

Methods for Analysis of Copper from WEEE Cables When Present in High Weight Percent

Eleanor Lewis

P. Douglas, R. Charles, D. Bates Moss, G. Liversage



Swansea University
Prifysgol Abertawe



Overview

Introduction to the Project

Overview of the Recycling Process

Project Aim

Methods Explored

Samples

Results

Conclusions and Future Work

Introduction to the Project

- MSc by Research student at Swansea University working in partnership with Mekatek Ltd.
- WEEE pre-processing company
- Copper scrap cables are received at ~25, 45 and 65 wt% copper
- Value of copper output fraction is critically dependent on its wt% Cu
- Key grades are 98, 99 and 99.5 wt %
- Current method: scoop sampling and XRF gun average



Figure 1. Cables in their raw form (top), cables after shredder (middle), copper from cables in final form (bottom)





the Recycling Process

Shredder



plastic through

Shaking Table

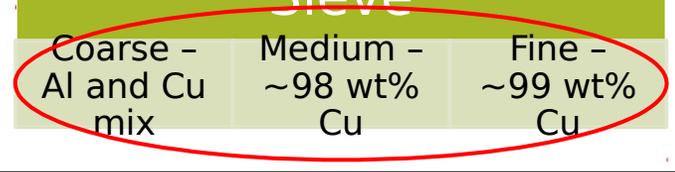
Plastic Copper

Sieve

Coarse - Clean plastic Fine - Cu and plastic (re-run through EES)

Sieve

Coarse - Al and Cu mix Medium - ~98 wt% Cu Fine - ~99 wt% Cu



Project Aim

Evaluation of methods for in-house analysis of copper from cable recycling with high accuracy and precision (i.e. to within one standard deviation of $\leq 0.25\%$)

- Analytical methods were assessed against a number of criteria, including:
 - Accuracy
 - Precision
 - Relative operator skill
 - Relative cost
 - Waste produced
 - Sample preparation
- In order to:
 - Prevent economic loss when selling fractions
 - Solve conflicts between recycler and refiner



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Methods Explored

Titration

Atomic
Spectroscopy
(Emission)

Spectrophotometry (UV/VIS)

Gravimetry

X-Ray
Fluorescence
(XRF)

EDTA Titration

Gravimetry

UV/VIS

Atomic Emission

XRF

Samples digested and bulk analysis performed

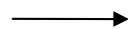
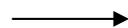
Measurement based on complexation

Volume of complexing agent used (EDTA)

Weight of the complexed precipitate (ammonium thiocyanate)

Absorption intensity at specific wavelength for characteristic copper-EDTA complex

Analyses small fraction of the sample (1.5 cm diameter circle) in its original form and gives an average based on secondary x-ray emissions



Samples

- Two ~100 g samples of the copper output fraction were obtained in granular (sample 1) and powder (sample 2) form
- 4 sub-samples created, ~6 g each
- Samples for bulk analysis methods were digested in 50/50 nitric acid/water
- Samples for XRF analysis were kept in original form and also ground to smaller particle size



Figure 2. Sample 1 (top) and sample 2 (bottom)



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Figure 3. Samples digested in 50/50 nitric acid/water
(Titration, Atomic Emissions, UV/VIS,
Gravimetric)



Figure 4. Sample 1 (top) and sample 2 (bottom)
after grinding
(XRF)

Assessment of the bulk analysis methods against the

Method	Selectivity to Copper	Sources of Error	Precision	Accuracy	Relative Cost	Relative Skill	Sample Preparation	Volume of Waste	Suitability
EDTA Titration	Low	Interference through EDTA complexation with other metals.	Excellent	Good	Low	Medium	Medium	High	Low
Atomic Emission Spectroscopy	High	No obvious interferences.	Good	Excellent	High	High	Medium	Medium	Medium
UV/VIS	High	Coloured complexes from other metals. Plastics scattering light.	Very Good	Excellent	Medium	Medium	Medium	Medium	High
Gravimetry	Medium	Loss of precipitate. Incomplete precipitation.	Excellent	Excellent	Low	High	Medium	High	Medium

Precision and accuracy key: Excellent (≤ ± 0.25%), Very good (≤ ± 0.5%), Good (> ± 0.5%) or insoluble
Green - more desirable, red - less desirable

Assessment of XRF analysis

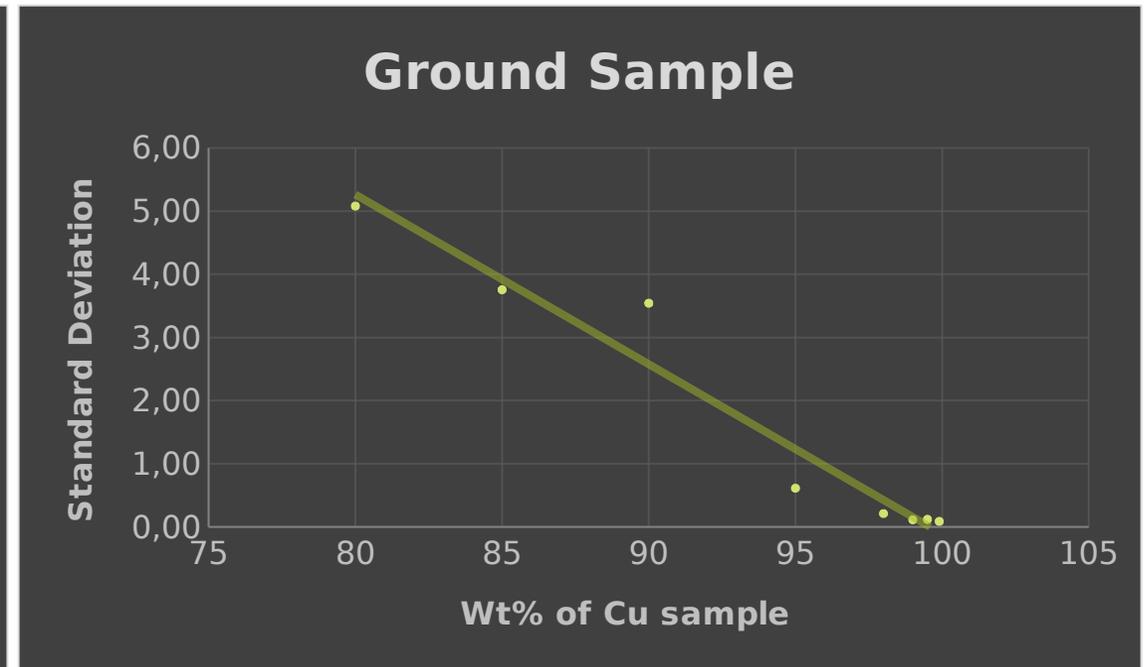
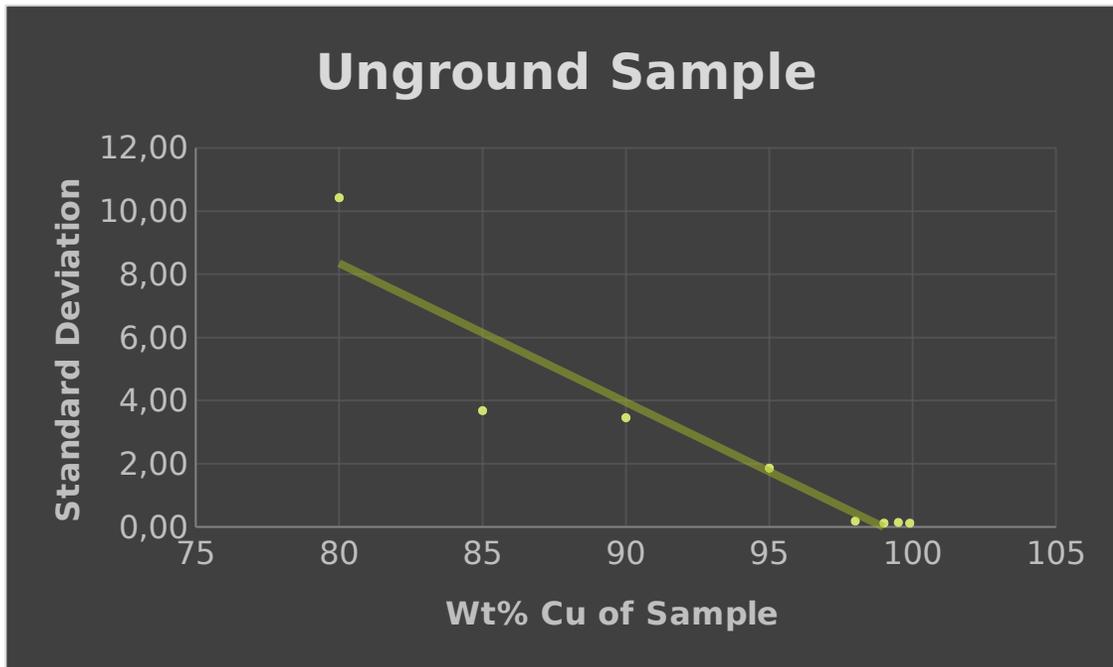
Method	Selectivity to Copper	Sources of Error	Precision	Accuracy	Relative Cost	Relative Skill	Sample Preparation	Volume of Waste	Suitability
XRF (unground)	High	High presence of organics reduces reliability · Insensitive to organics.	Excellent	Excellent	Medium-High	Medium	Low	Low	High
XRF (ground)	High		Excellent	Excellent	Medium-High	Medium	Low	Low	High

Precision and accuracy key: Excellent ($\leq \pm 0.25\%$), Very good ($\leq \pm 0.5\%$), Good ($> \pm 0.5\%$)
Green - more desirable, red - less desirable

- Remove plastics via alternative method prior to analysis

Effect of plastic content on the reliability of XRF analysis

Standard deviation between readings on the same sub-sample at different wt% plastic content



Wt% of plastic:Copper
20:80, 15:85, 10:90, 5:95, 2:98, 1:99,
0.5:99.5, 0:99.9

UV VIS vs XRF

Method	Pros	Cons
UV/Vis	<ul style="list-style-type: none"> • Meets required precision • Analysis of absolute copper wt% regardless of plastic content • Tests whole sub-sample via homogenous solution 	<ul style="list-style-type: none"> • Cost of instrument • More sample preparation • More waste produced
XRF	<ul style="list-style-type: none"> • Meets required precision • Already own the instrument 	<ul style="list-style-type: none"> • Only tests a fraction of the sub-sample • Insensitive to organics



Conclusions and Future Work

- Have identified UV/VIS as a reliable method for accurate and precise sample analysis
- XRF displayed high enough precision but its reliability decreases significantly after 2 wt% plastic content
- Need more work on sampling procedure to make sure sampling variation is within required precision and accuracy
- Develop technique to maximise XRF suitability by sample pre-treatment to remove plastic



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Thank you

Eleanor Lewis

eleanorlewis07@gmail.com

07949385804



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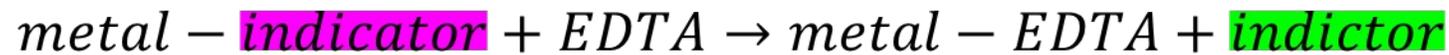
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EDTA Titration

- The free indicator displays a different colour to when in a complex with the metal



- The concentration of copper in solution can be calculated using the volume and concentration of EDTA used and the volume copper solution used
- The concentration of copper in solution can be calculated using the volume and concentration of EDTA used and the volume copper solution used

$$\frac{C_1 V_1}{V_2} = C_2$$



Atomic Emission Spectroscopy

- The wavelength of light emitted is characteristic to each element, therefore the concentration of the element can be determined by intensity of the emission and ch

Instrument: Agilent
Technologies 4200 MP-AES

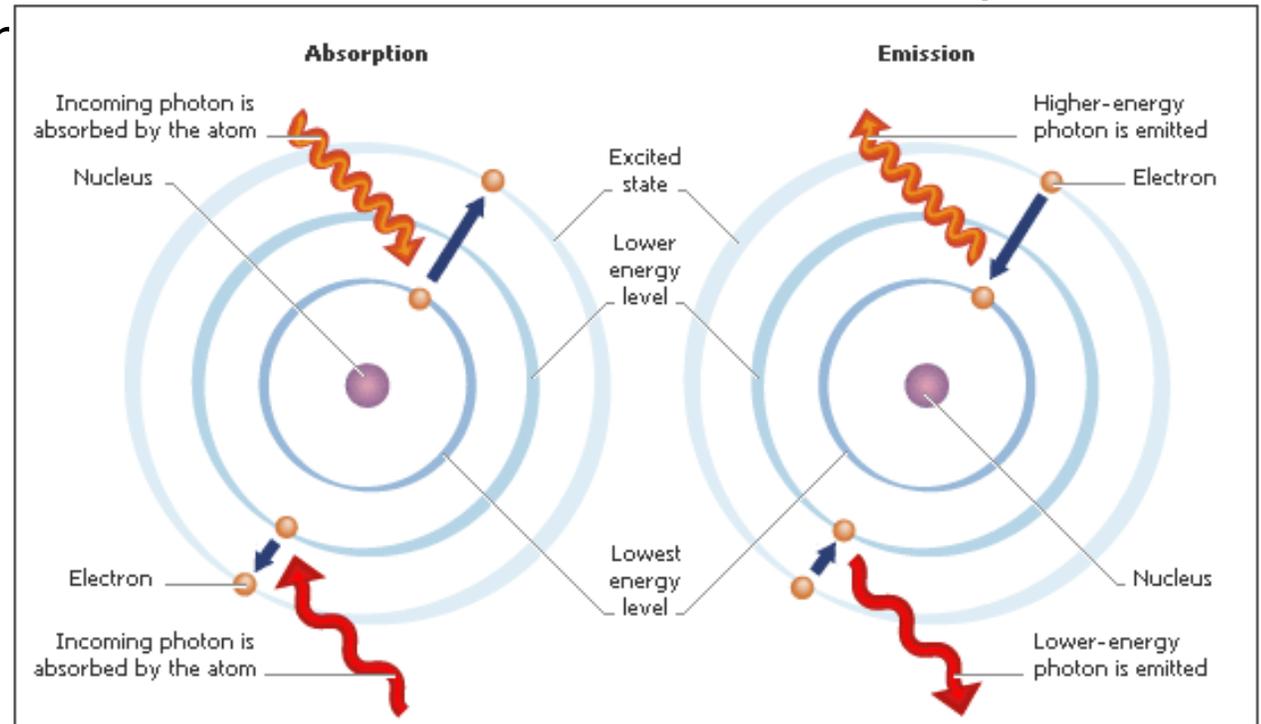


Figure 2. Illustration of the measured emission photons from atoms after entering the excited state (Source: http://light.physics.auth.gr/enc/wavelength_en.html)



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UV/VIS

- Complexation with EDTA under specific pH to form a coloured complex
- The coloured complex is run against a blank and the difference in absorbance is used to calculate the copper concentration in solution
- Beer-Lambert Law
- Intensity of absorption is prop. To the concentration of copper
- Beer-Lambert Law

$$Abs = \epsilon lc$$

Instrument: Unicam UV300 UV/VIS



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Gravimetry

- Copper in solution forms a solid compound with the help of a precipitating agent and precipitates out of solution as a white solid
- The weight of the precipitate is compared to the original weight of the sample and a wt% calculated
- Copper is precipitated as an insoluble complex and the precipitate is filtered and the complex is weighed



XRF

- Electrons are ejected due to excitation by primary x-ray
- Vacancy is filled by electron from a higher shell, emitting a secondary x-ray of characteristic energy specific to each element

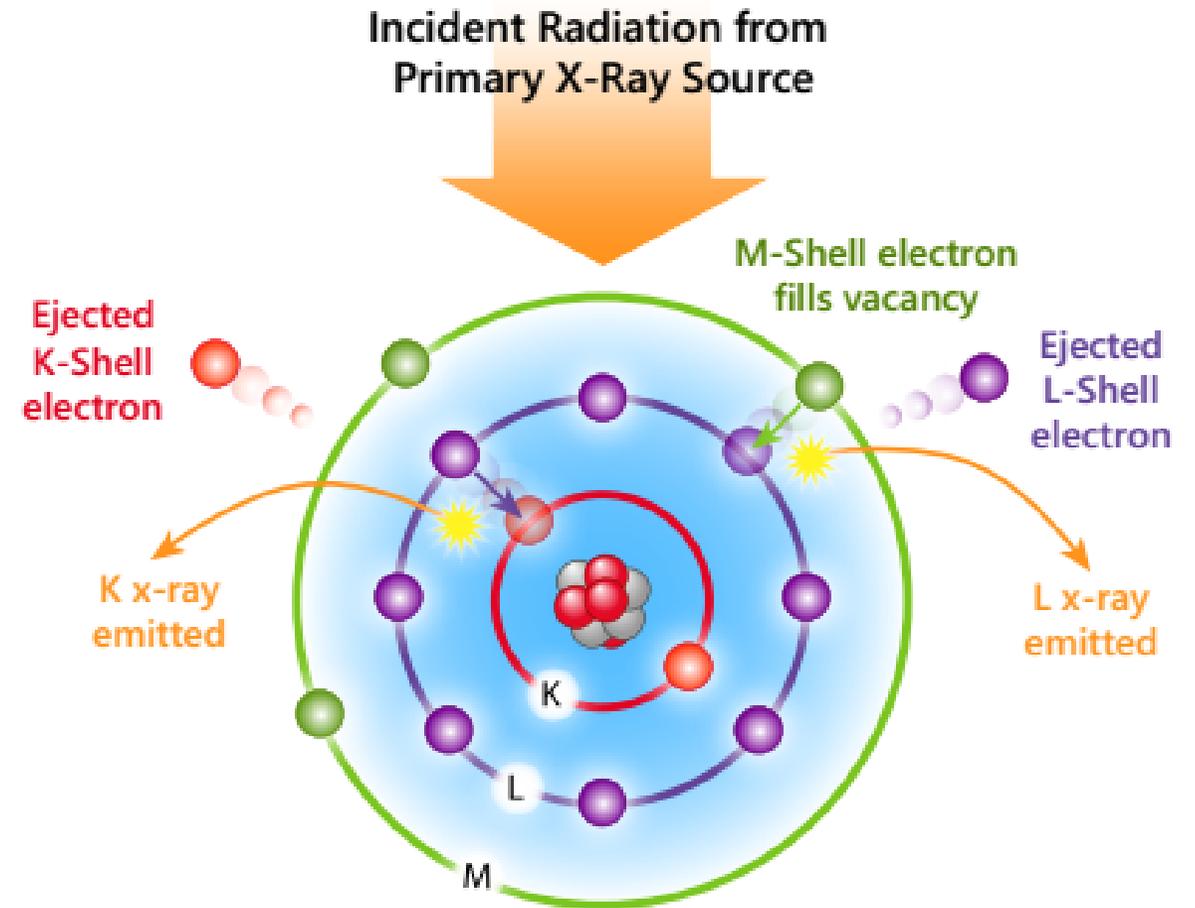


Figure 3. Illustration of the electron ejection and emission of secondary x-rays (Source:

<http://www.nitonuk.co.uk/pdf/Niton%20XRF%20Guide.pdf>)

Instrument: Niton XL2 GOLDD XRF Analyser



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Method	Sample	Copper content wt%	Standard Deviation	Instrumental Standard Deviation	Sample to sample Standard Deviation
Titration	1	100.27	±0.40	±0.13	±0.44
	2	-	-	-	-
MP-AES	1	97.66	±3.80	±2.17	±3.68
	2	98.06	±2.19	±1.43	±2.07
UV/VIS	1	99.44	±1.60	±0.46	±1.72
	2	99.67	±1.29	±0.36	±1.41
Gravimetric	1.1	99.33	±0.17	±0.17	-
	2	-	-	-	-
XRF (unground)	1 (raw)	99.64	±0.18	±0.13	±0.16
	2 (raw)	99.76	±0.07	±0.09	±0.00
XRF (ground)	1 (ground)	99.77	±0.06	±0.07	±0.00
	2 (ground)	99.78	±0.06	±0.04	±0.00

Results: EDTA Titration

Sample	Copper content wt%	SD	95% CI	99% CI	Instrumental SD	Sample SD
1	100.27	±0.40	±0.26	±0.36	±0.13	±0.44
2	-	-	-	-	-	-



Results: Atomic Emission Spectroscopy

Sample	Copper content wt%	SD	95% CI	99% CI	Instrumental SD	Sample SD
1	97.66	±3.80	±2.41	±3.41	±2.17	±3.68
2	98.06	±2.19	±1.39	±1.96	±1.43	±2.07

- Instrument: Agilent Technologies 4200 MP-AES



Results: Spectrophotometry (UV/VIS)

Sample	Copper content wt%	SD	95% CI	99% CI	Instrumental SD	Sample SD
1	99.44	±1.60	±1.01	±1.43	±0.46	±1.72
2	99.67	±1.29	±0.78	±1.10	±0.36	±1.41

- Instrument: Unicam UV300 UV/VIS



Results: Gravimetric

Sample	Copper content wt%	SD	95% CI	99% CI	Instrumental SD	Sample SD
1.1	99.33	±0.17	±0.42	±0.96	±0.17	-
2	-	-	-	-	-	-



Results: XRF

Sample	Copper content wt%	SD	95% CI	99% CI	Instrumental SD	Sample SD
1 (raw)	99.64	±0.18	±0.11	±0.16	±0.13	±0.16
2 (raw)	99.76	±0.07	±0.07	±0.11	±0.09	±0.00
1 (ground)	99.77	±0.06	±0.04	±0.06	±0.07	±0.00
2 (ground)	99.78	±0.06	±0.06	±0.09	±0.04	±0.00

- Instrument: Niton XL2 GOLDD XRF Analyser