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Determination of metallic impurities in the copper deposit obtained by electroextraction from solution resulted in the recycling of Waste Printed Circuit Board

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Abstract

The content of Sn, Pb, Ni, Zn and Fe in deposits of copper obtained by electrodeposition from acidic solution resulted in the recycling of Waste Printed Circuit Board (WPCB) were determined by inductively coupled plasma optical emission spectrometry. The determinations were carried out using a simultaneous Spectro CIROS^{CCD} spectrometer equipped with an axial viewing torch. The copper samples were dissolved in aqua regia, and the metals determined in optimum working conditions of plasma torch. Contents as low as 0.1 % Fe, 0.2 % Ni, 0.3 % Zn and Sn, and 0.5 % Pb were found. The copper purity was in the range 95.3 – 98.6%. Based on these data, the analytical protocol for metal trace quantification in the copper deposit was validated using synthetic solutions prepared from monoelemental stock solutions. For this purpose, the limit of detection, limit of quantification and recovery of metals were evaluated.

Introduction

The United Nations (UN) and the Environmental Protection Agency (EPA) estimated that only ~ 20 % of e-waste is recycled each year, the rest goes to landfills or are incinerated (Hageluken 2010), both causing environmental and health concerns. As a consequence of Waste Electrictrical and Electronic Equipments (WEEE) being deposited as landfills, toxic heavy metals can leach out and contaminate the ground and drinking water by up to 100 times compared to residential areas (Ghosh 2015). On the other hand, incineration's main drawback is that it generates in high amounts toxic gaseous substances (e.g. dioxins, furans) and also, its energy demand is very high (Awasthi 2017). The second alternative to recycling is represented by the leaching methods, but they also come with disadvantages, such as, low processing speed, use of highly corrosive/oxidative conditions or less corrosive but high cost reagents (e.g. thiourea leaching of Au) (Tesfaye 2017). Therefore, eco and budget friendly extraction methods are highly needed.

Desktop PCs printed circuit boards weighs approximately 200-300 g (Hanafi 2012) and contains about 20 weight % Cu, 7 % Fe, 5% Al, 5 % Pb and 1% Ni (Hangeluken 2006, Yamane 2011), but can vary depending on the type of board, manufacturer and period of production (Isildar 2018). These metal quantities represent a higher metal density than those found in primary ores, and the energy needed for their extraction is almost 90% lower (Crowson 2012, Tesfaye 2017). Besides, with the current demand of the electronics sector for metals, their primary resources are being depleted, slowly making urban mining a necessity. As a consequence, proper analytical methods are needed to analyse the obtained results.

The main goal of this research was the validation of the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method for determination of metallic impurities in copper deposits obtained by electroextraction from desktop PC motherboard leachate solution. Based on previous research conducted by our group (Dorneanu 2017) and other researches published in scientific journals, it was found that copper extraction can be achieved successfully with a purity very close to 100%, containing impurities as low as 0.1%, Ni, Pb, Sn, Zn and Fe. With these in mind, it was proposed for validation a method capable to determine at least 0.1% metallic impurity in the presence of $80 - 100$ % copper. Nine synthetic solutions were prepared, considering deposit solubilization in aqua regia and a 10-fold subsequent dilution. Results were discussed in terms of accuracy, precision and method figures of merit.

Experimental

Materials, methods and instrumentation

Nine synthetic solutions containing 80 -100 % copper and 0.1 – 1.5 % metallic impurities (Table 2) were prepared from monoelemental stock solutions produced by Merck (Darmstadt, Germany) in presence of 2% (v/v) HCl in order to avoid Sn precipitation.

The concentrations of Cu, Pb, Sn, Zn, Ni and Fe were determined simultaneously by an axial viewing inductively coupled plasma optical emission spectrometer using the SPECTRO CIROS^{CCD} spectrometer (Spectro, Cleve, Germany). The operating parameters of the spectrometer were as follows: 1400 W plasma power, 27.12 MHz radiofrequency, 12 L min^{-1} outer gas, 1 L min^{-1} nebulizer gas and 0.6 L min^{-1} auxiliary Ar 5.0 (Linde, Cluj-Napoca, Romania) flow rate. The samples were introduced into the plasma by a cross-flow nebulizer at a flow rate of 2 mL min^{-1}, 40 s of flushing time and with a delay time of 20 s. Axial plasma viewing was carried out at torch position X= -3.9 mm; Y= +3.6 mm and Z= +2.6 mm. Optical detection of spectral lines was achieved with a double grating Paschen-Runge polychromator (160 – 800 nm) equipped with 22 CCDs and its chamber filled with N$_2$.

Instrument calibration was performed in the 0 – 10 mg L^{-1} range (8-point) for Cu, and 0 – 1 mg L^{-1} (8-point) for Pb, Sn, Zn, Ni and Fe. Metals were determined at analytical lines 324,754 nm Cu (I), 189.991 Sn (II), 220.351 nm Pb (II), 259.940 nm Fe (II), 341.476 nm Ni (I) and 213.856 nm Zn (II), where (I) are atomic lines and (II) ionic lines. Emission signals were processed as peak heights with an integration time of 48 s.

Results and discussion

Figures of merit and validation

Figures of merit obtained for the ICP-OES measurements are presented in Table 1. The calibration curves, in the range of 0 – 10 mg L^{-1} for Cu and 0 – 1 mg L^{-1} for the rest of the metals, provided very good linearity, with coefficients of determinations of at least 0.9992. Limits of detection (LOD), calculated with equation (1) (Miller and Miller 2000) in liquid samples provided values between 0.010 – 0.034 mg L^{-1}, while limits of quantification (LOQ), calculated as 3 times LOD, varied between 0.030 – 0.102 mg L^{-1}.

$$LOD = \frac{3s_{y/x} - y}{m} \tag{1}$$

where ($s_{y/x}$) is the residual standard deviation, (y) is the intercept and (m) is slope of the calibration curve. The residual standard deviation was calculated as:

$$s_{x/y} = \sqrt{\frac{\sum_{i}^{n}(y_i - \hat{y}_i)^2}{n-2}} \tag{2}$$

where (y_i) are measurement values of the calibration standards, ($\hat{y}_i$) are fitted y_i values and (n) is the number of standard solutions employed in the plotting of calibration curves.

Because the LOQs were at least 3 times lower than the lowest concentration in the synthetic solutions, it can be concluded that from the methods limit of quantification point of view, metallic impurities as low as 0.1% can be determined.

Table 1. Figures of merit for ICP-OES measurements

Element	Calibration range (mg L^{-1})	Coefficient of determination (R^2)	LOD (mg L^{-1})	LOQ (mg L^{-1})
Cu	0 – 10	0.9999	0.019	0.057
Pb	0 – 1	0.9994	0.034	0.102
Sn	0 – 1	0.9992	0.010	0.030
Zn	0 – 1	0.9992	0.025	0.075
Ni	0 – 1	0.9999	0.018	0.054
Fe	0 – 1	0.9993	0.010	0.030

Recoveries obtained in synthetic solutions (Table 2) ranged between 94 and 109 % with confidence intervals, calculated for 95% confidence level, between 3 and 10 %. Because the obtained recoveries in all cases contained the 100 % value, it proves that the method provides accurate results within the generally accepted confidence intervals, *i.e.* ±10%.

Measurements precision was evaluated from individual relative standard deviation values obtained in the synthetic solutions. The results ranged between 1.3 – 3.9 %, proving good precision of results.

Table 2. Recovered metal concentrations found in the multielemental synthetic solution

	Sample 1				Sample 2			
Metals	c_{prep} (mg L^{-1})[1]	$c_{det}\pm$C.I. (mg L^{-1})[2]	RSD[3] (%)	R$\pm$C.I. (%)	c_{prep} (mg L^{-1})	$c_{det}\pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)
Cu	80	81.0$\pm$3.6	1.8	101$\pm$4	80.0	82.2$\pm$3.9	1.9	103$\pm$5
Pb	0.500	0.521$\pm$0.034	2.6	104$\pm$6	1.00	0.970$\pm$0.075	3.1	97$\pm$8
Sn	0.300	0.305$\pm$0.019	2.5	102$\pm$6	0.500	0.515$\pm$0.029	2.3	103$\pm$6
Zn	0.300	0.306$\pm$0.018	2.4	102$\pm$6	0.500	0.504$\pm$0.023	1.8	101$\pm$5
Ni	0.200	0.211$\pm$0.013	2.5	106$\pm$6	0.400	0.382$\pm$0.024	2.5	96$\pm$6
Fe	0.100	0.107$\pm$0.010	3.8	107$\pm$9	0.200	0.210$\pm$0.009	1.8	105$\pm$5

[1] analytical concentration

[2] determined concentration; C.I. is the confidence interval for 95% confidence level and n=3 measurements

[3] RSD is the relative standard deviation.

Table 2. (Continuation)

	Sample 3				Sample 4			
Metals	c_{prep} (mg L^{-1})	$c_{det}\pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)	c_{prep} (mg L^{-1})	$c_{det}\pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)
Cu	80.0	81.5$\pm$3.9	1.9	102$\pm$5	90.0	89.7$\pm$4.7	2.1	100$\pm$5
Pb	1.50	1.56$\pm$0.06	1.5	104$\pm$4	0.500	0.498$\pm$0.044	3.6	100$\pm$9
Sn	0.800	0.824$\pm$0.026	1.3	103$\pm$3	0.300	0.305$\pm$0.028	3.7	102$\pm$9
Zn	1.00	1.06$\pm$0.07	2.7	106$\pm$7	0.300	0.299$\pm$0.018	2.4	100$\pm$6
Ni	0.600	0.561$\pm$0.039	2.8	94$\pm$7	0.200	0.199$\pm$0.019	3.8	100$\pm$9
Fe	0.300	0.306$\pm$0.015	2.0	102$\pm$5	0.100	0.102$\pm$0.008	3.2	102$\pm$8

Table 2. (Continuation)

	Sample 5				Sample 6			
Metals	c_{prep} (mg L^{-1})	$c_{det}\pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)	c_{prep} (mg L^{-1})	$c_{det}\pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)
Cu	90.0	90.2$\pm$5.9	2.6	100$\pm$6	90.0	89.3$\pm$3.3	1.5	99$\pm$4
Pb	1.00	1.10$\pm$0.09	3.4	108$\pm$8	1.50	1.54$\pm$0.15	3.9	103$\pm$10
Sn	0.500	0.512$\pm$0.029	2.3	102$\pm$6	0.800	0.837$\pm$0.050	2.4	105$\pm$6
Zn	0.500	0.510$\pm$0.029	2.3	102$\pm$6	1.00	0.948$\pm$0.086	3.6	95$\pm$9
Ni	0.400	0.412$\pm$0.026	2.5	103$\pm$6	0.600	0.624$\pm$0.023	1.5	104$\pm$4
Fe	0.200	0.212$\pm$0.013	2.5	106$\pm$6	0.300	0.314$\pm$0.018	2.3	105$\pm$6

Table 2. (Continuation)

	Sample 7				Sample 8			
Metals	c_{prep} (mg L^{-1})	$c_{det} \pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)	c_{prep} (mg L^{-1})	$c_{det} \pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)
Cu	100	98.9±2.8	1.1	99±3	100	99.3±3.8	1.5	99±4
Pb	0.500	0.482±0.039	3.2	96±8	1.00	1.04±0.09	3.5	104±9
Sn	0.300	0.299±0.026	3.5	100±9	0.500	0.507±0.026	2.1	101±5
Zn	0.300	0.298±0.012	1.6	99±4	0.500	0.489±0.021	1.7	98±4
Ni	0.200	0.199±0.014	2.8	100±7	0.400	0.405±0.026	2.6	101±6
Fe	0.100	0.109±0.010	3.7	109±9	0.200	0.199±0.015	3.0	100±8

Table 2. (Continuation)

	Sample 9			
Metals	c_{prep} (mg L^{-1})	$c_{det} \pm$C.I. (mg L^{-1})	RSD (%)	R$\pm$C.I. (%)
Cu	100	98.4±3.8	1.6	98±4
Pb	1.50	1.54±0.09	2.4	103±6
Sn	0.800	0.803±0.034	1.7	100±4
Zn	1.00	1.08±0.10	3.7	108±9
Ni	0.600	0.652±0.062	3.8	109±10
Fe	0.300	0.314±0.026	3.3	105±8

Conclusions

It was demonstrated that ICP-OES method is suitable for the determination of metallic impurities in concentrations as low as 0.1%, in the presence of high concentration of copper. Based on results obtained on synthetic samples prepared in laboratory, it was observed that ICP-OES provides accurate and precise results, and could be applied for such analysis.

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