



Determination of 22 elements in Copper (Cu)

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For the development of civilization, copper has played an important role and its history goes back to 9,000 BC. Copper objects have been found as tools, weapons and also as jewellery objects. They were manufactured at this time by cold hammering of copper. Around 5,500 BC copper started to be produced from oxidized ores first in the Sumerian region and then around 4,500 – 3,500 BC in the Nile Valley. The Romans also developed the knowledge to handle copper and they obtained most of knowledge from Cyprus. They called firstly aes cyprium, later cyprium which was converted to cuprum and finally to copper. The mining and processing of copper ores started in the tenth century in Germany (Saxony and Harz region) and in the thirteenth century in Mansfeld.

The average copper content in the earth's crust is 55 ppm. Copper appears as natural and in more than 200 minerals, but only 10 minerals are economically useful with the main reservoirs of copper in Canada, Chile, Congo, Mexico, USA, Russia and Zambia. Depending on the ore, copper can be associated with noble elements like gold, silver and elements of the platinum group, but also with molybdenum, cobalt, nickel, selenium, tellurium, lead and tin. Copper is also used for construction, in electric and electronic products and in industrial machinery and equipment. Copper combines with lots of other elements to form alloys (brass, bronze, cupro-aluminium, cupro-nickel, nickel silver ("German silver" with 15 to 30 % Zn and 8 to 30 % Ni). These alloys have a good corrosion resistance against the atmosphere, but also against sea-water (propellers and rudders, sea-water condenser and sheathing material in off-shore objects). Copper compounds are also used as fungicides, algicides and for wood preservation and copper oxides are used in glass-making and CuO as a catalyst in the production of acrylates. It is because of its huge economic importance (the production of refined copper was estimated at 15 million tonnes for the year 2000), that it is necessary to analyze the ores, the metallic copper, the alloys and also the anode slime in the electrolysis process of pure copper, which contain many precious metals.

Thanks to its speed and multi-element detection possibility the use of Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) is well established for the determination of minor and major elements concentrations in copper analysis laboratories. The development of the method is a key issue to get accurate results. This application note describes the development of a method for the determination of Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn and Zr in a copper matrix. The method is validated by the analysis of two synthetic copper solutions as well as the analysis of two copper certified reference materials (CRM).

Principle

The elemental analysis of these samples was done by ICP-OES where the sample is nebulized and then the aerosol transferred with an argon carrier gas stream into an argon plasma. The sample aerosol 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 Jobin Yvon ACTIVA M 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.

Table 1: Specification of the ICP spectrometer ACTIVA M

Parameter	Specification
Optical mounting	Czerny Turner
Focal length	0.64 m
Nitrogen purge	Yes
Gratings: number of grooves per mm	2400 groove/mm and 4320 groove/mm back-to-back gratings used in first order
Resolution	9 pm 120 - 440 nm 18 pm 440 - 800 nm
Type of RF generator	Solid state, water-cooled
Frequency	40.68 MHz
Torch	Vertical with Radial viewing and Total Plasma View*

* Total Plasma View: Measurement of the whole Normal Analytical Zone for enhanced sensitivity and reduced matrix effects

Table 2: Specification of the sample introduction system

Parameter	Specification
Nebulizer	Seaspray
Spray chamber	Cyclonic glass
Sample uptake	1 mL/min
Argon humidifier	Yes
Nebulizer pressure/Argon flow	2.6 bar / 0.71 L/min
Injector tube internal diameter	3 mm

Table 3: Operating conditions of the spectrometer

Parameter	Specification
RF generator power	1300 W
Plasma gas	12 L/min
Auxiliary gas	0.1 L/min
Sheath gas	0.3 L/min

Preparation of the copper samples

HCl and H₂SO₄ do not dissolve metallic copper at room temperature, but it can be dissolved with hot H₂SO₄. Metallic copper is easily dissolved by HNO₃ by forming Cu(NO₃)₂. The dissolving process can be described by the following equation:



For the dissolution of the copper samples it is recommended to use the following procedure: Weigh 2 g of the sample in a 100 mL flask. Add 10 mL of doubly distilled H₂O and 10 mL of conc. HNO₃ (65 %). Wait until the reaction is nearly complete (the development of gas around the copper in the flask is very slight) and then add an additional 5 mL of conc. HNO₃.

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. This procedure was used for the certified reference samples BAM-385 and BAM-386.

Development of the method - wavelengths selection

Wavelength selection was done by acquiring several profiles. Due to the high concentration of copper in the samples, only a few emission lines per element can be used. The profiles were acquired using single element standards of the different elements and also a copper solution with

1 g/L and 20 g/L respectively. This procedure is necessary to select interference free wavelengths with appropriate sensitivity and also to set background correction. Before the CRM solutions were analyzed, the method and the wavelength selection, were checked using two synthetic copper solutions which were produced for a round robin from Aurubis AG, Hamburg. For the acquisition one point with an integration time of 4 s was used.

Calibration samples

For the analysis of the synthetic solutions the calibration samples were distributed together with samples from Norddeutsche Affinerie, Hamburg. In the case of the analysis of the CRMs the calibration samples were manufactured by using high purity copper for matrix matching and commercial standard solutions from Spex CertiPrep®.

Results

The results obtained for the analysis of the synthetic solutions are given in Table 4, the results for the reference materials BAM-385 and BAM-386 are given in Table 5, respectively.

Table 4: Analysis of the synthetic solutions with 1 g/L Cu and 20 g/L Cu

		synthetic solution with 1 g/L Cu			synthetic solution with 20 g/L Cu		
Element	Wavelength	Expected value	experimental value	Recovery	expected value	experimental value	Recovery
	nm	g/t	g/t	%	g/t	g/t	%
As	188.983	4992	4976	99.7	330	327	99.1
	193.695		4930	98.8		323	97.9
	197.198		4952	99.2		326	98.8
Bi	190.178	5778	5863	101.5	327	327	100.0
Cd	214.438	4959	5093	102.7	329	329	100.0
	226.502		5063	102.1		329	100.0
	228.802		5051	101.9		331	100.7
Cr	206.149	4910	4883	99.5	246	251	102.0
	267.716		4934	100.5		244	99.2
	283.563		4912	100.0		245	99.6
	284.325		4914	100.1		245	99.6
	357.869		5052	102.9		246	100.0
Fe	234.349	5597	5613	100.3	339	335	98.8
	238.204		5626	100.5		336	99.1
	259.940		5657	101.1		333	98.2
	261.187		5648	100.9		333	98.2
Ni	227.021	6215	6283	101.1	239	237	99.2
	231.604		6301	101.4		235	98.3
	232.003		6218	100.1		240	100.4
	341.476		6106	98.3		236	98.7
P	178.229	6159	6166	100.1	295	293	99.3
	185.880		6335	102.9		294	99.7
Pb	168.155	5590	5370	96.1	296	282	95.3
	220.353		5777	103.4		291	98.3
	283.306		5641	100.9		285	96.3
S	180.676	5804	5793	99.8	282	281	99.7
	181.978		5890	101.5		280	99.3
Sb	187.052	6188	6132	99.1	295	286	97.0
	206.833		6245	100.9		284	96.3
	217.581		6295	101.7		288	97.6
Se	196.026	6667	6698	100.5	294	292	99.3
	206.279		6695	100.4		288	98.0
Te	214.281	5988	5976	99.8	277	270	97.5
	238.578		5950	99.4		267	96.4
Zn	206.200	6097	6074	99.6	338	338	100.0
	334.502		6225	102.1		328	97.0

Table 5: Analysis of the certified reference materials BAM-385 and BAM-386

		BAM-385		BAM-386	
Element	Wavelength nm	Certified value µg/g	Experimental value µg/g	Certified value µg/g	Experimental value µg/g
Ag	328.068	28.6 ± 0.8	28.20 ± 0.29	47.4 ± 1.2	47.31 ± 0.05
	338.289		28.72 ± 0.24		47.67 ± 0.05
Al	167.020	28.6 ± 2.5	29.84 ± 0.16	36.5 ± 2.5	37.05 ± 0.22
	396.152		29.03 ± 0.10		37.39 ± 0.91
As	189.042	11.4 ± 0.8	11.37 ± 0.04	24.2 ± 1.0	23.79 ± 0.10
	193.759		11.11 ± 0.25		23.82 ± 0.14
	197.262		11.14 ± 0.25		23.99 ± 0.47
Bi	190.241	5.81 ± 0.17	5.76 ± 0.46	9.6 ± 0.5	9.72 ± 0.39
Cd	214.438	5.80 ± 0.3	5.91 ± 0.03	7.8 ± 0.4	7.88 ± 0.11
	226.502		6.06 ± 0.02		7.79 ± 0.01
Co	228.616	6.93 ± 0.15	6.94 ± 0.03	5.2 ± 0.14	5.21 ± 0.02
	238.892		6.87 ± 0.03		5.13 ± 0.01
Cr	357.869	9.81 ± 0.20	9.98 ± 0.07	12.4 ± 0.4	12.72 ± 0.11
Fe	234.349	45.4 ± 1.4	44.28 ± 0.17	64.7 ± 1.8	64.23 ± 0.30
	238.204		44.59 ± 0.12		63.58 ± 0.16
	259.940		44.51 ± 0.21		64.02 ± 0.16
Mg	279.553	29.1 ± 1.3	29.44 ± 0.11	36.1 ± 1.2	36.29 ± 0.12
	285.213		29.18 ± 0.22		35.99 ± 0.14
Mn	257.610	10.1 ± 0.2	10.11 ± 0.1	13.3 ± 0.2	13.19 ± 0.09
Ni	227.021	11.9 ± 0.8	12.57 ± 0.03	25.0 ± 1.0	24.96 ± 0.07
	231.604		12.65 ± 0.02		24.95 ± 0.06
P	178.229	12.9 ± 1.0	12.22 ± 0.46	7.2 ± 0.7	7.42 ± 0.54
	185.880		12.96 ± 0.29		7.21 ± 0.44
Pb	168.155	11.3 ± 0.5	8.91 ± 0.23	23.4 ± 1.2	23.82 ± 1.34
	220.353		13.46 ± 1.7		23.21 ± 0.17
S	180.676	31.2 ± 1.5	31.44 ± 0.67	21.9 ± 2.1	21.39 ± 0.13
	181.978		31.94 ± 0.93		21.56 ± 0.26
Sb	187.052	19.9 ± 0.8	18.58 ± 0.58	31.2 ± 1.1	31.20 ± 0.24
	206.833		19.18 ± 0.14		31.05 ± 0.74
	217.581		19.32 ± 0.08		31.76 ± 0.46
Si*	251.611	7.2 ± 1.5	6.91 ± 0.11	14.3 ± 4.3	10.41 ± 0.12
	288.158		6.98 ± 0.08		10.72 ± 0.20

* = values not certified, indicative value

		BAM-385		BAM-386	
Element	Wavelength Nm	Certified value µg/g	Experimental value µg/g	Certified value µg/g	Experimental value µg/g
Sn	189.989	18.0 ± 0.9	17.69 ± 0.11	28.3 ± 0.8	28.38 ± 0.09
	242.949		17.43 ± 0.12		28.95 ± 0.52
Te	238.578	10.0 ± 0.4	10.209 ± 0.38	38.3 ± 0.9	38.58 ± 0.58
Ti	323.452	3.83 ± 0.17	3.89 ± 0.05	33.1 ± 1.3	33.66 ± 0.10
	336.121		3.88 ± 0.02		33.69 ± 0.15
	337.280		3.83 ± 0.03		32.96 ± 0.16
Zn	206.200	57.9 ± 4.0	59.22 ± 0.18	49.5 ± 1.6	49.22 ± 0.19
	334.502		58.68 ± 0.82		49.24 ± 0.37
Zr*	256.887	< 7	3.01 ± 0.10	8.9 ± 1.7	9.65 ± 0.35
	339.198		3.10 ± 0.15		8.82 ± 0.20
	343.823		2.88 ± 0.17		8.96 ± 0.20

*= values not certified, indicative value

For an estimation of detection limits in copper please refer to HORIBA Jobin Yvon's application note number 09 "Analysis of several elements in a copper matrix".

Conclusions

The results obtained with the ACTIVA M ICP-OES spectrometer show that it is possible to analyze low traces of elements in difficult matrices without any complicated sample preparation.

This is mainly due to the excellent optical resolution, the stability and the sensitivity of this instrument that allows determining elements without manipulation and extra work through mathematical procedures like inter-element correction or deconvolution. The avoidance of software corrections improves accuracy and precision. The vertical torch with the 3 mm internal 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 associated with the high resolution of the spectrometer, which has a direct impact on the detection limits, allows the analysis of low concentrations of elements known as difficult like As, Bi, Sb and Te.

The reference materials analyzed in this study are available from BAM in Berlin. For more information see www.bam.de.

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