Leibniz Institute
for Solid State and
Materials Research
Dresden

Fortschritte bei der Analyse leichter Elemente mit der Glimmentladungs-Spektrometrie

Volker Hoffmann

Colloquium Analytische Atomspektroskopie, 23. – 26. September 2019

18. GDS-Anwendertreffen, 26. – 27. September 2019

TECHNISCHE UNIVERSITÄT
BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.

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Outline

Introduction

- (Importance of Light Element Analysis (H, O, N))
  - Depth resolved, metrological characterization of pure elements (EMRP)
- Effects of Light Elements in GDS
- Quantification

Preparation and Validation of Sintered Calibration Samples

Calibration and Application

- Oxygen
- (Hydrogen and Nitrogen at IGDSS 2018 in Berlin)

Summary

Effects of Light Elements in Glow Discharge Spectrometry

- **Plasma physics**, e.g. gases are removed by flow, discharge parameters and excitation/ionization processes may change

  Zdenek Weiss, Spectrochim. Acta B61 (2006) 121-133

- **Plasma chemistry**, e.g. dissociation + recombination, combination/gettering.

  These processes (e.g. equilibrium of X and X_2) depend on the matrix.

- **Contamination** of gas, source and/or sample, (H_2O, C_xH_y) or by leakages (N_2, O_2, CO_2), chemisorption, adsorption, desorption

But many, many applications

$\Rightarrow$ 1. Instrumental developments (sources, spectrometers, vacuum system, software tools)

$\Rightarrow$ 2. Fundamental investigation (mostly using gas mixtures)

Compare the effect with sputtering of samples containing the light elements!

Absolute Calibration of Light Elements (H, N and O)

$$I_i = f_i (c_i \bullet q) + background + interference$$

GD-OES: f_i= Emission Yield factor - constant, if no self-absorption or other effects

GD-MS: f_i=Sensitivity factor

N. Jakubowski et al., J. Anal. At. Spectrom., 1992, **7**, 951
R. Muñiz et al., Spectrochim. Acta Part B, 2017, **135**, 34

Accurate sputtering rate measurements are essential for calibration.
3 D crater volume: $\Delta V/V \approx 1\%$ possible, usually between 5-10%.

Compact conductive H-, N- and O-calibration samples with different matrix are missing, but essential to check matrix independence (efficient method). Layered material useful, but determination of composition, thickness, density is more difficult and samples are destroyed during calibration.

$\Rightarrow$ Preparation of sintered calibration samples including light elements (H, O, N)

Preparation of Sintered Powder Mixtures

Matrices: Cu, Al, Mg

Compounds: TiH_2, ZrH_2, MgO, Al_2O_3, CuO, Cu_2O, AlN, Si_3N_4 for light elements H, O, N
NaCl, KCl, KBr, RbCl, CaF_2, CaO, LiCl, $SrCO_3$ for other purpose

Powder is Mixed (5 min)

Sintering Process (30 min)

Al matrix Al Al_2O_3

Mg matrix Mg MgO

Sintering conditions
Temperature: 400 °C
Pressure: 150 kN
Inert gas: Ar

Cu matrix Cu CuO

Cu Cu_2O

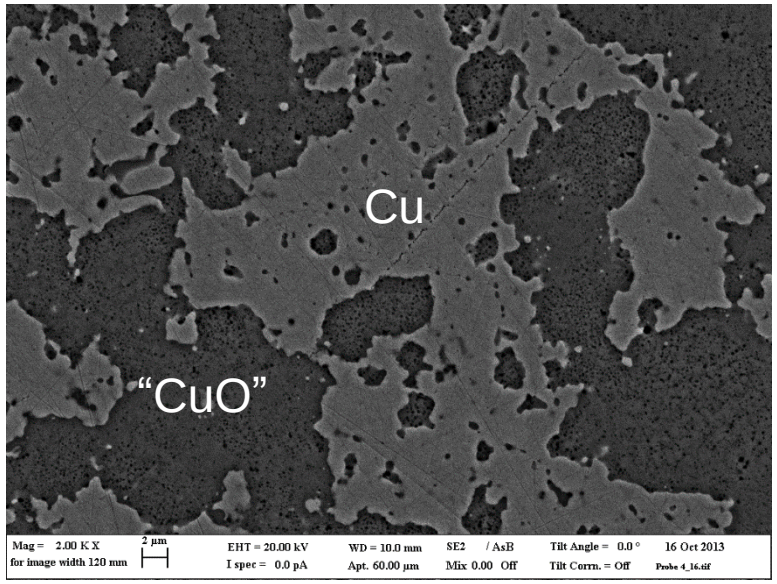
Sintering conditions
Temperature: 600 °C
Pressure: 150 kN
Inert gas: Ar

Sintered Samples

Properties: ∅ = 20 mm, h ≈ 20 mm, grindable
density > 95% - vacuum tight
homogeneous in mm range - 5% reproducibility

SEM Pictures of Sintered Samples

10 g Cu+2 g CuO (≙ 3.35 m% O)



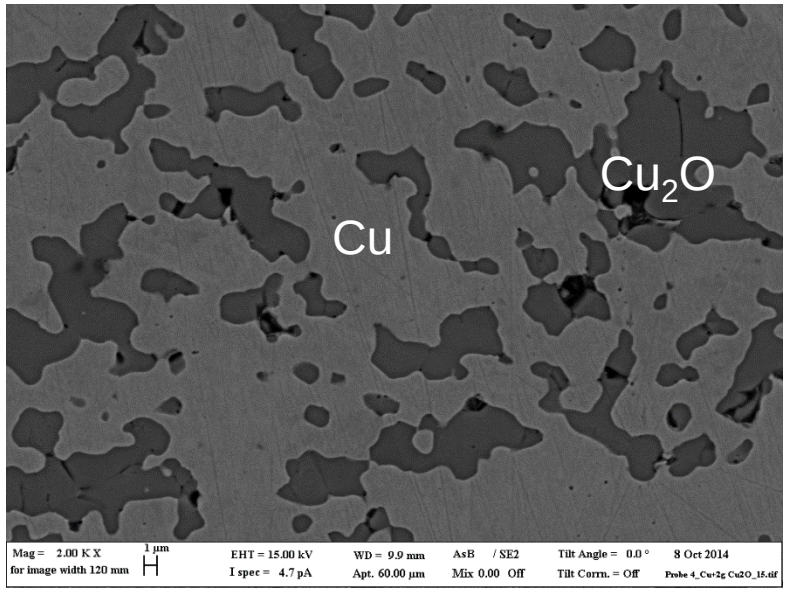
40 µm

CuO converts into Cu_2O at sintering (XRD)

⇒ low density (≈ 89%) and closed porosity

CGHE: c(O) = 3.58 m%

10 g Cu+2 g Cu_2O (≙ 1.87 m% O)



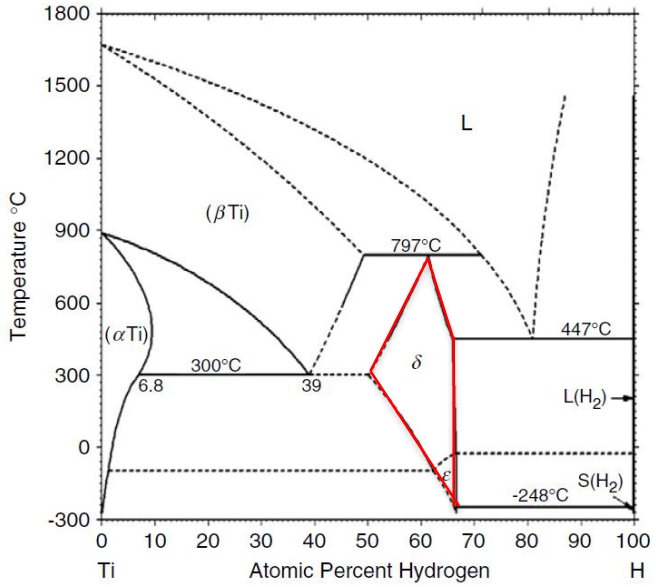
40 µm

Cu_2O is stable (XRD), > 99% density

CGHE: c(O) = 1.88 m%

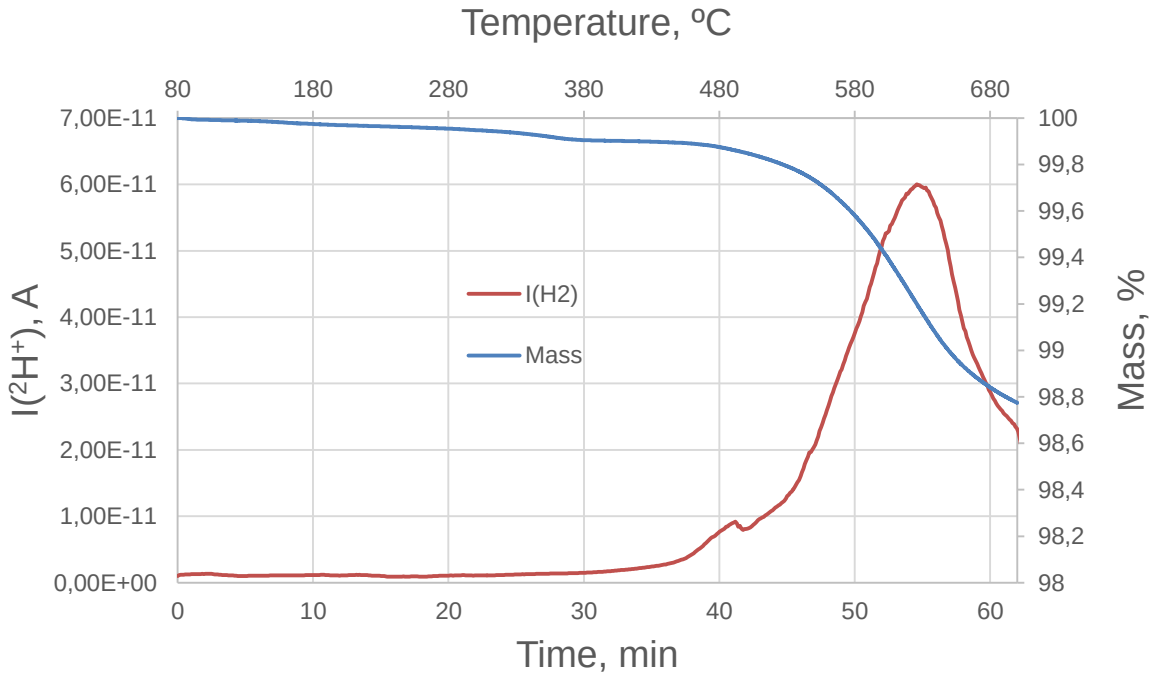
⇒ Validation of concentration is essential

Thermogravimetry (TGA) and Evolved Gas Analysis (EGA)
10 g Cu + 6 g TiH_2, c(H) = 1.5 m%



$T_S(\delta,TiH_2)$ = 797 ºC

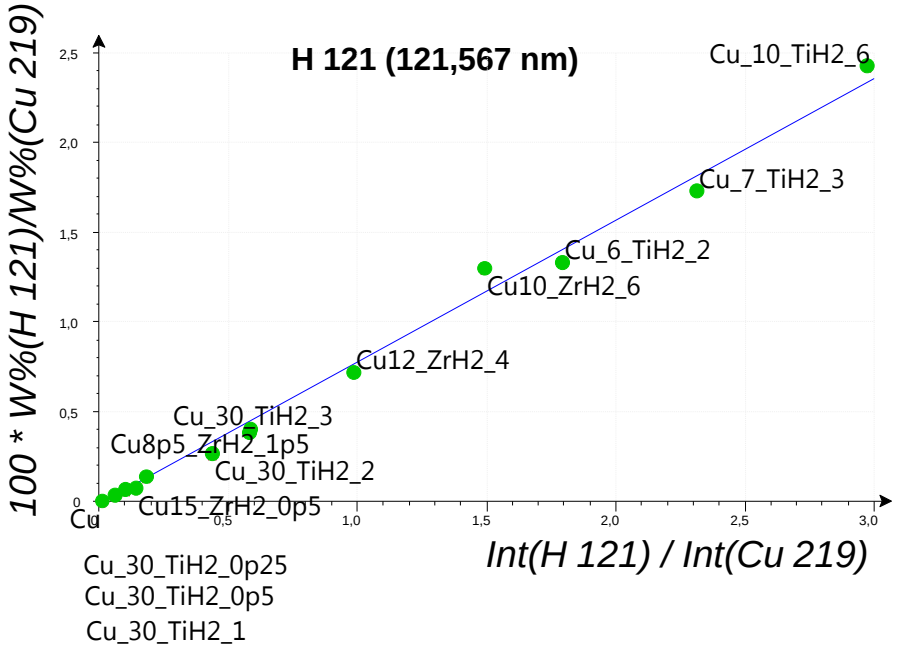
Yuh Fukai,
J. Japan Inst. Met. 55,1991, 17

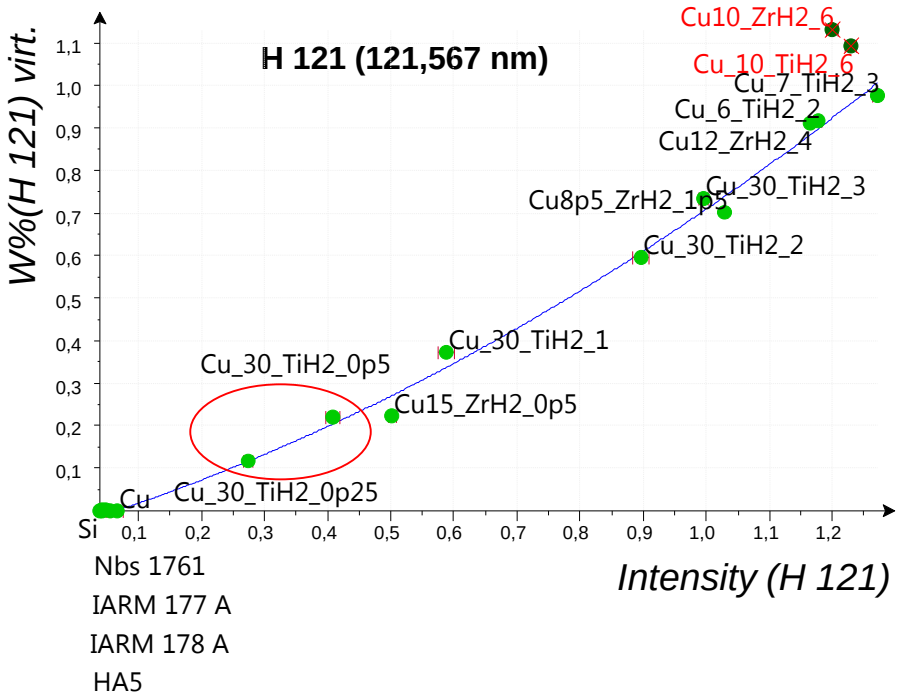


- Decomposition starts at ≈ 450 ºC.
- All H is lost at 700 ºC and atmospheric pressure!

⇒ Validation of concentration is essential

H calibration using sintered Cu+TiH_2 and Cu+ZrH_2 (700 V, 20 mA)





Ratio to Cu 219 compensates saturation and self reversal.

But, quantification is matrix dependent!

Absolute model works up to 1 m% H in Cu(Ti,Zr)

New: 30 g Cu + 0.25 g TiH_2 ≙ c(H) = 331 µg/g

30 g Cu + 0.50 g TiH_2 ≙ c(H) = 657 µg/g

For applications with other matrix, e.g. DLC.

Validation by Carrier Gas Hot Extraction

Successfully for TiH_2, ZrH_2, CuO, Cu_2O, Si_3N_4 in Cu

Failed at MgO, Al_2O_3, AlN in Mg and Al

- Al_2O_3 , AlN and MgO with high melting point > 2000°C
- Mg and Al getter efficiently.

Because

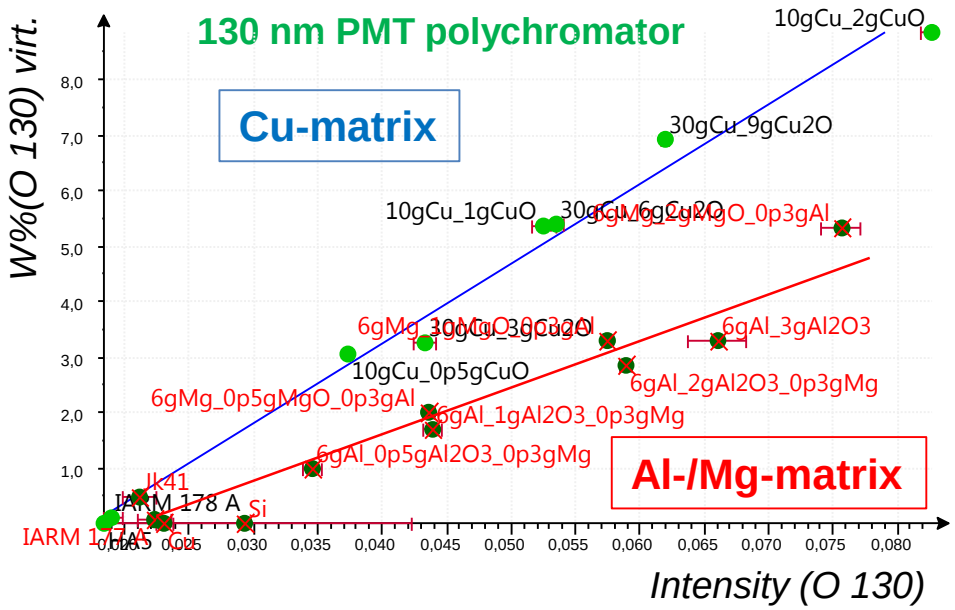
- Decomposition of AlN, Al_2O_3 and MgO is unlikely at 600 °C.
- Introduction of important amounts of additional H, O and N is not possible.
- Densities of sintered samples agree with phase densities better than 95%.

$\Rightarrow$ Calculated concentrations were used.

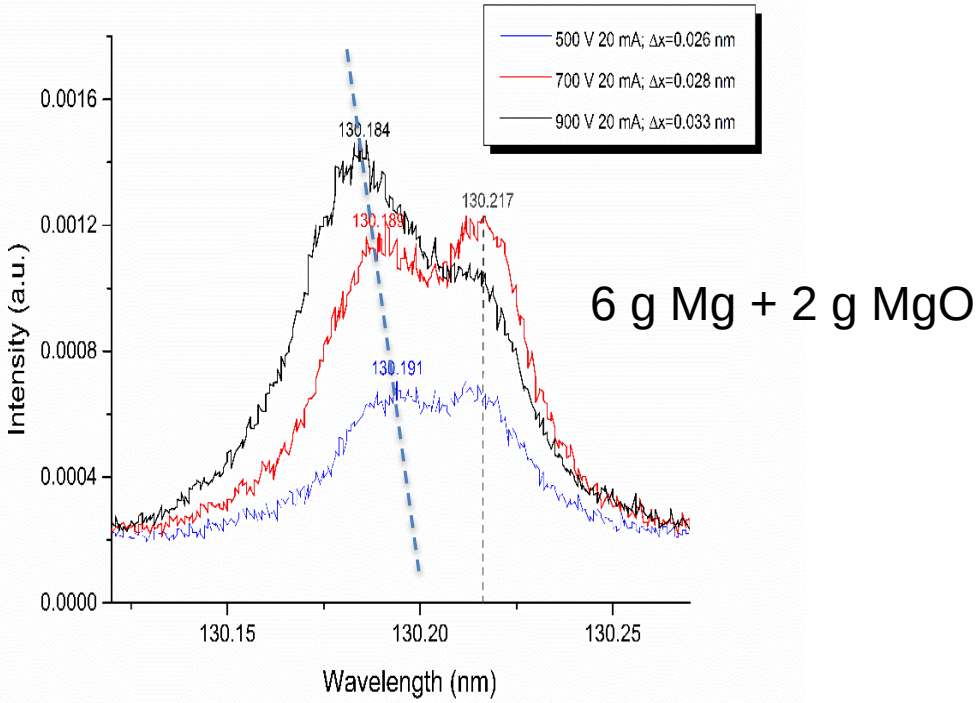
GDS is very welcome for light element analysis, if matrix independent and accurate.

Quantification of Oxygen (700 V, 20 mA)

Line Shift at 130 nm, already reported 2009 at CSI by Michael Köster (Payling Award)



$$\Delta\lambda \propto \sqrt{U}$$



⇒ Matrix dependent for Cu-, Mg- and Al-matrix (EMRP project SIB09 Elements 2013/14)

Cristina Gonzalez-Gago et al., The use of matrix-specific calibrations for oxygen in analytical glow discharge spectrometry, Anal Bioanal Chem (2014) 406:7473

Quantification of Oxygen

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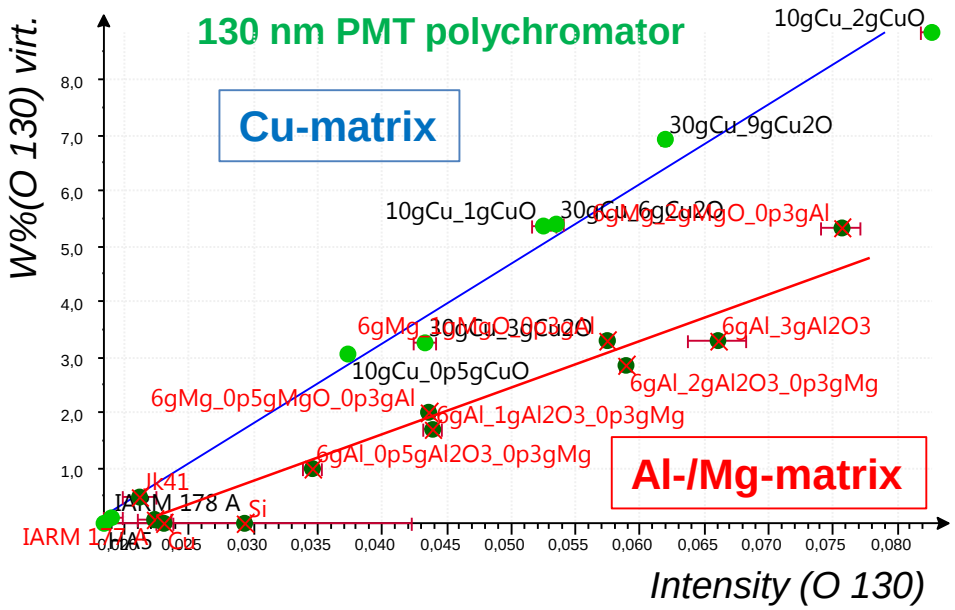
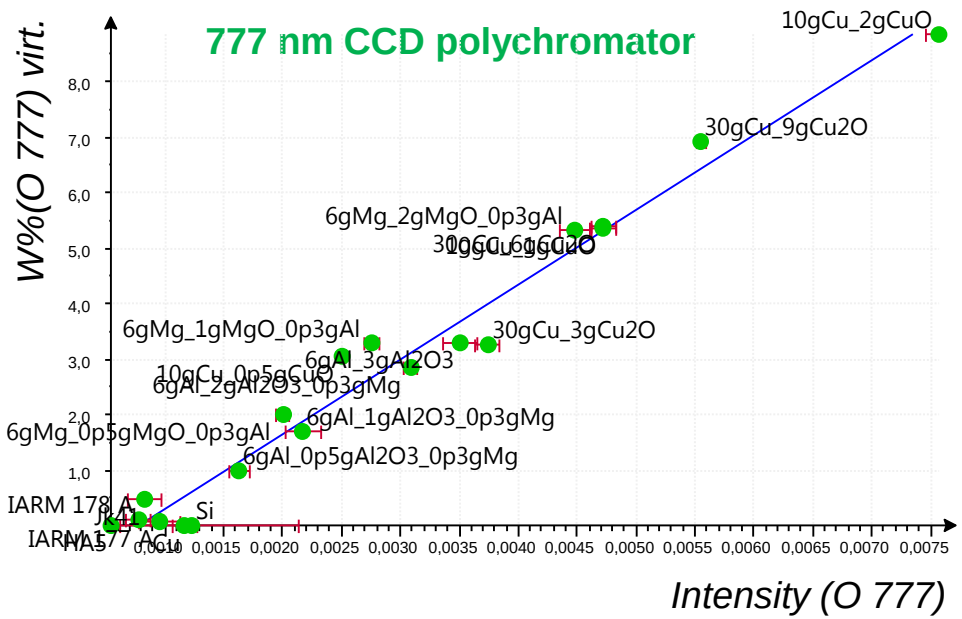
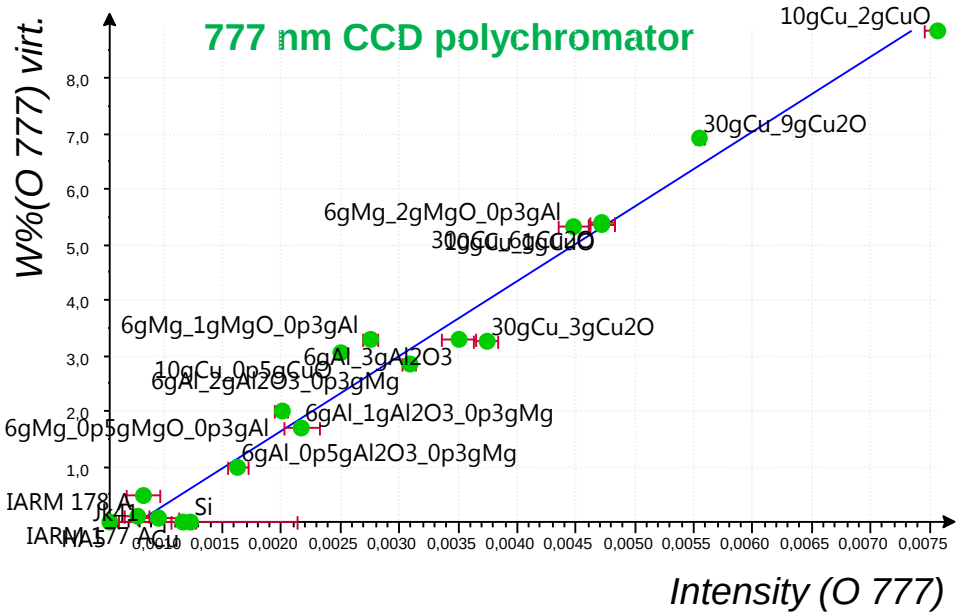




⇒ Matrix dependent for Cu-, Mg- and Al-matrix (EMRP project SIB09 Elements 2013/14)

Use of 777 nm line and CCD at Spectruma (2014/15)
⇒ Matrix independent for Cu-, Mg- and Al-matrix

Quantification of Oxygen



Use of 777 nm line and CCD at Spectruma (2014/15)
⇒ Matrix independent for Cu-, Mg- and Al-matrix

Spectruma

Digikröm monochromator (2015)

- Installation of new grating (1200 g/mm), second order filter (500 nm) and NIR-PMT (R6357 Hamamatsu)

⇒ Resolution@777 nm > 20 pm

GDA750 polychromator (2016)

- Installation of new optics with HR CCD
- Installation of NIR-PMT@777 nm

⇒ Dark current of NIR-PMTs depends on T

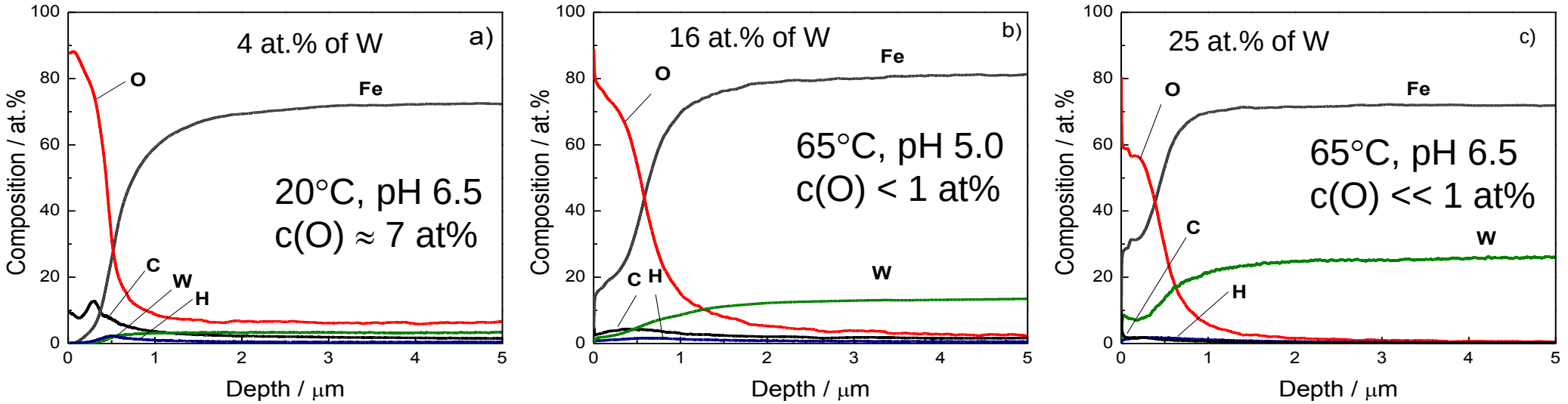
⇒ use of CCD for application

Analysis of Electrochemically Deposited FeW

A. Mulone, A. Nicolenco, V. Hoffmann et al., Electrochimica Acta 261, 2018,167

≈ 500 nm FeO_x (C,H,W) and FeW layer for HT applications

1.0 glycolic acid, 0.3 citric acid, 0.1 $Fe_2(SO_4)_3$ and 0.3 Na_2WO_4, NaOH and H_2SO_4 for pH regulation



c(W) and c(O) in FeW_x depend on T and pH at deposition and are essential for HT behaviour.

1. Calibration correct for Fe?
2. Application of PMT possible for thin layers or low c(O)?

FeO-layers from Literature

S. Suzuki, K. Suzuki, K. Mizuno from Nippon Steel, Japan
Quantitative GDOS Analysis of Oxide Films on Steels, Surf. Interface Anal., 22 (1994) 134-138.

- Matrix specific calibration of 130 nm O-line with Fe_3O_4-layer (background/zero not reported)
- Fe_3O_4- and FeO-layers on construction steel in air at 600°C and 800°C (time not reported)
- Comparison of EY with HIP of Fe+MnO and Fe+SiO_2 (c not reported) ⇒ ± 5% same EY

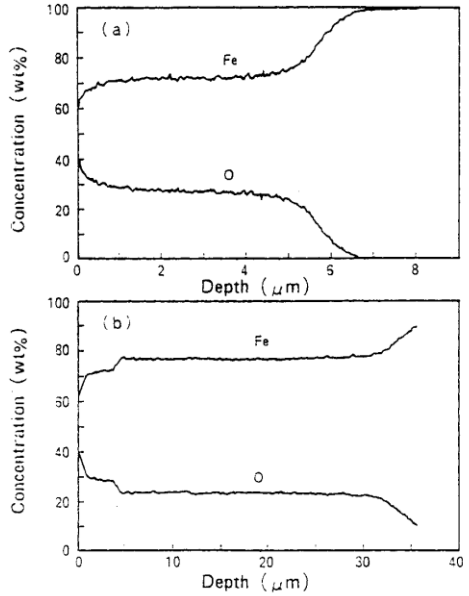
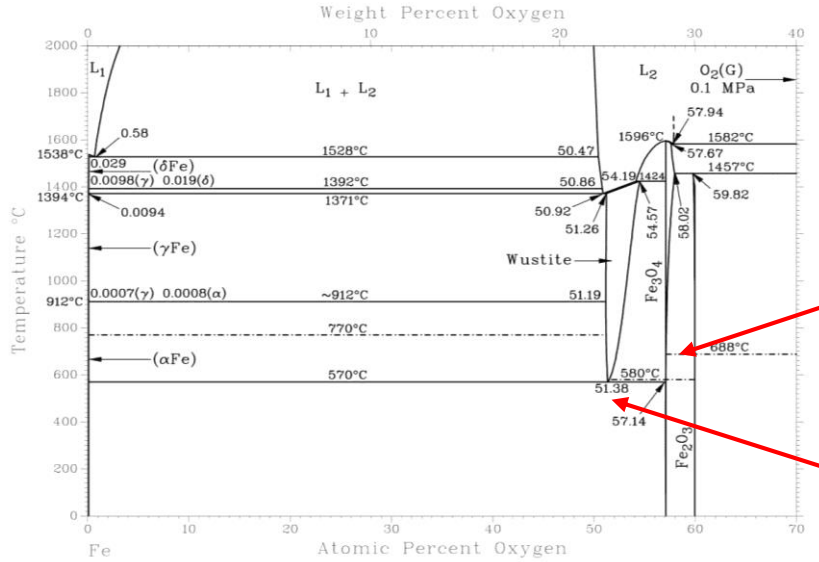


Figure 5. Depth profiles of Sample A oxidized (a) at 873 K and (b) at 1073 K which were corrected based on the present method.

Magnetit
6 µm Fe_3O_4-layer used for 1 point calibration

Wüstite
„thick“ FeO-layer



(C) 1996 ASM International

Fe_3O_4/Fe_2O_3-layer
c(O)=57-60 at%
(27-30 m%)

FeO-layer
c(O)=51.38 at%
(23.19 m%)

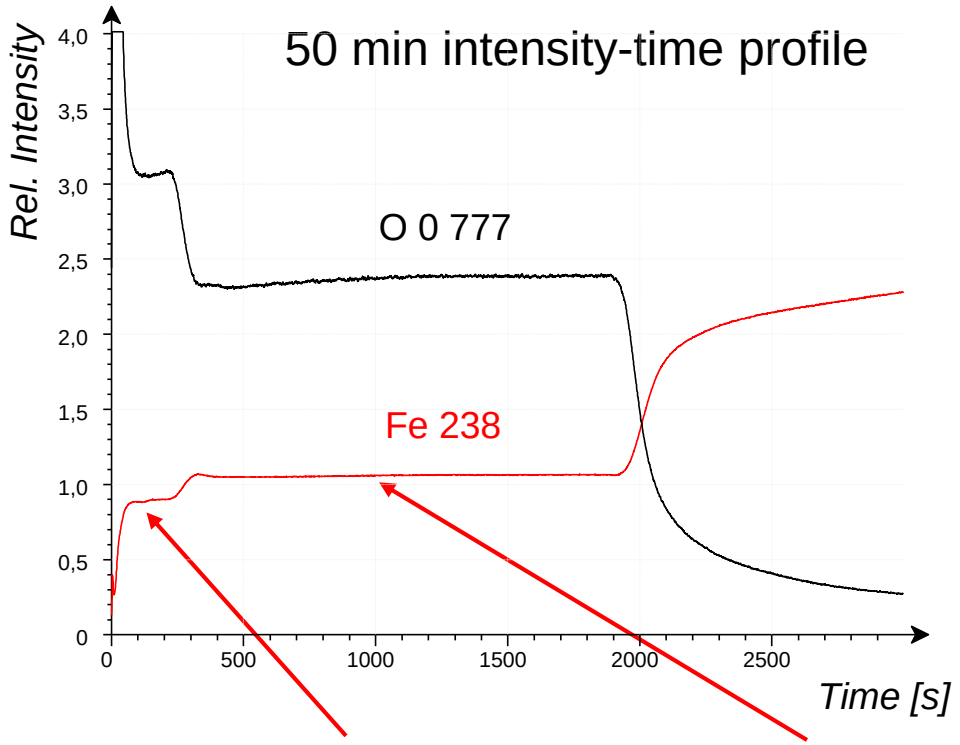
Preparation of FeO-layers at IFW

Construction steel
> 99 m% Fe

1200°C, 1 h, air

800°C, 10 min, air

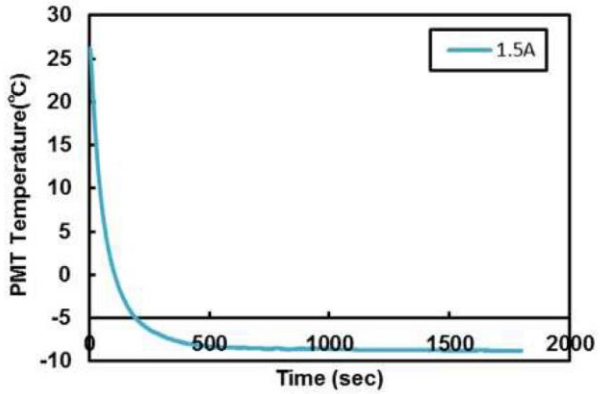
800°C, 10 min, 200 mbar O_2
6.5 µm Fe_3O_4 + 43 µm FeO

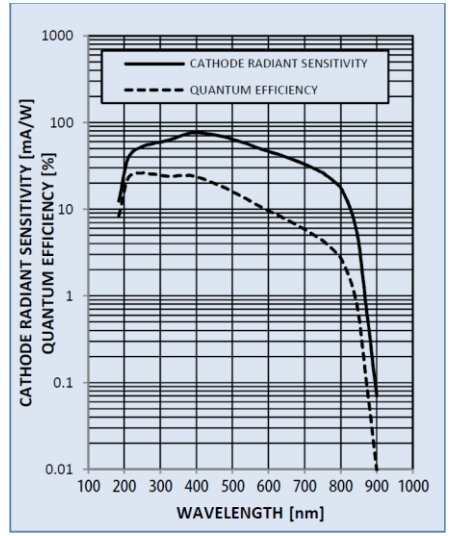


phases (XRD)	Fe_3O_4/Fe_2O_3	FeO
d(Profilometer), µm	6.5 µm	43 µm
c(O, RBS), m%	60 at%	52 at%

PMT H14768 (Hamamatsu) with Peltier cooling

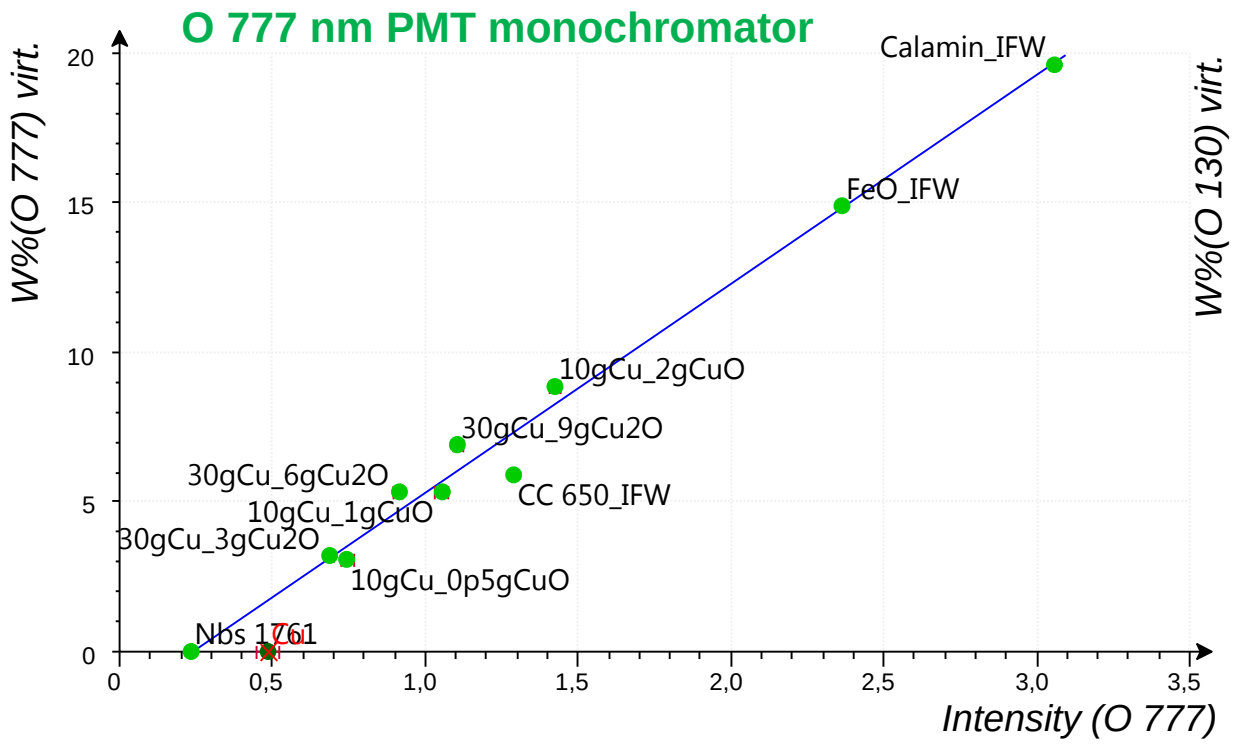
Installation at monochromator Digikröm (Spectral Products)

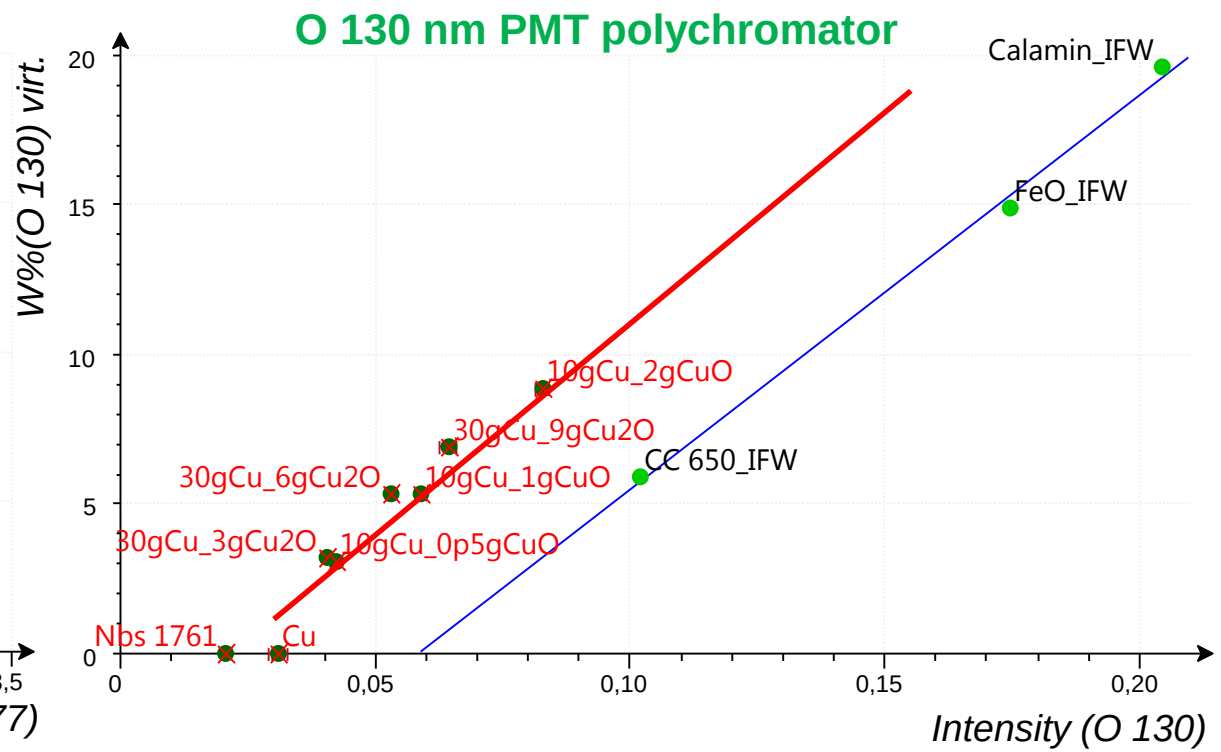




Figures from H14768_Technical Information_181210.pdf (Hamamatsu)

Comparison of O-Calibration at 777 nm and 130 nm with PMT





900 V PMT voltage

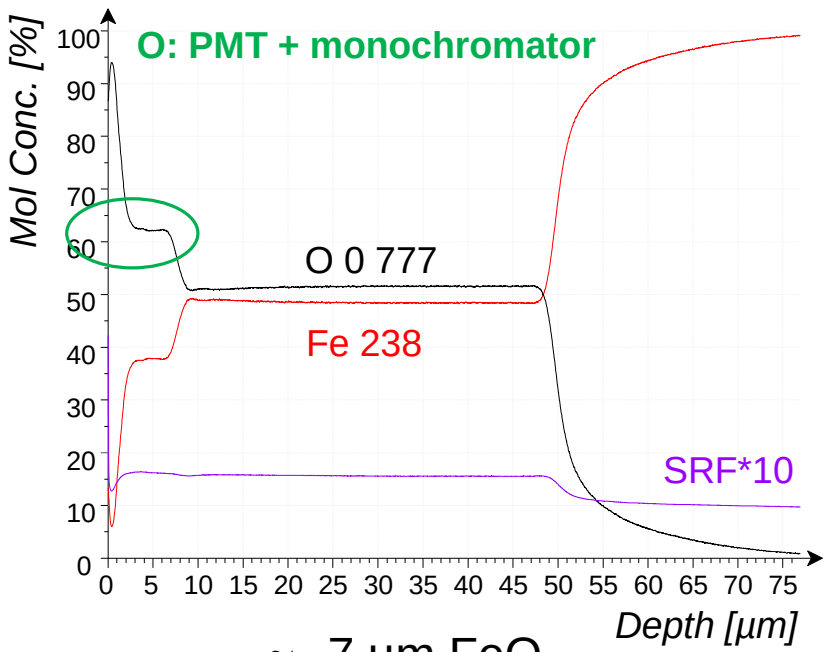
HS3 ≈ 900 V PMT voltage

⇒ 777 nm line is more sensitive, EY(O) similar in Cu, Al, Mg, Fe and CC650

⇒ Less scattering at 130 nm, but clear dependence of EY on matrix

⇒ Background depends on matrix at both lines

Compositional Depth Profile of FeO-layers from IFW



≈ 7 µm FeO_x

c(O) ≈ 62 at%, ARF=1.56

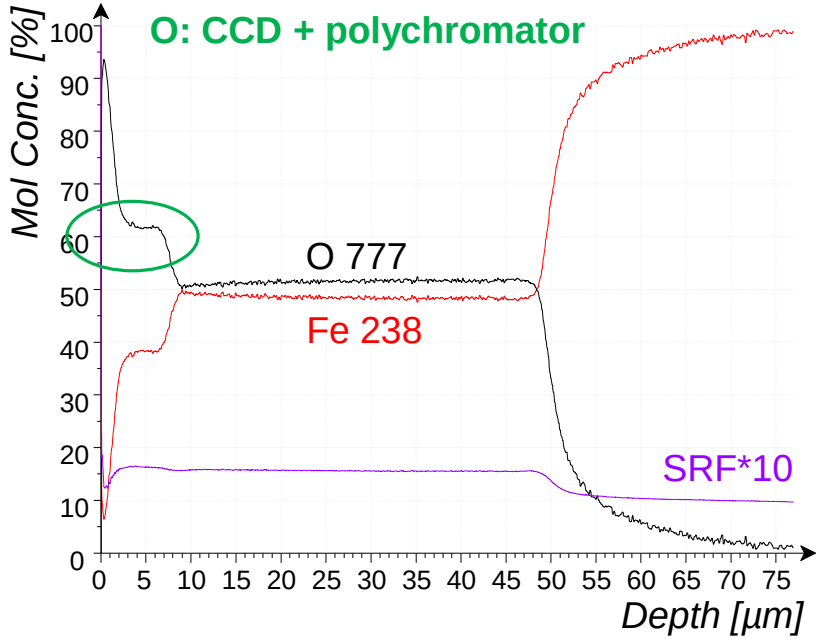
$\rho(O, Fe_3O_4) = 2.75\ g/cm^3$

<

used $\rho(O) = 2.9\ g/cm^3$

<

$\rho(O, FeO) = 3.14\ g/cm^3$



≈ 45 µm FeO

c(O) ≈ 52 at%, ARF=1.53

⇒ Cooled PMT H14768 successfully coupled to monochromator

Possible improvements: reduction of O background and scattering, better Fe calibration

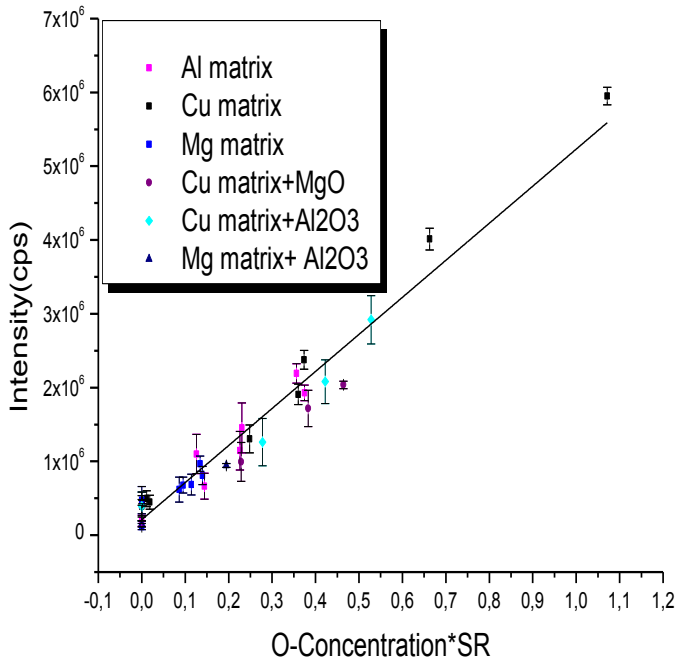
Calibration of Oxygen **in GD-MS**

Main investigations with Element GD at Evonik (VG9000 for comparison) using a set of certified Al, Cu and Zn samples. *(Evonik, BAM, IFW @ EMRP project)*

- At constant flow and current (400 sccm and 50 mA) StdRSF method and absolute method are matrix-independent.
  - Deviations < 15% from reference value in the middle mass range.
  - StdRSFs(Cu, Al) depend on samples or concentration?
- The stability of discharge (especially, if Oxygen is present at higher concentrations) is much better at matrix-specific conditions, which is needed for good intensity and sputtering rate measurements. Sensitivity must be checked ⇒ deviations < 15%

⇒ Calibration of Oxygen at matrix-specific conditions in absolute mode

Multi-matrix calibration for Oxygen at Element GD and VG9000



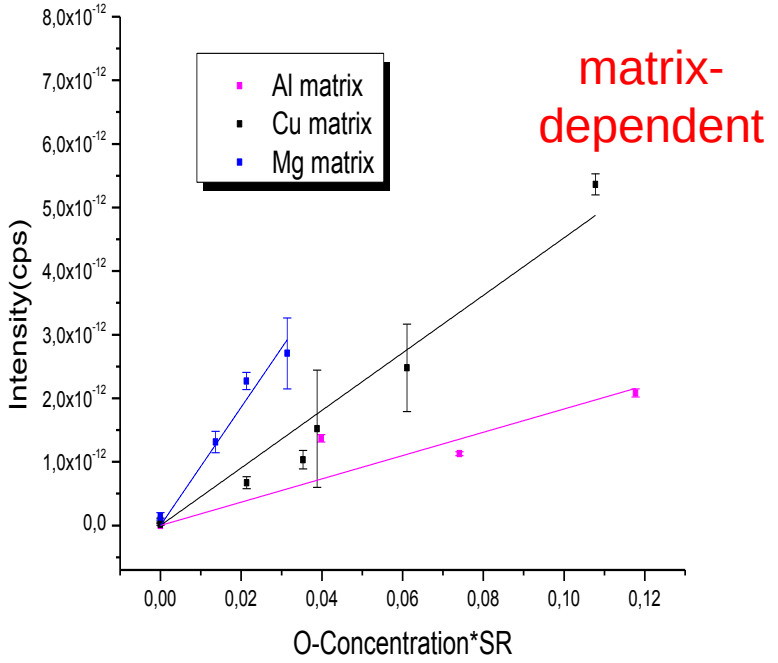
ELEMENT GD
Matrix-specific conditions
Al: 320 sccm, 80 mA
Cu: 400 sccm, 50 mA
Mg: 320 sccm, 80 mA

Deviations for c(O) < 15% using the absolute model and matrix specific conditions

Sensitivity of O is independent of chemical form of the oxide and matrix

C. Gonzalez-Gago et al., Investigations of matrix independent calibration approaches in fast flow glow discharge mass spectrometry, J. Anal. At. Spectrom., 2019, 34, 1109-1125 (Evonik, BAM, IFW @ EMRP project)

VG9000
Matrix-specific conditions
Al: 5 mA, 1.25 kV
Cu: 5 mA, 1 kV
Mg: 3 mA, 1 kV



matrix-dependent

Latest Publication about Quantification in GD-MS

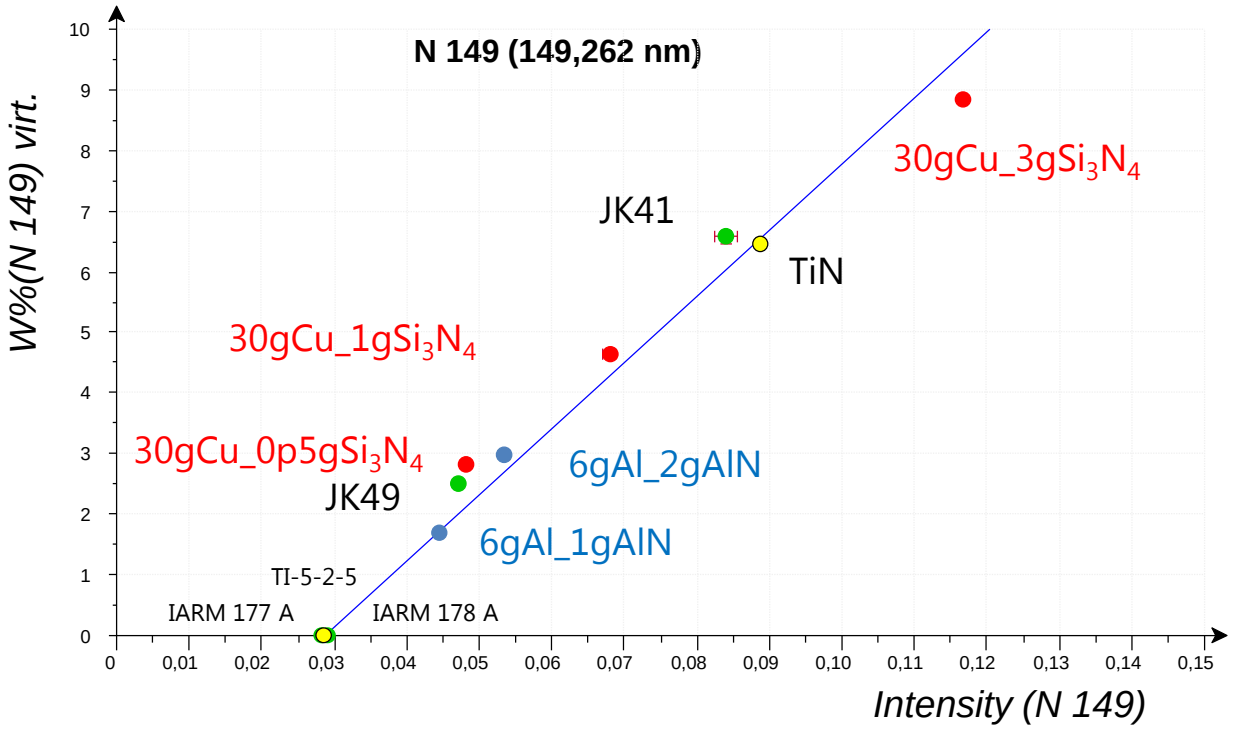
C. Gonzalez-Gago et al., Investigations of matrix independent calibration approaches in fast flow glow discharge mass spectrometry, J. Anal. At. Spectrom., 2019, 34, 1109-1125 (Evonik, BAM, IFW @ EMRP project)
Element GD from Thermo, flat samples, systematic study of quantification using Cu, Al and Zn standards

G. Paudel, M. Kasik, M. Di Sabatino, Investigation of the intensity dependence of glow discharge mass spectrometry quantification on the discharge parameters, J. Anal. At. Spectrom., 2019, 34, 1829-1837
Astrum instrument from Nu, pin samples, systematic study of discharge parameter changes using a Ta sample

⇒ **RSD ≤ 5%,** discharge parameters must be considered at quantification

⇒ Continuation of investigations, instrumental and software improvements are needed, including Astrum from Nu and considering
T. Saka, M. Yamaguchi, K. Ito, Concentration Dependence of Relative Sensitivity Factors in Glow Discharge Mass Spectrometry, Anal. Sci., 2001, 17, i841-i844
VG9000 from former VG, flat and pin samples ⇒ Cu and Al matrix show deviations using the StdRSF concept assuming non-linearities of RSFs.

Results for Nitrogen

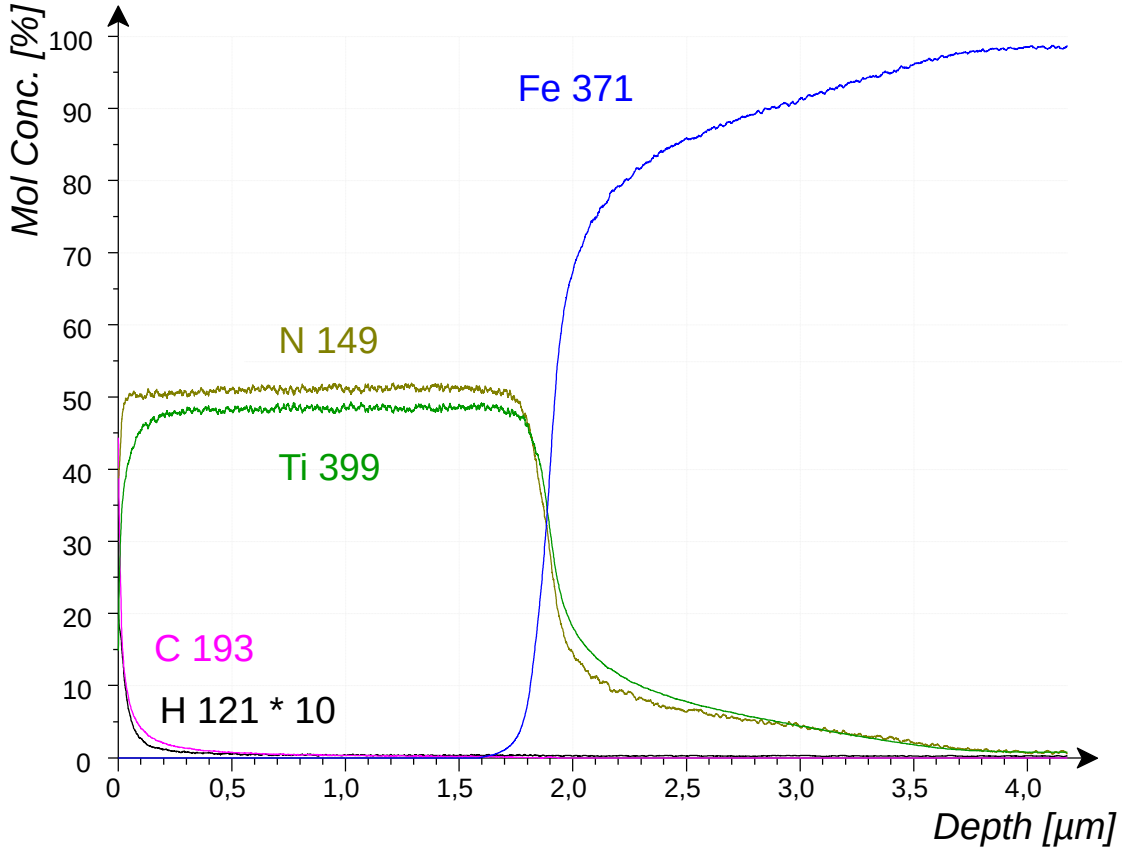


GD-OES Calibration at 149 nm

- 4 mm DC source, 700 V, 20 mA
- Validated c(N) for Cu + Si_3N_4
- EY(N) of sintered Cu + Si_3N_4 agrees with
  - EY(N) in sintered Al + Al_2O_3
  - EY(N) in TiN and in certified
  - JK41 (c(N)=6.9 m% - out of stock)
  - JK49 (c(N)=1.89 m%)

⇒ No dependence on matrix (Al, Cu, Ti, Fe) and chemical form of the nitride was observed.

Quantification of ≈ 2 µm thick TiN-Layer



4 µm sputtered in 5 min

$\Delta c(N, Ti) \approx 5\%$ after 100 nm
(C_xH_y contamination)

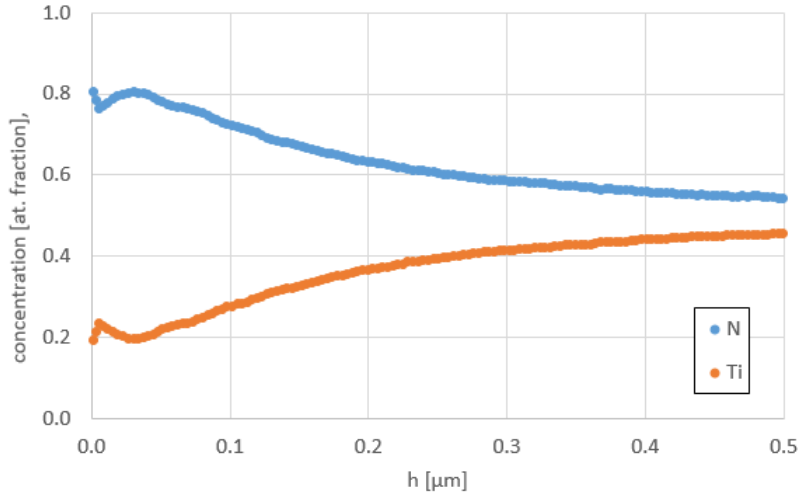
$\rho(N, TiN) = 11.3\ g/cm^3$ was used

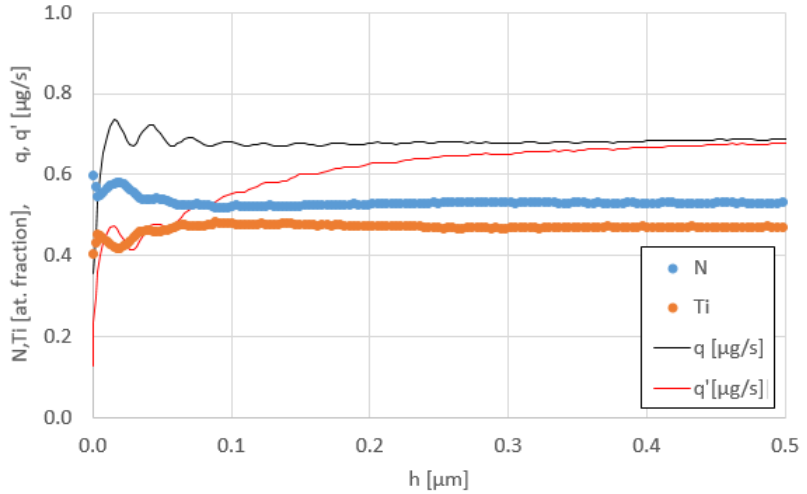
Hard-core model

$$\frac{1}{\rho} = \sum\left(\frac{c_i}{\rho_i}\right) \qquad z = \sum\left(\frac{q}{\rho \cdot A} \cdot \Delta t\right)$$

Effect of other light Elements on the Analysis of TiN-Layers

- *Arne Bengtson, H-effect*
- *Vasile-Dan Hodoroaba, Volker Hoffmann, Edward Steers, H-effect*
- *Richard Payling, Max Aeberhard, Daniel Delfosse, 2001, J. Anal. At. Spectrom., 2001, 16, 50-55, Improved quantitative analysis of hard coatings by rf-GD-OES*
- *...*





Influence of H, C on Ti, N until 500 nm ⇒ Interelement effects must be corrected

Zdenek Weiss, Petr Vlcak, J. Anal. At. Spectrom., 2017, 32, 2476–2484
Analysis of shallow depth profiles of titanium nitride and N-implanted titanium by GD-OES: the 'hydrogen effect' after the discharge startup and a correction thereof

Summary

1. **Hydrogen**
   - Absolute calibration in GD-OES (< 1 m%) and GD-MS (< 1.5 m%)
   - No matrix effect until now (CuTi, CuZr)

   7 sets (3 samples) with Cu+TiH_2 prepared with c(H) = 0.13 – 0.36 m%
   0.0331 and 0.0657 m% positively tested

2. **Oxygen**
   - EY(O 130 nm) is matrix dependent
   - EY(O 777 nm) in GD-OES **and** sensitivity(O) in fast flow GD-MS are independent of matrix (Al, Cu, Mg) and chemical form of oxide
   - Cooled PMT H14768 successfully coupled to monochromator

   7 sets with Cu+Cu_2O prepared with c(O) = 1.1 – 2.6 m%

3. **Nitrogen**
   - EY(N 149 nm) is independent of matrix (Cu, Al, Ti, Fe) and chemical form of nitride

   c(N) of Cu+Si_3N_4 is validated. c(N) = 0.9 – 3.5 m%

Much progress at light element analysis by GDS

Acknowledgement

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Wolfgang Löser, Andrea Voss

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SIB09-Primary Standards for Challenging Elements
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Heinrich Kipphardt

AQura / Evonik
Cristina Gonzalez-Gago, Petr Smid
Thomas Hofmann, Cornel Venzago

HZDR René Heller

Thank you for your attention!