

# Determination of 1 ppm Iron and Phosphorus in Ultra Pure Copper

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A round robin was held under the direction of the German Federal Institute for Materials Research and Testing, BAM (Bundesanstalt für Materialforschung und prüfung), as part of the development of three new Cu reference materials (BAM-M390, BAM-M391 and BAM-M392) with very low mass fractions of Fe, P and Sn. Several members of the German GDMB Working Group for Copper, who are able to analyze Fe, P and Sn at very low concentrations in the solid (Fe: 1 ppm, P: 1 ppm to 6 ppm and Sn: < 0.1 ppm) participated in this round robin. Several analytical techniques were used for the analysis:

- Photometry (colorimetric method)
- ICP-OES
- ICP-OES after Lanthanum precipitation
- ICP-MS
- GD-MS

As the photometric method and the ICP-OES method after Lanthanum precipitation are time consuming methods and as Mass Spectrometry techniques are more expensive and sometimes increase the uncertainty and the time for sample preparation due to dilutions, ICP-OES remains as the most interesting technique due to its ease of use. The high resolution of the HORIBA Scientific ULTIMA 2 ICP-OES Spectrometer allows analyzing these samples directly after dissolution without any special sample treatment or dilution. Due to the very low concentration of Sn (< 0.1 ppm) it was decided not to try to analyze it. The analysis may be possible with an increased initial sample weight or with the use of a hydride generation system.

Several issues arise for the analysis of such high purity materials. Careful cleaning of flasks and all spare parts like the caps for the flasks with a mixture of HCl and H<sub>2</sub>O<sub>2</sub> on a hot plate is required. For the sample preparation procedure, ultra pure nitric acid has to be used to avoid any contamination of the samples. Some issues that are directly related to the development of new CRM materials remain. To perform the calibration, you have to find calibration standards or at least a material with fewer impurities than the material to be analyzed. In this case this is nearly impossible. For this reason, for ICP-OES and ICP-MS the standard addition method was used. To avoid any error propagation for the new reference material, using other certified reference material for the calibration is strictly forbidden.

#### Principle

The elemental analysis of these samples was done by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The sample is nebulized and then transferred with an argon carrier gas stream into an argon plasma. The sample is desolvated, atomized and ionized, whereby the atoms and ions are excited. The intensity of the light is measured when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths, which can be used for the identification of the element. The intensity of the light is used for the quantification.

# Instruments and operating specification

The work was done on a HORIBA Scientific ULTIMA 2 Dual grating ICP spectrometer. The specifications of the instrument are listed in Table 1, the specifications of the sample introduction system in Table 2, and the operating conditions of the instrument in Table 3.



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Table 1: Specification of the ICP spectrometer ULTIMA 2 Dual grating

Parameter	Specification
Optical Mounting	Czerny-Turner
Focal Length	1 m
Nitrogen purge	Yes
Gratings (number of grooves/mm)	2400 g/mm and 4343 g/mm used in first order
Resolution	5.5 pm 120-440 nm 10 pm 440-800 nm
Thermoregulation	32 ± 0.1°C
Type of generator	40.68 MHz Solid State, water cooled
Torch	Vertical with Radial viewing

Table 2: Specification of the sample introduction system

Parameter	Specifications
Nebulizer	Seaspray
Spray chamber	Cinnabar cyclonic
Sample uptake	1mL/min
Argon humidifier	Yes
Injector tube diameter	3 mm

Table 3: Operating conditions of the spectrometer

Parameter	Specification
Power	1300 W
Plasma gas	12 L/min
Auxiliary gas	0.1 L/min
Sheath gas	0.3 L/min
Nebulizer pressure/argon flow	2.6 bars / 0.71 L/min

## Sample preparations of the Cu samples

To analyze the Cu samples by ICP-OES it is necessary to dissolve them with the following recommended procedure: Weigh 2 g of the sample in a 100 mL flask. Add 10 mL of doubly distilled water and 10 mL of ultra pure nitric acid (65 %). Wait until the reaction is nearly complete (the evolution of hydrogen is very slight) and add an additional 5 mL of ultra pure nitric acid. After the complete dissolution of the material the flasks are filled to 100 mL. It is also necessary to make an acid and water blank value for the calibration. Since 20 g/L of Cu are used, there will be, at the 1 ppm level, 20 µg/L of Fe, P or Sn in the solution. This procedure was used for all the samples analyzed.

## Wavelength selections

Due to the high concentration of Cu in the samples, only a few emission lines can be used for the analysis of Fe and P. Common emission lines for P like 213.618 nm and 214.914 nm are interfered by Cu and for this reason the emission line at 177.229 nm is used. For Fe the emission line at 238.204 nm and 259.940 nm are used. The acquisition parameters for the emission lines are listed in Table 4.

Table 4: Acquisition parameter

Acquisition mode	Max mode
Measurement points	1
Integration time	8 s
Entrance slit	20 µm
Exit slit	15 µm

## **Calibration samples**

As mentioned in the introduction it is necessary to use the standard addition method for the analysis. The sample with the lowest concentration of Fe and P (BAM-M390) is used to prepare four 10 mL aliquots. An amount of Fe and P standard solutions is added to create standards that cover the range of interest in the solid. These concentrations are given in Table 5.

Table 5: Concentrations of the different additions of Fe and P expressed as  $\mu g/g$  in the sample

Fe	0	1.0	1.5	2.0
Р	0	2.5	5.0	7.5

# **Results**

The results obtained for the analysis of Fe and P are given in Tables 6 and 7, respectively. The values obtained with the ULTIMA 2 are very close to the average value. The average value is computed from the results obtained with ICP-AES, ICP-AES after Lanthanum precipitation, ICP-MS and GD-MS for both Fe and P. For P, the average also includes the results obtained with photometry.

Table 6: Fe concentration (ppm) in the Cu samples

Fe average	0.812	0.967	0.892
Fe HJY result	0.902	1.060	0.877

Table 7: P concentration (ppm) in the Cu samples

		N-1- /	1
Fe average	1.255	3.231	6.969
Fe HJY result	1.274	3.260	6.710

## **Conclusions**

The results obtained with the ULTIMA 2 show that it is possible to analyze very low traces of elements in difficult matrices without any complicated sample preparation. The vertical torch with the 3 mm inner diameter injector and the sheath gas module allow unmatched stability over hours, even with the 20 g/L Copper samples. The total plasma view, i.e. the measurement of the entire normal analytical zone of the plasma and the high resolution of the spectrometer, which has a direct impact on the detection limits, allow the determination of 1 ppm of Fe and P in the solid sample.

The reference material analyzed in this study will be available soon from BAM in Berlin. For more information see www. bam.de.

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# Appendix A: individual results for Fe in the samples BAM-M390, BAM-M391 and BAM-M392



# Appendix B: individual results for P in the samples BAM-M390, BAM-M391 and BAM-M392



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