

Determination of Trace Metals in Electrolytic Copper by ICP OES and ICP-MS

Éder José dos Santos¹, Amanda Beatriz Herrmann¹, José Luiz Olkuszewski¹, Tatiana D. Saint’Pierre² and Adilson José Curtius^{2*}

¹Instituto de Tecnologia do Paraná - TECPAR; C. P. 357; eder@tecpa.br; 81350-010; Curitiba - PR - Brasil.

²Universidade Federal de Santa Catarina - UFSC; C. P. 476; curtius@qmc.ufsc.br; 88040-900; Florianópolis - SC - Brasil

ABSTRACT

The performance of axial view ICP OES and ICP-MS techniques were compared through the determination of As, Fe, Mn, Pb, Sb and Sn in electrolytic copper. Samples were prepared by two procedures: 1. Total dissolution with 5 % v/v HNO₃ and 2. Dissolution with 1.4 % v/v HNO₃ plus 2.0 % v/v H₂SO₄, followed by separation of the Cu by electrodeposition. The methods were applied for the analysis of standard copper solutions, using calibration against aqueous solutions with or without the addition of Cu. The results obtained by the two techniques were similar, but the separation of Cu from the sample matrix proved to be more adequate for practical reasons.

Key words: ICP-MS, axial view ICP OES, electrolytic copper, electrodeposition

INTRODUCTION

Copper is a major component of several metal alloys because of its malleability and excellent electrical and thermal conductivities. Copper alloys are employed in many industrial sectors. Electrolytic copper is used mainly in electricity, electronic devices and in many other applications (Lemos and Arantes, 1982; Fodes, 1973; ASM, 1988). The allowed concentration limits of trace metals, such as Fe, Pb and Sn, in electrolytic copper are very low, according to ASM (1988), ASTM (1990), and JIS (1988), since some elements can deteriorate the alloy characteristics, such as the electric conductivity. The allowed concentration limits vary according to the utilization purpose of the sample and, for

electrolytic copper, they are, in mg kg⁻¹: As: 10; Fe: 100; Mn: 50; Sb: 10; Sn: 10 and Pb: 50 (Metals Handbook, 1979). For this reason, the concentration of impurities should be under control to guarantee the quality of copper alloys. The analysis of this kind of material is recommended to be carried out by atomic absorption spectrometry and UV/VIS spectrophotometry, according to ASTM and JIS. In addition, the sample preparation is a very important step of the analysis and should be optimized to each matrix.

The ICP techniques, inductively coupled plasma optical emission spectrometry (ICP OES) (Nham, 1999) and inductively coupled plasma mass spectrometry (ICP-MS) (Jarvis, Gray and Houk, 1992), allow multielemental detection, low limits of detection and good precision, ideal for the industrial routine analysis that, usually, require fast and

* Author for correspondence

highly sensitive techniques. In this sense, the determination of trace metals in copper samples can be difficult by the presence of high quantities of copper in solution, which can promote interferences and contamination of the nebulization system. In ICP-MS, the corrosion of the sampler and skimmer cones should also be taken under consideration.

Some works have developed methods for the determination of trace elements in electrolytic copper. Chiba et al. (1990) determined Sb and Ag in electrolytic copper by isotope dilution (ID ICP-MS) with preconcentration of the analytes by coprecipitation. A more efficient method was proposed by Park et al. (1992) using previous electrodeposition of the Cu before the determination of Ni, Zn, Ag, Sb and Pb by ID ICP-MS. Milella et al. (1993) investigated impurities in high-purity electrolytic copper by Zeeman graphite furnace atomic absorption spectrometry and more recently Kumar et al. (2004) investigated two different procedures, (i) co-precipitation of metal hydroxides using La as carrier and (ii) electrodeposition of Cu for determination of impurities by F AAS and GF AAS.

In this work, the performances of ICP-MS and axially ICP OES were compared through the determination of As, Fe, Mn, Pb, Sb and Sn in electrolytic copper. Two methods for sample preparation were also compared, i.e., total dissolution without and with copper separation by electrodeposition.

MATERIALS AND METHODS

Instrumentation

A Varian Vista Pró (Melbourne, Australia) axially inductively coupled plasma atomic absorption spectrometer (ICP OES) and a Perkin Elmer Sciex Elan 6000 (Tornhill, Toronto, Canada) inductively coupled plasma mass spectrometer with pneumatic nebulization were used to carry out the measurements. A Yanaco Co. (Kobe, Kyoto, Japan) AES 2D - Y1550 electroanalyser, equipped with high purity Pt electrodes was employed to separate Cu from the analytes. The ICP OES and ICP-MS operational conditions are described in Table 1.

Table 1 - ICP OES and ICP-MS operational conditions.

Parameters	ICP-MS	ICP OES
RF power, W	1000	1000
Plasma gas flow rate, L min ⁻¹	15	15
Auxiliary gas flow rate, L min ⁻¹	1.2	1.5
Carrier gas flow rate, L min ⁻¹	1.04	1.0
Scan/reading	50	10
Reading/replicate	1	1
Replicates	3	3
Detector	Dual	CCD
Cones sampler/skimmer	Pt	Pt

The spectral lines and the analytes isotopes selected for the analysis by ICP OES and ICP-MS, respectively, were chosen in order to obtain maximum sensitivity and minimum interference, and are shown in Table 2. For ICP OES, all selected spectral lines were free from interference. The background emission was compensated by the preparation of the sample and calibration solutions in the same media.

For ICP-MS, ²⁰⁸Pb, ¹²¹Sb and ¹²⁰Sn were the chosen isotopes, since these were the most abundant

isotopes and free from interference in this sample matrix. Manganese is monoisotopic, ⁵⁵Mn, and can suffer spectral interference by ArN, ClO and HClO ions. However, these interferences are not significant at low nitric and chloride concentrations (Jarvis et al. 1992; ELAN 6000, 1989). Arsenic is also monoisotopic, ⁷⁵As, but the possible interferences are not significant in this situation.

Table 2 - Selected spectral lines and isotopes for the analysis by ICP OES and ICP-MS, respectively.

Analyte	ICP OES (Spectral lines, nm)	ICP-MS (Isotope abundance, %)
As	193.696	⁷⁵ As (100)
Fe	238.204	⁵⁷ Fe (2.2)
Mn	257.610	⁵⁵ Mn (100)
Sb	206.834	¹²¹ Sb (57)
Sn	189.925	¹²⁰ Sn (33)
Pb	220.353	²⁰⁸ Pb (52.3)

The most abundant Fe isotopes, ⁵⁶Fe (92 %) and ⁵⁴Fe (6 %), are subjected to critical interference by ArO and ArN ions. In this case, a less abundant isotope has to be selected, ⁵⁷Fe (2.2 %), since the interference by ArO over this isotope is much less significant.

Reagents and Solutions

All chemical reagents were of analytical grade. Water (resistivity of 18.2 MΩ cm) was de-ionized in a Milli-Q system (Millipore, Bedford, MA, USA). A 65 % v/v nitric acid (No. 100452) and 95-97 % v/v sulfuric acid (No. 100731) both from Merck (Darmstadt, Germany) were used for the preparation of samples, calibration solutions and blanks. Individual 1000 mg L⁻¹ aqueous stock solutions of As (No.119773), Fe (No.109972), Mn (No.19789), Pb (No.119776), Sb (No.109920) and Sn (No.9929) were also from Merck and a 10.000 mg L⁻¹ of Cu solution (No.14372) was from Specpure (Warn Hill, MA, USA).

Calibration solutions

Two series of calibration solutions containing 5, 10 and 20 µg L⁻¹ of As, 50, 100 and 200 µg L⁻¹ of Fe, Mn, Sb and Sn, each one, and 100, 500 and 1000 µg L⁻¹ of Pb were prepared in two different media: calibration 1 (matrix matching): 5 % v/v HNO₃ containing 0.2 % w/v Cu and calibration 2 (conventional calibration): 2 % v/v H₂SO₄ and 1.4 % v/v HNO₃, without addition of Cu.

Certified standard solutions

Calibration solutions were prepared by dilution of certified standard solutions APS 1031, 1032 and 1033 from Alpha Resources (Stevensville, Michigan, USA) in the same media of the calibration solutions, with and without addition of 0.2 % w/v Cu, to a final concentration of 50 µg L⁻¹

of As, Fe and Mn; 100 µg L⁻¹ of Sb and Sn and 500 µg L⁻¹ of Pb.

Samples

Eight samples were analyzed: three commercial electrolytic copper and five more from different industries.

Sample 1 was from Divisão QM Reagentes (São Paulo, SP, Brazil, catalog no. 13060), sample 2 was from Vetec Química Fina (Rio de Janeiro, RJ, Brazil, no. 676) and sample 3 from Merck (no. 2715). They were prepared by two different procedures and then analyzed by ICP OES and by ICP-MS: *Total dissolution*: 0.2 g were dissolved in 10 mL 50 % v/v HNO₃ under heating (around 90 °C) and diluted to a 100 mL final volume. *Electrodeposition*: 1 g was dissolved in a mixture of 10 mL H₂SO₄ plus 7 mL HNO₃ plus 30 mL water, under heating (around 90 °C), and diluted to 300 mL. The solution was submitted to the Cu electrodeposition process in the electroanalyzer by applying a current of 3 A to the electrodes for 2 h. This process follows the ASTM and JIS methodologies for the determination of Cu by electrogravimetry (ASTM, 1990; JIS, 1988). The resulting solution was colorless and the volume was made up with water to 500 mL. The same procedure was applied to the standard solutions containing Cu, in order to verify the efficiency of the separation step. The samples 4 to 8 from: Volvo do Brasil Veículos Ltda, Tupy Fundições Ltda, Summer Ltda and Daher Tecnologia were analyzed by ICP-MS and ICP OES through the electrodeposition procedure.

RESULTS AND DISCUSSION

Two methods of calibration (matrix matching and conventional calibration) were employed for the

analysis by two different techniques (ICP OES and ICP-MS). The linearities of the calibration curves, expressed as the correlation coefficient, were good, better than 0.99 for all analytes by both techniques. The limits of detection (LOD) were very low, better by ICP-MS than by ICP OES, except for Fe, as expected, and especially for Sb and Sn, as could be seen in Table 3.

The limit of detection is defined (Thompson, 1987) as the analyte concentration equivalent to three times the standard deviation of ten measurements of

the blank. The LOD for Fe in solutions containing Cu was better by ICP OES than by ICP-MS, probably because of the low sensitivity of Fe in consequence of the low abundance of the selected isotope. It can be also observed that, by ICP OES, the LODs were similar for all analytes in the solutions containing Cu or not, except for Pb. This happens by the formation of $PbSO_4$ by the presence of H_2SO_4 in the solutions with Cu that could decrease the efficiency of emission of this analyte, producing lower sensitivity.

Table 3 - Correlation coefficients (R^2) and limits of detection (LOD) in the solution*, in $\mu g L^{-1}$, for conventional calibration and matrix matching calibration by ICP OES and ICP-MS.

Analyte	Conventional calibration				Matrix matching			
	ICP OES		ICP-MS		ICP OES		ICP-MS	
	R^2	LOD	R^2	LOD	R^2	LOD	R^2	LOD
As	1.00000	10	0.999999	4	1.00000	10	0.999907	0.1
Fe	0.999929	1	0.999994	0.5	1.000000	1	0.999909	3
Mn	0.999999	0.5	0.999975	0.1	0.999942	0.5	0.999999	0.3
Sb	0.999459	30	0.999613	0.005	0.996018	30	0.999656	0.01
Sn	0.998682	25	0.999409	0.03	0.999837	30	0.999582	0.4
Pb	0.999937	10	1.000000	0.1	0.999983	5	0.999957	0.2

*The LOD in the sample, in $mg kg^{-1}$, is the LOD in solution divided by 2 (considering the sample dissolution procedure).

The sensitivity of As, Sb and Sn by ICP OES were close to or lower than the limit concentrations in electrolytic copper samples, recommended by the ASM (1988). That means that the determination of these elements in electrolytic copper could not be accurate by ICP OES, requiring a lower sample dilution. Alternatively, the determination of As, Sb and Sn close to the limit concentrations could be efficiently carried out by the coupling of a hydride generator to the ICP OES, since this sample introduction accessory allowed higher sensitivities than the pneumatic nebulization, for these elements (VARIAN, 2000; Caruso and Wolnik, 1987).

Evaluation of the electrodeposition efficiency

In an ideal separation procedure, the separation efficiency should be as close to 100 % as possible. However, normally some co-precipitation or partial separation can occur, leading to analyte loss or even to some contamination.

In order to verify the separation procedure efficiency, certified standard solutions with the addition of 0.2 % w/v Cu were submitted to the separation process and the concentrations of the analytes were determined by ICP OES. The recovery of the analytes were close to 100 %, except for Fe and Sn, which recovery values were high, possibly indicating the occurrence of some contamination during the copper electrodeposition. The same procedure was applied to a blank solution and the average concentrations and recovery values for a calibration solution and for the blank are shown in Table 4.

The measured values in the blank solution confirmed the contamination by Fe and Sn during the procedure, probably due to the contact of the acid vapors with the electrode holders, during the heating. An adequate optimization of the procedure, not tried in this work, would probably minimize the contamination.

Table 4 - Measured concentrations and recoveries of the analytes, in $\mu\text{g L}^{-1}$, in standard solution and blank, after electrodeposition of the Cu, by ICP OES.

Analyte	Certified conc.	Measured conc.	Recovery, %	Blank conc.
As	50	50 ± 0.7	100 ± 1.4	nd
Fe	50	129 ± 62	256 ± 124	153 ± 30
Mn	50	50 ± 0.1	100 ± 0.2	nd
Sb	100	101 ± 2	101 ± 2	nd
Sn	100	117 ± 15	117 ± 15	77 ± 8
Pb	500	429 ± 5	98.4 ± 1.0	nd

nd = not detected

Determination of the analytes in standard solutions by ICP OES and ICP-MS

The calibration solutions prepared with the certified standards, with and without the addition of Cu, were analyzed by ICP OES and by ICP-MS and the measured concentrations are shown in Table 5.

The results obtained by ICP OES were satisfactory using calibration samples with or without Cu.

However, the measured concentrations by ICP-MS for solutions without Cu were closer to the certified values than for solutions containing Cu. It was observed that, the presence of high quantities of Cu in the solution led to the formation of deposits on the torch and cones and, after some time, could promote the corrosion of the sampler cone surface.

Table 5 - Concentrations, in $\mu\text{g L}^{-1}$ obtained for the analytes in standard solutions with or without Cu, by ICP OES and ICP-MS.

Analyte	Certif. conc.	Conventional calibration		Matrix matching	
		ICP OES	ICP-MS	ICP OES	ICP-MS
As	50	51 ± 3	48 ± 0.5	44 ± 8	45 ± 0.2
Fe	50	47 ± 1	48 ± 1	48 ± 1	45 ± 0.1
Mn	50	47 ± 1	50 ± 0.2	48 ± 1	45 ± 0.2
Sb	100	102 ± 5	102 ± 0.7	101 ± 3	92 ± 1
Sn	100	96 ± 3	101 ± 0.5	99 ± 3	89 ± 2
Pb	500	501 ± 5	490 ± 3	498 ± 14	497 ± 2

This was observed in both techniques, but the corrosion of the cone was more critical in the ICP-MS instrument. In addition, by ICP-MS, the high quantities of Cu in solution led to lower than expected concentration values, in spite of the matrix matching calibration. Probably, the deposit of copper on the cones surface promote the decreasing of the sensitivity for the other analytes. For this reason, the analysis of electrolytic copper by ICP-MS is recommended only after the previous separation of the Cu, i.e., the matrix matching is not recommended in this case. Since the ICP-MS technique has a very high sensitivity for these analytes, an alternative approach, not attempted in this work, would be to dilute the sample and calibration solutions, in order to reduce the amount of Cu in the solution, probably, improving the accuracy of the method. However, for the

determination of As, usually in low concentrations, an additional dilution would make the analysis not feasible. For this reason, in spite of the risks of contamination, the dissolution followed by the copper electrodeposition appeared to be the best choice for sample preparation in the analysis of electrolytic copper by ICP-MS.

The *Student's t* test was applied to the obtained concentration values, according to Leite (2002) and Vogel (1992) and the results were satisfactory at 95 % confidence level for both techniques. Comparing both techniques, no was observed significant differences a 95 % confidence level, when the paired t-test was applied. However, the precision obtained by ICP-MS was better than by ICP OES, as could be seen by the relative standard deviation values in Table 5.

The measured concentrations of the analytes in the three studied electrolytic copper samples were lower than the LODs of the methods, except for Fe in all samples, and for As, Pb, Sb and Sn in sample 2. The contamination of Fe during the copper electrodeposition process also occurred in this case for all samples, confirmed by the high obtained Fe concentration values. By ICP OES, the concentration of Fe in the samples subjected to the separation were, in general, one order of magnitude higher than the obtained values using matrix matching calibration, which were, in mg kg⁻¹: 2.5 ± 0.2 (sample 1), 4.5 ± 1.2 (sample 2) and 4.7 ± 0.1 (sample 3). Only in sample 2, the other analytes could be measured: As (2.5 ± 0.1 mg kg⁻¹), Sb (5.6

± 0.3 mg kg⁻¹) and Sn (13.0 ± 0.7 mg kg⁻¹) by ICP-MS using external calibration, after separation by electrodeposition. In Sample 2, Sb (4.2 ± mg kg⁻¹) could also be measured by ICP-MS, without separation, using matrix matching calibration. In this sample, Pb was obtained by ICP OES (42.6 ± 2.4 mg kg⁻¹) and by ICP-MS (36.6 ± 0.9 mg kg⁻¹) using matrix matching calibration. For samples 4 to 8, the determination of the impurities was carried out by ICP-MS and ICP OES using external calibration, after separation by electrodeposition. The results are presented in Table 6. All found concentrations were below the limits established by ASM, 1988 for electrolytic copper with the exception for Sn in the samples 5 and 6.

Table 6 - Concentrations, in mg kg⁻¹, obtained for the analytes by ICP-MS using external calibration, after separation of Cu by electrodeposition, in samples 4 to 8 (n=3).

Sample	Technique	Analyte					
		As*	Fe	Mn**	Sb**	Sn**	Pb**
04	ICP-MS	nd	12.1 ± 0.1	0.08	0.15 ± 0.00	1.18 ± 0.01	0.78 ± 0.01
	ICP OES	nd	13.6 ± 0.7	nd	nd	nd	nd
05	ICP-MS	nd	73.6 ± 0.7	0.12 ± 0.01	2.24 ± 0.01	74.15 ± 1.10	5.32 ± 0.03
	ICP OES	nd	74.4 ± 0.8	nd	nd	76.4 ± 2.7	5.3 ± 0.2
06	ICP-MS	nd	53.5 ± 0.4	0.64 ± 0.01	1.85 ± 0.01	141.60 ± 0.12	14.80 ± 0.12
	ICP OES	nd	54.2 ± 0.9	0.67 ± 0.02	nd	143.2 ± 3.1	15.1 ± 1.0
07	ICP-MS	nd	30.1 ± 1.3	0.18 ± 0.02	4.84 ± 0.05	1.54 ± 0.15	1.15 ± 0.15
	ICP OES	nd	31.9 ± 0.2	nd	nd	nd	nd
08	ICP-MS	nd	10.6 ± 0.1	0.10 ± 0.01	0.70 ± 0.01	0.38 ± 0.01	0.45
	ICP OES	nd	11.5 ± 0.5	nd	nd	nd	nd

*nd: not detectable at level of 2 mg kg⁻¹ (ICP-MS) and of 5 mg kg⁻¹ (ICP OES). ** For ICP OES, not detectable at level of 0.25 mg kg⁻¹ (Mn), 15 mg kg⁻¹ (Sb), 12.5 mg kg⁻¹ (Sn) and 5.0 mg kg⁻¹ (Pb).

CONCLUSION

The determination of As, Fe, Mn, Sb, Sn and Pb in electrolytic copper could be successfully carried out by ICP OES and ICP-MS. A previous separation of Cu by electrodeposition is recommended, in order to reduce the metal load introduced into the plasma, being mandatory for the ICP-MS technique, in order to avoid the corrosion of the cones. The ICP-MS provide higher sensitivity and precision, allowing the determination of all analytes in concentrations lower than the limit values, demonstrating to be a powerful technique for the quality control of electrolytic copper manufacturing.

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RESUMO

O presente trabalho apresenta um estudo comparativo das técnicas ICP-MS e ICP OES com configuração axial e também de dois métodos diferentes de tratamento das amostras, ou seja, por dissolução total com e sem separação do cobre por eletrodeposição, para as determinações de As, Fe,

Mn, Pb, Sb e Sn em amostras de cobre eletrolítico. Amostras comerciais e industriais foram dissolvidas com HNO₃ 5% v/v e o cobre foi eletrodepositado em meio de HNO₃ (1,4% v/v) e H₂SO₄ (2,0% v/v). Verificou-se que a separação do cobre foi eficiente, contudo se constatou contaminação de Fe e Sn durante o processo de eletrodeposição. As determinações foram realizadas utilizando-se um ICP OES Axial Varian (Vista Pro) e um ICP-MS Perkin Elmer (Elan Sciox 6000). Foi aplicada a calibração externa, com soluções padrão contendo ou não cobre na concentração equivalente à da amostra. Os limites de detecção (3s, n=10) para a técnica de ICP OES foram bastante semelhantes na presença ou não do cobre). Já usando ICP-MS, os limites foram melhores na ausência do cobre. Com o objetivo de estabelecer o nível de significância entre as técnicas de quantificação, ou seja, entre ICP OES e ICP-MS, foi aplicado o teste *t* emparelhado, que demonstrou, para um nível de confiança de 95%, não haver diferença significativa, tanto para as soluções sem ou com cobre. Os resultados obtidos no presente trabalho demonstraram que as técnicas ICP-MS e ICP OES fornecem resultados similares em determinadas faixas de concentração dos analitos, podendo ambas serem utilizadas, no controle de qualidade do cobre eletrolítico. Contudo, a técnica ICP-MS foi superior em termos de limite de detecção.

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