in a mode with discharge voltage of 1 kV at a constant 2 mA current. For compact samples  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> the ion beam stabilized after 15-20 min of discharge process, for nanopowder samples  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after 30-40 min. Quantitative analysis was performed with refined relative sensitivity factors (RSFs) compared to found previously [1] that were measured using own standard samples and NIST-standard SRM 699.

The results showed the possibility of using GDMS to determine the full composition of trace elements in Al<sub>2</sub>O<sub>3</sub> samples at  $<1$  ppm level. Problematic to measure are only elements that are have strong interference, such as:  $^{38}\text{Ar}^1\text{H} - ^{39}\text{K}$ ,  $^{40}\text{Ar}^1\text{H} - ^{41}\text{K}$ ,  $^{181}\text{Ta}^{16}\text{O} - ^{197}\text{Au}$ ,  $^{181}\text{Ta}^{13}\text{C} - ^{194}\text{Pt}$ ,  $^{181}\text{Ta}^{14}\text{N} - ^{195}\text{Pt}$ , etc. However, these elements are rarely found in the composition of high-purity aluminum oxide and can be determined using another substrate metal. Despite high resolution of instrument attention should be paid for other elements. This problem was resolved by mathematical modeling of mass-spectra, allowing to avoid incorrect interpretation of mass-spectra [2]. Computer program developed allows also analyzing of non-conductive samples by special algorithm that takes into account residual impurities in the tantalum cathode.

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## SPATIO-TEMPORAL STUDY OF A DBD ATMOSPHERIC PRESSURE PLASMA SOURCE FOR ANALYTICAL APPLICATIONS

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Dielectric barrier discharge (DBD) can be used as plasma source to generate low temperature plasmas at atmospheric pressure and create soft ionization [1-2]. According to their properties some sources could be used for analytical investigations [3-5]. In this work, the source is composed of a cylindrical dielectric chamber with a tube termination. The cylinder and the capillary tube are covered with conductive electrodes connected to the power supply. Using a gas flow, a plasma jet can be generated out of the tube (fig. 1).



Figure 1: Helium atmospheric plasma in ambient air at the end of the tube

This study is based on electrical and optical diagnostics. The source is operated with Helium flow and is powered by square pulsed voltages (20 kHz) with a 50% duty cycle. The influence of the applied voltage and the gas flow will be presented and discussed according to the ICCD imaging results and spectral results (excited species, line intensities and outer plasma length).

Out of the tube, emissions of He, O, OH, N<sub>2</sub> and primary N<sub>2</sub><sup>+</sup> ions are observed. They are coming from Penning ionization due to helium metastable and electron impact. According to the applied voltage and the flow rate, the variations of these species line intensities will be presented and discussed as a function of the distance from the capillary end.

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## ANALYSIS OF POWDERED GEOLOGICAL SAMPLES USING ISOTOPE DILUTION ANALYSIS AND RADIOFREQUENCY PULSED GLOW DISCHARGE - TIME OF FLIGHT MASS SPECTROMETRY.

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Metal contamination in soils and sediments is a current concern having implications in health, ecological and legislation issues. Traditional methods to determine metal concentration involve an acid digestion step which is time consuming, prone to contamination and with analyte loss risks; moreover, a complete dissolution of the sample can sometimes prove difficult when refractory phases are present. Several solid-state analysis techniques can be used to determine metals at the ppm level or below in soils and sediments but all of them have their pros and cons.

Glow discharges (GDs) have been widely investigated as atomization, excitation and ionization tools for direct analysis of materials. GD sources coupled to mass spectrometry (MS) offer fast sputtering rate, high depth resolution, multielement and isotopic capabilities, high sample throughput, minimal matrix effects and good detection limits. Additionally, pulsed GDs (PGDs) have been proposed as attractive analytical alternatives to the more common continuous GD operation mode. Among the different mass analyzers, GD-time-of-flight (TOF) MS systems are increasingly used. PGD-TOFMS permits the quasi-simultaneous detection of ions along the GD pulse period and, thus, the observation of the different time domains (denoted as prepeak, plateau and afterpeak regions) along the pulse period [1]. This allows the selection of the integration time detection window providing the highest analyte signals with the minimum spectral interferences.

A main limitation of direct solid analysis techniques is related to the lack of certified reference materials for quantification purposes. Isotope dilution mass spectrometry (IDMS) is internationally regarded as a reference measurement method directly traceable to the International System of Units. In contrast to other calibration strategies, the analytical result is not affected by signal drifts, matrix effects or analyte losses provided that the isotope equilibration is achieved.

In this communication, the analytical potential of radiofrequency PGD-TOFMS is investigated in combination with IDMS for fast quantitative analysis of soil and sediment samples fused with lithium borate. The advantages of using such sample preparation procedure include: homogeneous mixing of analytes, possible dilution for highly concentrated elements and stability over time. The study was focused on the selection of the pulse region for each isotope of interest to achieve accurate measurement of isotope ratios. Limits of detection were evaluated and the validity of the proposed quantification approach is demonstrated through the analysis of certified reference materials. In this way, Cu, Zn, Ba and Pb were successfully determined by PGD-TOF(IDMS) in two standard reference materials (SRM 2586 and SRM 2780) representing two different matrices of geological interest: soil and rock samples.

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## DEPTH PROFILE CHARACTERISATION OF PHOTOVOLTAIC DEVICES BY PULSED GLOW DISCHARGE - TIME OF FLIGHT MASS SPECTROMETRY.

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The combination of radiofrequency (RF) glow discharge (GD) to time of flight mass spectrometry (TOFMS) is recently demonstrating to be a promising analytical tool, allowing a fast collection of the complete mass spectrum with high precision and sensitivity regardless of the number of isotopes being measured, low matrix effects, analysis of conducting and insulating materials, limits of detection in the range of  $\mu\text{g/g}$ - $\text{ng/g}$ , nanometric depth resolution and fast analysis time.

GDs can be operated in continuous or pulsed powering mode. Pulsed GDs (PGDs) give rise to temporally increased ion signals, provided that a fast time-gated detector is used such as TOFMS. The PGD-TOFMS combination allows, for example, the selection of the integration time window of the GD pulse period which provides the highest analyte signals with the minimum spectral interferences [1].

The analytical potential of RF-PGD-TOFMS for fast quantitative depth profiling will be presented by resorting to the analysis of thin film solar cells (TFSC) based on hydrogenated amorphous silicon (a-Si:H) as a practical example. Determination of compositional depth profiles of a-Si:H TFSC was performed with a multi-matrix calibration procedure and the effect of hydrogen has been properly corrected. Results show that RF-PGD-TOFMS allows to discriminate the different parts of the photovoltaic devices: the first contact layer with  $\text{ZnO}_2$  and  $\text{Al}_2\text{O}_3$  (AZO), the a-Si:H layer (where it can be distinguished between the doped films and the intrinsic a-Si:H), the second AZO and the back contact layers and, finally, the substrate. A good agreement with the nominal values for elements concentration and layers thicknesses was obtained. Moreover, diffusion processes between the coating layers, which could have an important influence on the final efficiency of TFSC, can be identified. Hence, the findings support the use of RF-PGD-TOFMS as a powerful analysis technique in the characterization of thin films.

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## ANALYTICAL POTENTIAL OF RF-PGD-TOFMS TO EVALUATE OXIDATION IN REVERSE OSMOSIS MEMBRANES

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Thin film composite (TFC) membranes are semipermeable membranes used for water purification or desalinization. These membranes used in reverse osmosis (RO) are typically made of a thin film of polyamide on top of a polysulfone porous layer deposited on a support sheet [1]. This configuration gives the needed properties of high rejection of undesired materials (salts), high filtration rate and good mechanical strength. However, a limitation in the use of TFC membranes is the degradation through common oxidants employed in water treatment such as sodium hypochlorite (NaClO) and chlorine dioxide (ClO<sub>2</sub>). Oxidation is one of the worse problems that TFC membranes could suffer since it is an irreversible process which turn into lower salt rejection. Mechanism proposed to explain the degradation produced by chlorine in RO membranes involving a sequence of two stages: first, a polymer deformation (produced by N-chlorination and/or ring chlorination) and then a depolymerization [2].

Fujiwara test has been traditionally used to check if the membrane is affected by chlorine exposure (a small quantity of a dye solution is dropped on the membrane surface, the dye will adhere to the support material that has been oxidized, and these damaged areas will appear as bright pink spots) [3]. Nevertheless, other techniques as ATR-FTIR (Attenuated Total Reflection–Fourier Transform Infrared) and XPS (X-ray photoelectron spectroscopy) have also shown to be useful tools to determine the oxidation in RO membranes related with the presence of NaClO [4, 5]. In fact, these spectroscopic techniques are able to detect the degradation on the active layer when Fujiwara test is still negative [5]

In this work, the analytical potential of radiofrequency pulsed glow discharge time of flight mass spectrometry (rf-PGD-TOFMS) [6] is evaluated as complementary technique to characterize the oxidation suffered by a commercial polyamide RO membrane after being immersed in seawater. Possible differences in the membrane degradation depending on the oxidants (NaClO and ClO<sub>2</sub>) added to the seawater are investigated and the results given by rf-PGD-TOFMS are compared with those provided by other techniques.

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## **FULL SURVEY AND DEPTH SPECIFIC ANALYSIS OF HIGH PURITY GRAPHITES, CARBON/CARBON COMPOSITES AND SILICON CARBIDE BASED MATERIALS AND COATINGS.**

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Great progresses have been made recently on development of analytical protocols for measuring trace element concentrations in those ultra-high purity solids, which are exceptionally difficult to analyze by solution based techniques, such as nuclear grade graphite, carbon/carbon composites and SiC. Much of the progress have been achieved on solid sampling analytical methods, like laser ablation inductively coupled plasma-atomic emission spectroscopy (LA-ICP-AES), solid sampling electrothermal atomic absorption and/or atomic emission spectrometry using the boat technique (ETAAS, ETAES), instrumental neutron activation analysis (INAA), and X-ray fluorescence spectroscopy (XRF). INAA is an important approach for certifying trace analyte contents in high purity solids, but this technique is certainly not easily accessible for routine analyses in production environment. All other solid sampling methods require strict standardization procedures for quantitative determinations using certified reference materials. Unfortunately, availability of solid reference materials with certified analyte concentrations is very limited, and virtually non-existent for high-purity grades. As a result, synthetic laboratory standards or liquid alternative standards are generally used to circumvent this issue. Wet digestion of graphite and/or composites with mineral acid mixtures has been problematic, regardless if it is done in open or pressurized closed vessels, in microwave ovens, or by combustion. The situation even worsens relating to nuclear grade graphite samples. Since nuclear grade graphite is able to endure the stringiest corrosive conditions, it also means that it is extremely difficult, if not impossible, to break down under commonly available clean digestion conditions. As a result, solution analysis of high purity nuclear grade graphites and composites after digestion has been subject to great uncertainties. In general, the industrial and academic communities are still debating on a preferred method for their routine chemical analysis.

Highly efficient analytical approaches for routine chemical analysis of ultra-high purity graphites, composites and solid SiC samples by fast flow glow discharge mass spectrometry will be presented in this contribution. Special focus will be set on calibrations and full survey analysis of high purity carbon, graphite and SiC grades. Other promising applications of this analytical method, such as depth specific analysis of SiC coatings will be also demonstrated.

# ENHANCED EXCITATION OF VARIOUS ANALYTE ATOMIC LINES IN ANALYTICAL GLOW DISCHARGES IN THE PRESENCE OF MOLECULAR GASES

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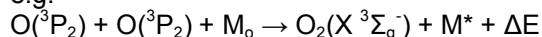
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Comprehensive investigations of the effects of molecular gases on analytical glow discharges (GD) have been carried in the last two decades. The main results reveal that the presence of molecular gases affects considerably the electrical characteristics of the discharge, the sputter rate of the analyte, the number density of plasma gas ions and metastable atoms and so affects the intensities of spectral lines of plasma gas and analyte material, often by Penning ionization or excitation or by asymmetric charge transfer. However, Smid *et al.* [1] reported that in the presence of hydrogen in an argon GD, there is enhanced excitation of Fe I and Ti I lines with upper energies of about 5 eV. No similar effect occurred with added nitrogen. Subsequently Mushtaq *et al.* [2] reported enhanced excitation in a similar energy region with added oxygen and for other sample elements, including titanium, copper and manganese (Fig 1.). We have also observed this effect with neon as the discharge gas. Until now no explanation of this effect has been available.

Following a suggestion from Hoffmann (IFW Dresden), we now propose a partial explanation. The enhanced excitation of analyte atomic lines with upper energies close to 5 eV in the presence of hydrogen or oxygen is likely to be due to three body collisions involving two hydrogen or oxygen atoms and a sample atom, resulting in the formation of an H<sub>2</sub> or O<sub>2</sub> molecule and the excitation of the sample atoms by the recombination energy released by the molecule. There are also likely to be changes in the kinetic energies of the colliding particles.

e.g.



where the subscript <sub>o</sub> and superscript \* represent ground and excited state respectively and M is the sample atom. The dissociation (and

recombination) energies of oxygen and hydrogen molecules are 5.15 eV and 4.52 eV respectively, and the excess energy required for the excitation of the sample atoms in some cases can be supplied by the kinetic energy of the colliding particles or by excitation of the sample atoms from low lying metastable levels. On the other hand, the dissociation energy of the nitrogen molecule is 9.97 eV so any similar effect would only occur at much higher energies above the ionization energy of typical sample atoms. The majority of the molecular recombination is likely to take place at the walls of the source, but three body collisions within the gaseous volume can make a significant contribution to the excitation of sample atoms. The effect increases at higher molecular gas concentrations (see Fig 1.) due to increased concentrations of H and O atoms. The effect appears to be the strongest at low powers, possibly because the degree of ionization increases leading to a reduction in the concentration of oxygen or hydrogen atoms and also because normal electronic excitation increases and the enhanced excitation is less obvious.

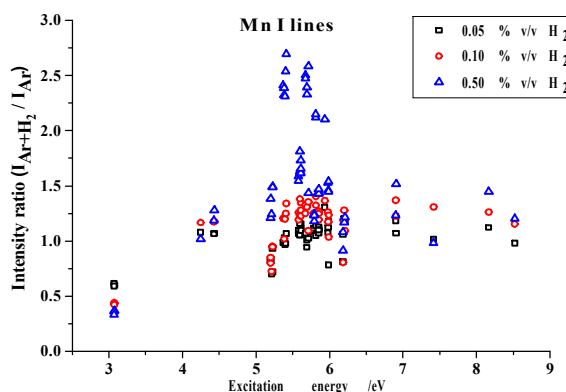


Fig. 1 Intensity ratios of Mn atomic lines as a function of their excitation energy, 700 V & 20 mA.

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## AN EXPLORATION OF SAMPLE PREPARATIONS AND DETECTION LIMITS FOR CONDUCTIVE, SEMI-CONDUCTIVE AND NON-CONDUCTIVE MATERIALS AS PERTAINING TO THE NU ASTRUM HR-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 a variety of materials. Some of the materials which lend themselves to GDMS analysis are predictable such as high purity metals and alloys that have conventional configurations of small blocks with smooth surfaces. However many other types of samples, both conductive and non-conductive of varying sizes, shapes and consistencies may be analysed by GDMS. The work presented here seeks to explore some non-traditional types of samples which may be analysed using the latest generation of HR-dc-GDMS technology, the Astrum from Nu Instruments. Typically GDMS instruments, historically the VG9000 from VG Elemental and currently the Astrum, are fitted with different holders to allow both pin and flat cell capabilities, the pin samples being ~2x2x20mm while the flat samples are ~20x20x10mm, optimally. These different cell geometries allow for a plethora of shapes and sizes of samples to be analysed. If a sample cannot be fashioned into a pin then perhaps it can be pressed onto a binder for analysis using the flat cell method. In this manner, the analysis of such unconventional samples as ball bearings, screws and orthopaedic pins are possible. Thin wires may be analysed by either twisting them into a pin shaped configuration or by cutting them into pieces that can be pressed onto an indium binder. In addition to the versatility afforded by the pin and flat cell geometries, the Astrum has other features which facilitate the analysis of non-conventional samples. Due to the low-flow GD source of the instrument, the Astrum has a sputter rate which can range from 10  $\mu\text{m}$  / 20 minutes for copper to 10  $\mu\text{m}$  / 2 hours for ceramics. This low sputter rate translates into ample time to acquire meaningful and reproducible data for thin and even ultrathin foils and coatings. The low sputter rate also allows for time resolved analysis of coated powders and bulk samples, obtaining information about the contaminants in each matrix layer. Another feature of the Astrum is the cryo-cooled source which allows for both pin and flat cell analysis of low melting point samples such as gallium (m.p. 30°C). Additionally, non-conductive samples can be analysed with the Astrum by using a supporting conductive binder. In this approach, the sputter-redeposition of the secondary electrode material forms a thin conducting layer on the non-conducting sample. Consequently, bombarding particles can penetrate this layer and atomize the non-conducting sample. The most common binder materials are indium and tantalum, due to their high purity and lack of interferences. The indium binder can assume a pin or a flat configuration, both forms allowing for a powder to be pressed onto the indium for analysis. The tantalum binder usually consists of a tantalum pin with a groove fashioned into it which functions to hold the analyte. The different cell geometries, the low sputter rate and the cryo-cooling of the source are among some of the many features of the Astrum which serve to make it a powerful and versatile technique in the determination of trace and ultra-trace contaminants in conductive, semi-conductive and non-conductive bulk materials and powders.

## RF GD-OES ANALYSES OF OPTICAL MULTILAYERS

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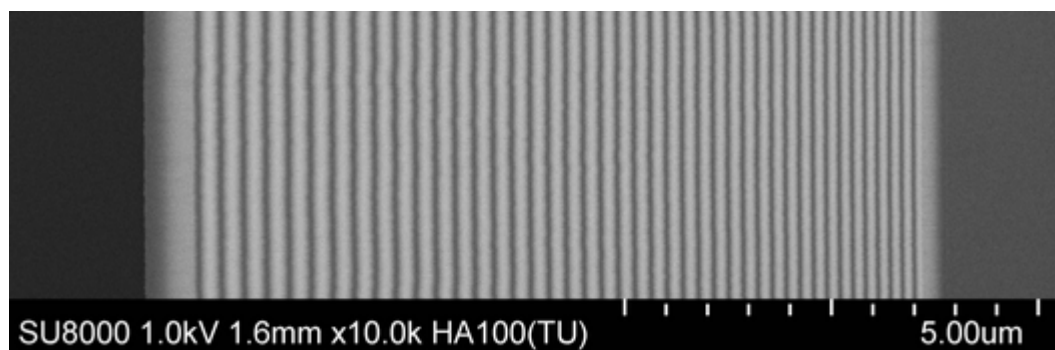
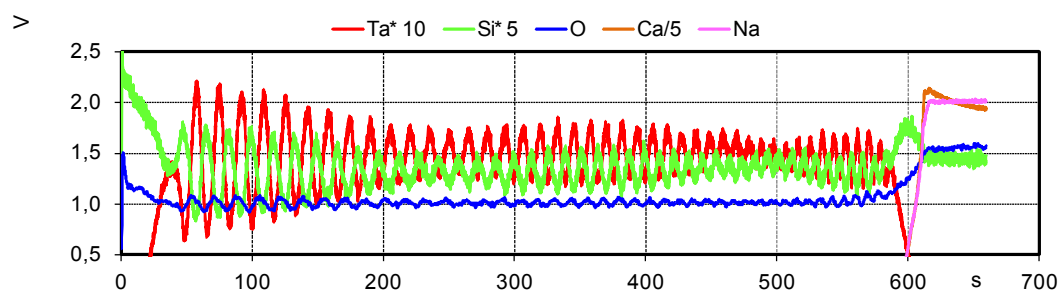
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Optical multilayers with antireflective, highly reflective or solar-control properties are used on different substrates like glass or polymer films. In the frame of our work we have tested the possibilities and limitations for the analyses of the chemical depth-profiles of different optical multilayers by RF glow discharge optical emissions spectrometry (RF GD-OES).

For the testing of the depth resolution a broad-band highly reflective optical Rugate filter with 46 periods of silicon oxide and tantalum oxide gradient layers with a total thickness of 9.65  $\mu\text{m}$  on 1 mm soda-lime was used. The optimization of a flat sputter crater was achieved by the variation of the total pressure, rf sputtering power and duty cycle. The flatness of the bottom of the sputter crater could be mainly affected by the sputtering pressure, whereas the steepness of the side walls could be drastically improved by optimization of sputtering power and duty cycle. The results show that with optimized sputter parameters the thinnest period of 140 nm could be still clearly resolved near to the bottom of the very deep sputter crater.

In addition the effect of spectral reflectivity on measured intensity of optical emission lines was tested using a 5 stack multilayer layer of silicon oxide and titanium oxide layers with a total about thickness 670 nm. This multilayer system exhibits a high reflectivity in the UV range and very low reflectivity in the visible range of spectrum. The effect of the changes in spectral reflectivity on the measured intensities of the optical emission lines were simulated as a function of the sputtering depth. The simulated results for the reflectivity of the used optical emission lines 365.35 nm for titanium and 288.158 nm for silicon versus sputtering depth are compared with the experimental results. It can be shown that for optimized crater profile the results corresponds very well to the simulated drastic changes in reflectivity.

Solar control layers for automotive applications are deposited on 50  $\mu\text{m}$  PET films. The multi-layer system with a total thickness of about 450 nm is composed of 5 periods with alternating thin silver and zinc-tin-oxide layers. For the RF GD-OES analyses the coated PET films are glued on an aluminum substrate, which enables the production of flat sputter craters for the optimized sputtering pressure. On the other hand relative low sputtering powers and duty cycles must be used to avoid thermal damage of the sensitive substrates. The used relative low sputtering powers of 15 or 20 W restricts unfortunately a little bit the steepness of the sputter craters. Nevertheless all present 5 silver layers with a thickness of about 8 nm can be still clearly resolved.



## APPLICATION OF GLOW DISCHARGE MASS SPECTROMETRY FOR THE ANALYSIS OF HIGH PURITY MAGNESIUM USING PRESSED POWDER SAMPLES WITH DIFFERENT DOPANT TYPES

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Direct current Voltage (DC) fast flow glow mass spectrometry is an important and versatile tool for multielemental analysis of conductive solid materials for the determination of trace element contents down to the  $\mu\text{g}/\text{kg}$  level. It provides high sensitivity, minimum demands on sample preparation, avoiding losses and contamination, and only short time is needed for the measurements.

The quantification strategy based on matrix-independent relative factors (RSF) is not sufficiently satisfying regarding accuracy for each matrix and element for fast flow GD sources [1]. Therefore matrix-matched calibration samples (MMCS) are required to achieve reliable quantification. In fact, the list of available certified reference materials (CRM) appropriate for calibration purposes is relatively short, especially looking at analyte contents at the sub-mg/kg level. Convenient synthesis of homogeneous MMCS can facilitate the application of fast flow GD-MS for quantification of impurities in different matrices.

An approach for the preparation of MMCS by pressing of metal powders was suggested earlier [2], the method was modified by use of analyte solutions for doping of rather pure metal powders such as Cu and Zn [3], but not yet for doping of pure Mg-powder. Liquid doping is suitable for the determination of metallic impurities at low contents, but there is a limitation using Mg-powder. Salt formation due to chemical reaction with the acids in the doping solution results in a tremendous decrease of the electric conductivity of the pellets; as a consequence they can not be used for DC-GD-MS measurements.

In the present work we describe the development and comparison of different doping approaches – using liquid, solid and combined doping – for the preparation of synthetic pressed Mg-powder samples used for the determination of both metallic (such as Li, Ca, Cr, Co and Ag) and non-metallic (O, Si and B) analytes. Silicon nitride, magnesium oxide and boron nitride were used as dopants for the determination of O, Si and B, correspondingly.

The obtained results demonstrate a satisfying suitability of the suggested approaches for comprehensive chemical characterization of challenging metals concerning metallic and certain non-metallic impurities by fast flow GD-MS.

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## Ar I and Ne I SPECTRAL LINE SHAPES IN CATHODE FALL REGION OF GRIMM-TYPE GLOW DISCHARGE

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Glow discharges are successfully used as an excitation source for analytical spectroscopy of metal and alloy samples [1, 2]. These glow discharge sources (GDS) are usually built on the basis of the Grimm original design [3] with direct current (dc) and more recently with radio frequency (RF) excitation.

With the growing number of applications of GDSs in optical emission spectroscopy (OES) it became evident that reliable wavelength tables of glow discharge spectra are needed. A group of authors decided to overcome this lack of data and began the formidable task of measuring and comparing GD wavelengths and line intensity data with other available sources of information [4]. One of used instruments was a high spectral resolution Fourier transform spectrometer (FTS). As a light source a Grimm-type GDS with 4mm anode hole operated in argon or neon was utilized. A discharge voltage of 720V and discharge current of 20mA are kept constant in all experiments, while the pressure is varied depending on the cathode material and working gas. All discharge observations are carried out end-on through the anode opening, i.e. perpendicular to the cathode surface. The lines of several cathode elements are studied and some of them are used as wavelength standards (Fe I lines for example). A considerable part of this study is devoted to argon and neon lines, i.e. gases which are used most frequently to operate an analytical GDS. Recently, it has been noted that some Ar I and Ne I lines have large widths, exceeding 4–5 times the instrumental half-width, and in addition to line broadening red shifting of lines has also been detected [5].

In order to determine the origin of large widths and shifts detected in [5], Ar I and Ne I line shapes in an abnormal argon or neon glow discharge were observed along the axis of a cylindrical glow discharge parallel (side-on) and perpendicular (end-on) to the cathode surface [6]. The side-on spectra show spectral line shifting and sometimes simultaneous shifting and splitting in the cathode fall region of the glow discharge. The results of the measured line shift with available data for the dc Stark effect are used for measurement of electric field strength in the cathode fall region of the glow discharge. The end-on recorded line profiles show 10–40% larger half-widths than the side-on recorded line profiles. This effect is a result of the superposition of line emission in the cathode fall region under the influence of the dc Stark effect on the line profile from the negative glow.

The explanation is of importance for the application of new wavelength tables and may be of some value for characterization of other discharges.

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## STUDY OF QUANTITATIVE DEPTH PROFILE ANALYSIS OF NANOMETER SCALE FILM ON STEEL BY GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY

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There are several types of Nanometer film on steel: normal oxidation, surface passivation and metal strike-plate process so on. Quantitative depth profile analysis of nanometer film of steel surface is helpful to optimize produce process, evaluate anti-corrosion ability and develop application research.

We developed the depth profile analysis method by GDOES. Bulk standards were used to cover O, Cr, Ni, P, Mn, Al, Si, C and Cr element in the method. DC source and 4mm anode was chosen. DC source control mode was constant voltage vs. current. After a set of discharge parameters experiments, the best condition for method development was set: 1300V-45mA as preburn, 700V-20mA as analysis. Profilometer was used to prove flat bottom crater of the sample. Sputtering rate of steel is around 2 $\mu$ m/min by the above discharge parameter, data acquisition rate was set as 100 per sec to get about 0.3nm surface information every burn.

Bulk standards, which were measured and calculated sputtering rate were analyzed by the above-mentioned analytical parameters to get raw intensity. By the sputtering rate correction, the calibration was developed. To check the accuracy of thickness determination by GDOES, we chose two different surface techniques. Angle-dependent XPS was used to quantify the film that was less than 10nm such as oxidation film of stainless steel. AES was utilized to analyze Ni strike-plate steel and tin free steel sheet, whose thickness were between 20-30nm. Those results were same as that of GDOES.

In order to study the collaborative analysis experiments of nanometer scale film by several labs, seven samples were chosen for round robin test and analyzed by seven laboratories, the relevant repeatability and reproducibility data was gained through calculating the analysis results of collaborative experiments.

This method can help evaluate the anti-corrosion ability of cold roll steel sheet. After a large number of analysis, the important phenomenon was found. The higher Mn enrichment exist within 10nm oxidation film, the worse anti-corrosion ability of cold roll steel sheet could be. When Mn enrichment was wiped off by acidic reagent during process, cold roll product had good anti-corrosion ability.