

Evaluation of Methods for Sampling and Analysis of Copper when Present in High Weight Percent in Recycled Material

E.R.Lewis¹, P.Douglas^{2,3}, R.G.Charles⁴, G.Liversage⁵, D.Bates-Moss⁵

¹M2A MSc By Research, Room 333, Grove Building, Swansea University, Singleton Campus, Swansea SA2 8PP, UK

²Chemistry Group, Medical School, Swansea University, Singleton Park, Swansea SA2 8PP, UK

³School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban 4000, South Africa

⁴College of Engineering, Swansea University, Bay Campus, Swansea SA1 8EN, UK

⁵Mekatek Limited, MBG House, Unit C, Maerdy Industrial Estate (South), Rhymney Tredegar, NP22 5PH UK

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Presenting author, Eleanor Lewis, email: 988610@swansea.ac.uk

Introduction

Copper is one of the most valuable recoverable metals in Waste Electrical and Electronic Equipment (WEEE) (Balde *et al.*, 2017). Mekatek Ltd. run a recycling facility in the Rhymney Valley, South Wales. One of their main outputs is copper recovered from cables, which is separated from the other materials to as high a grade as possible and sold on to smelters or refiners. The value of copper outputs is critically dependent on the wt% copper in the sample, particularly when dealing with material of high, i.e. 90-100 wt%, copper content. The value of the copper itself is proportionately much greater if the material is high grade. Key grades are ≥ 95 , ≥ 98 , ≥ 99 and ≥ 99.99 wt% copper with significant value increase at each level; so, the selling of nominal 95 wt% grade copper when it is actually closer to 97 wt%, is something to be avoided. Furthermore, disagreements between recycler and refiner over copper grade can create cash flow issues and result in lost revenue for recyclers. The accurate analysis of the output fraction to within 95% confidence limits of ~ 0.5 wt% is clearly crucial in preventing the currently experienced conflicts with smelters and refiners and loss of value when selling these output fractions. The research presented here is aimed at determining the most effective methods for sampling and analysis of tonne size batches of recycled copper to determine the purity of copper content in copper outputs, with high accuracy and precision, i.e. to within one standard deviation of $\sim 0.25\%$.

Table 1. Overview of the different techniques explored in this research

Method	Typical precision	Accuracy	Selectivity to copper	Relative Cost	Relative Skill
EDTA Titration*	$\sim \pm 0.1-0.25\%$	$\sim \pm 0.1-0.25\%$	Low (Vogel, 1978)	Low	Medium
Atomic Absorption/Emission*	$\sim \pm 0.5-1\%$ (Skoog and West, 1982)	$\sim \pm 0.5-1\%$ (Skoog and West, 1982)	High (Dean <i>et al.</i> , 2002)	High	High
Gravimetry	$\sim \pm 0.1-0.2\%$ (Skoog and West, 1982)	$\sim \pm 0.1-0.2\%$ (Skoog and West, 1982)	Moderate-High (Skoog and West, 1982)	Low	Medium
UV/VIS*	$\sim \pm 1-3\%$ (Skoog and West, 1982)	$\sim \pm 1-3\%$ (Skoog and West, 1982)	Moderate-high (Skoog and West, 1982; Dado and Rosenthal, 1990)	Medium	Medium
XRF (powder)	$\sim \pm 1-5\%$ (Ramsey <i>et al.</i> , 1995; Charles, 2017)	$\sim \pm 1-5\%$ (Ramsey <i>et al.</i> , 1995; Charles, 2017)	High (Skoog, Holler and Nieman, 1985)	Medium-High	Medium
XRF (fused bead)	$\sim \pm 0.2-1\%$ (Ramsey <i>et al.</i> , 1995; Charles, 2017)	$\sim \pm 0.2-1\%$ (Ramsey <i>et al.</i> , 1995; Charles, 2017)	High (Skoog, Holler and Nieman, 1985)	Medium-High	Medium

Many methods of analysis in the literature are designed for low copper content, trace metal analysis for example, but here we want a method suitable for easy precise determination with copper in the 90-100 wt% range. Techniques considered are; titrimetric, gravimetric, UV/VIS absorption, atomic emission/absorption, and X-ray

fluorescence. Table 1 gives a general overview of the advantages and disadvantages of the techniques as described in the literature. (N.B. Only those methods marked (*) have been tested thus far but this research will address all methods detailed).

Methods

Sample preparation: Two 100 g samples of copper output fraction from recycling in: a) granular form, and b) powder form, from the Mekatek Ltd. recycling process were used. These were both coned and quartered to give 4 subsamples each of about 6 g. Digestion in 50/50 nitric acid/water was followed by dilution with 0.1 M nitric acid, and these stock solutions diluted using calibrated pipettes, such that the error in solution preparation was less than $\pm 0.15\%$. Agilent Technologies 4200 MP-AES and Unicam UV300 UV/VIS spectrometers were used. Three repeat measurements were made on each of the solutions prepared from the subsamples. Instrumental precision was assessed from agreement between measurements within subsamples, while sampling variation was obtained from results across subsamples.

Results and Discussion

Table 2 gives our preliminary evaluation of MP-AES and UV/VIS for analysis. Initial work indicates that UV/VIS shows better precision than MP-AES. For MP-AES instrumental precision is not high enough for this application even though the method is specific to copper and accurate. It may be possible to improve the precision significantly when using a dedicated instrument, but this will increase instrumental costs to the analyst. UV/VIS is more precise. Agreement between the two methods is generally good within experimental error but the high value for sample 1 using UV/VIS may indicate a method error, or interferent, of which we are currently unaware. The higher sample standard deviations in both methods indicate variation from sampling, even for these 100 g samples; although this may decrease with particle size since the granular sample, 1, gives higher sampling variability than the powder sample, 2.

Table 2. Results from MP-AES and UV/VIS methods. Confidence limits, CI, obtained using *all* results for that sample, 1 or 2, standard deviation of results, SD, obtained from results within (instrumental SD) or across (sample SD) subsamples.

Method	Sample	Copper content/ wt%	95% CI	99% CI	Instrumental SD	Sample SD
MP-AES	1	97.7	± 2.4	± 3.4	2.2	3.7
	2	98.1	± 1.4	± 2.0	1.4	2.1
UV/VIS	1	101.3	± 1.2	± 1.8	0.85	2.1
	2	98.93	± 0.83	± 1.2	0.66	1.5

Following the in-depth analysis of each method, their suitability for the role of rapid in-house analysis will be determined based on the factors listed in Table 1 above. The results of this research will enable Mekatek Ltd. to effectively determine the wt% purity of copper in their recycling process output fractions, benefitting them economically and ensuring sufficient revenue to yield a positive cost-benefit form the process.

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