Improvement of Signal Sensitivity Using Hollow Cathode Effect in Glow Discharge Optical Emission Spectroscopy

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Introduction

In order to generate a hollow cathode effect, a 15 mm deep hole was drilled in six pure copper samples (*Fig. 1*). The hole was placed quite opposite to the anode tube of the GD-OES Leco SDP-750. The diameter of the cylindric hole was the same as the inner diameter of the anode tube (4 mm). This investigation was carried out with the pure copper Certified Reference Materials: BAM-M381, BAM-M382, BAM-M383, BAM-M384, ERM-EB385 and ERM-EB386.

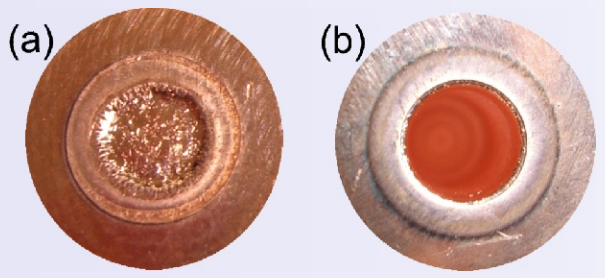

Fig. 1 Glow Discharge spot on:
(a) **F** samples, and
(b) **H** samples,

F = flat, **H** = hollow

Results and Discussion

Matrix (Cu)

Measurements of flat copper samples (**F** samples) and copper samples with hole (**H** samples) were carried out with the identical parameters of 300 V and 50 mA. It can be seen in *Fig. 2* that the copper atom line signal is significantly higher for **H** samples. The copper ion line signal is more intensive in measurements of **F** samples.

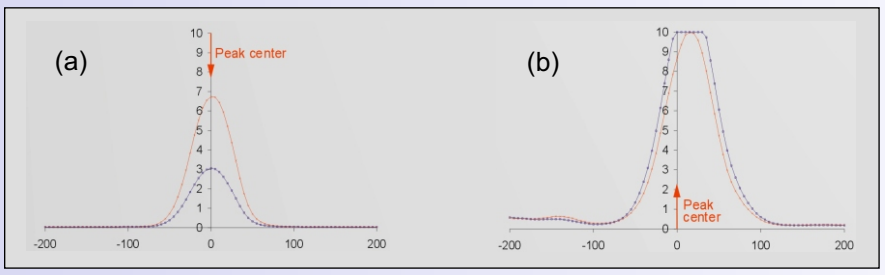

Fig. 2
Intensities of:
(a) a copper *atom* line (HV = 1), and
(b) a copper *ion* line (HV = 12)
for the **F** sample (blue) and **H** sample (red).

Examples of trace elements

	Si (mg/kg)	Ni (mg/kg)	Ti (mg/kg)
BAM-M381	<5	0.7	<0.3
ERM-EB386	14.3	25.0	33.1

Si (trace element)

The intensities of all investigated spectral lines of trace elements are much higher for **H** samples at optimal conditions (450 V, 250 mA) than for **F** samples at optimal conditions (500 V, ca. 100 mA). Even if the detector sensitivity (HV) is adjusted to higher values for **F** samples, sensitivity of the element determination is much better for **H** samples, as can be seen at an example of silicon (*Fig. 3*), where two samples BAM-M381(<5 mg/kg Si) and ERM-EB386 (14.3 mg/kg Si) are compared. Measured intensities are ca. 0.8 for the **F** sample (HV = 15) and 7 for the **H** sample (HV = 11), which would be an intensity of 112 corresponding to HV = 15. This is 140 times higher than for **F** sample measurement.

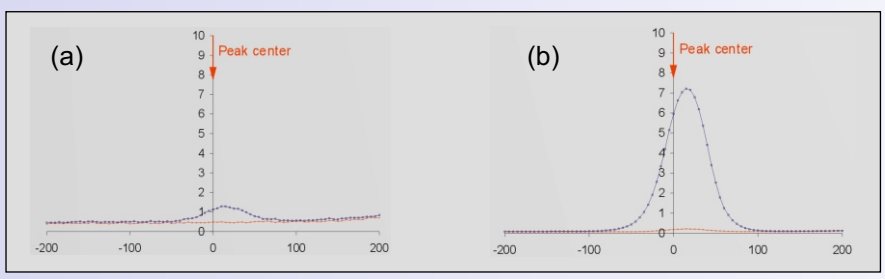

Fig. 3
Intensity of *silicon* atom lines in sample BAM-M381 (red) and ERM-EB386 (blue):
(a) **F** sample, HV = 15;
(b) **H** sample, HV = 11.

Ni, Ti (trace elements)

By combining the glow discharge with hollow cathode effect lower mass fractions of trace elements can be detected. For example a much better sensitivity was achieved with the hollow cathode for nickel atom line measurements (*Fig. 4*). The same is observed for titanium. Additionally, it can be seen, that interferences in **H** samples measurements appear differently than those seen in **F** samples analysis. Due to thisphenomenon many trace elements can be easier measured as shown in the example of titanium (*Fig. 5*).

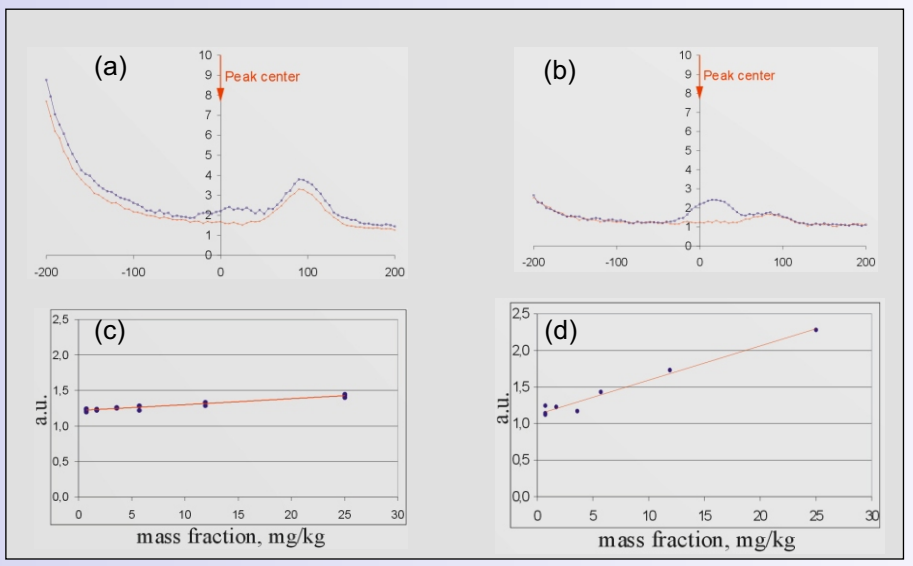

Fig. 4
Intensity of *nickel* ion lines in sample BAM-M381 (red) and ERM-EB386 (blue):
(a) **F** sample, HV = 15;(b) **H** sample, HV = 15;
(c) calibration curve for **F** sample, and (d) calibration curve for **H** sample

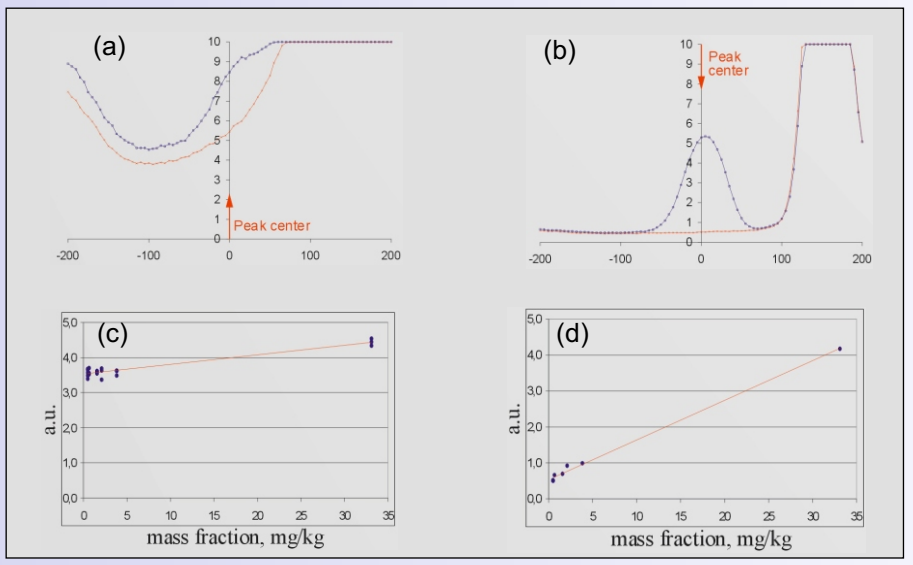

Fig. 5
Intensity of *titanium* ion lines in sample BAM-M381 (red) and ERM-EB386 (blue):
(a) **F** sample, HV = 14; (b) **H** sample, HV = 13;
(c) calibration curve for **F** sample, and (d) calibration curve for **H** sample

Conclusions

Combining the glow discharge with hollow cathode effect is a good way to achieve higher sensitivity in Optical Emission Spectroscopy applied to pure metals. A signal enhancement for all measured trace elements lines was observed. The special technique allows the determination of even those elements, which cannot be detected by usual GD-OES analysis. Plotted calibration curves show significantly better slopes. This demonstrates higher sensitivity for trace element determination in pure copper samples.

2006-121ga