Determination of Mopani Copper Mine MCM2 Copper Cathode Sampling Regime

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This paper highlights the importance of analytical chemistry in the mining industry; particularly in defining an internationally acceptable analytical regime for electrorefined copper cathodes as a precursor to the London Metal Exchange (LME) Grade A Copper. The change of technology for copper refining from the use of copper starter sheets to the more efficient ISA Process, which uses stainless steel or titanium blanks, at MCM Mufulira Refinery stimulated the need for this study. Twenty-four randomly selected MCM2 copper cathode pieces from the Refinery Tankhouse were sampled in a specified pattern, one piece each day over a period of three weeks. The individual cathode pieces were sub-sampled by punching at specific points of each cathode blade. The punches were analysed using a spark optical emission spectrometer and the results evaluated with respect to impurity distribution and quality consistency. The quality of MCM2 copper cathodes produced using the ISA Process were found to be of good consistency, with low level and homogeneously distributed impurities. From the evaluation of the analytical data, a sampling protocol of 15 pieces per section, diagonal sampling pattern and five points sub-sampling regime was selected and validated. This sampling protocol is in line with LME analytical criteria for copper exporters.

INTRODUCTION

General Overview

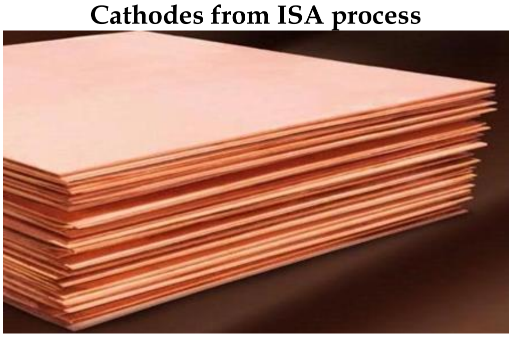
Mining accounts for 12% of Zambia´s gross domestic product and 70% of its total export value (World Bank, 2016). Copper mining, in particular, is the major contributor to the Zambian economy. Despite efforts by the Zambian government to diversify the economy, the Zambian copper mining industry has remained the engine driving the economy diversification programmes (Sikamo, 2016). Therefore, production of high-quality London Metal Exchange (LME) Grade A copper is vital for sustainable economic development because it attracts a high premium in international markets. The stringent quality specifications being demanded on the world market for copper metal are instructive for producing companies to develop accurate, efficient and cost-effective sampling protocols that should account for total characterization of impurity distribution in copper cathodes, which is not an easy task. The challenges of sampling of high-purity copper cathodes have been reported by several authors (Whebell, 1992; Carasco 2010). Whebell (1992) reported that cathodes are heterogeneous in nature, making their sampling labour-intensive and difficult to accomplish. Carasco (2010) observed that, despite several efforts in the past to implement best practices, guidelines and standards on sampling, assaying and variability issues, many people, particularly top managers and operators, still do not see the relevance of applying the best principles and practices of geostatistics, sampling theory, analytical chemistry and the understanding of processes variability from rock to cathodes.

Historical Background
Since inception of production of electrorefined copper at Mopani Copper Mines (MCM) Copper Refinery in 1937 and throughout the company's lifecycle from Roan Consolidated Copper Mines (1937–1972), Zambia Consolidated Copper Mines (1972–2000) and now Mopani Copper Mines, the sampling protocol was the random selection of 24 copper cathode pieces using a random number generation system from each section, followed by punching of each of the 24 pieces in a diagonal pattern when impurity distribution was consistent and in a 'Z pattern' in high impurity heterogeneity times. The resultant sample buttons were shredded and subdivided to obtain portions for analysis. This protocol is based on the British Standard BS EN 1978:1998, which specifies the composition and property requirements for cathodes of two copper grades, designated Cu-CATH-1 (CR001A) and Cu-CATH-2 (CR002A). Annex A (normative) of the standard describes methods for sampling cathodes for use in cases of dispute between the purchaser and the supplier and Annex B (informative) gives information on the relationships between electrical resistivity and conductivity of copper.

Following MCM Mufulira Refinery's drive to improve on the quality of copper cathodes and productivity, the Refinery Upgrade project was developed, which resulted in a change of copper refining technology from the use of copper starter sheets to the ISA Process, which uses stainless steel or titanium blanks (Aslin *et al.*, 2010). The old copper refining technology posed many challenges, with the quality of copper cathodes produced failing to meet both physical and chemical LME specifications. The cathodes had higher impurity levels with heterogeneous distribution characteristics. The ISA copper cathodes, however, meet both physical and chemical LME specifications, with lower impurity levels and less heterogeneous distribution characteristics. This change presented a challenge of determining an accurate sampling regime tailored to meet the high-quality expectations of copper derived from the ISA production process. Figure 1 illustrates the details of the cathodes produced from the former and later technologies.

Cathodes from starter sheet technology

Cathodes from ISA process



MCM cathode dimensions and mass

No. of pieces per bundle	20
Length L1 (without loop)	960–980 mm
Length L2 (with loop)	1030–1040 mm
Width	965–970 mm
Thickness	15–25 mm
Cathode mass	60–130 kg
Bundle mass	1.2–2.6 t

ISA cathode dimensions and mass

No. of pieces per bundle	40
Cathode mass	40–70 kg
Bundle mass	1.6 – 2.8 t
Thickness	6–10 mm
Bundle size (W × H)	912 mm × 900 mm, height 600 mm

Figure 1: Pictorial illustration of cathodes produced from former and later technologies.

SAMPLING BASICS

Correct sampling entails satisfying the fundamental requirements for correct sampling, which include the sampling frame, sample size, techniques, error sources or biases, and sampling intervals. For commercial purposes, customer satisfaction is critical; hence, the sampling protocol should include sound processes and practices that yield a representative sample commensurate with specific customer requirements (Morrison, 2008).

Establishing a Sampling Regime

Sampling challenges

Mufulira Analytical Services Department (ASD) was faced with a challenge of coming up with a sampling protocol commensurate with the new technology and achieving a shorter turnaround time (TAT) of results. The sampling challenges encountered were similar to those observed by Carasco (2010):

- sampling is seen as a third-class activity: cheap, nonskilled workers can do it;
- incorrect sampling protocols are implemented;
- generally, insufficient budgets are set for sampling equipment; often the equipment offered by the market is incorrect;
- operators do not care about sampling: it is seen as a nuisance;
- chemists use a very small sample mass for analysis: the sample is composed of only one increment.

Sampling methodology

Twenty-four randomly selected cathode pieces were individually sampled in a specified pattern, one piece each day over a three-week period. Each piece was marked with circles of sequentially reducing radii. Individual cathodes were punched at specific points of the sectioned copper cathode. Sample buttons obtained from similar points of each piece over the sampling period were composited into one sample representative of that position. Composite samples from each point were then split into three portions and melted separately. Two extra buttons (the green points shown in Figure 2) were taken from each of the nine sections of the cathode piece to obtain one daily composite sample, which was analysed in duplicate. The samples were analysed by Spectro Lab M10-spark–optical emission spectroscopy (OES).

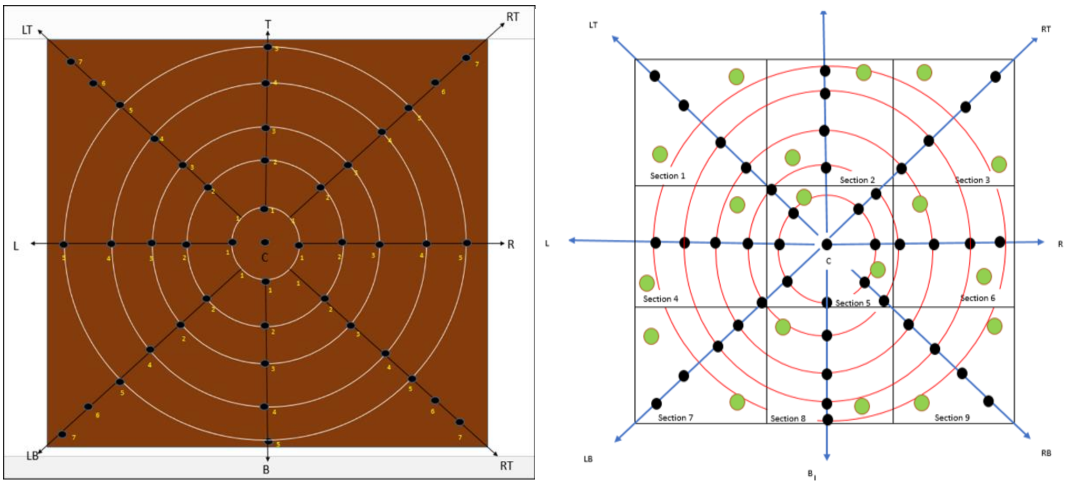


Figure 2: Pictorial illustration of the subsampling pattern used.

RESULTS

Statistical Evaluation

There are six elements of interest: Ag, As, Bi, Pb, S and Se. The statistical tools employed included trend graphs, standardisation test (outlier test), Levene's test (homogeneity of variance) chi square test (homogeneity), standard error and standard deviation, and permutation or combination of sampling patterns.

Evaluation of Cathode Quality Consistency

MCM2 cathode quality consistency was determined with respect to all six elements of interest on each cathode piece for a period of 24 separate days. As shown in Figure 3, the impurity levels of the cathodes were well below the LME specifications and consistently so over the whole period.

Evaluation of Impurity Distribution

Impurity distribution was examined by determining the homogeneity of variance using Levene's test and overall homogeneity using the chi square test. The Levene's and chi square tests' results indicated overall good homogeneity and even and consistent distribution of impurities over the copper cathode blade. This was done for all six elements of interest and all indicated similar results. This result was very critical for determining a reliable sampling technique. Results for silver and arsenic are shown in Figures 4 and 5, respectively, as an illustration.

Determination of Sub-Sampling Pattern

The sub-sampling pattern was determined by statistical evaluation of a variety of permutations on the copper cathode blade, i.e., diagonal left top (Lt) to right bottom (Rb); diagonal Rt to Lb; cross and 'Z' pattern. The mean assays for each element in the various sub-sampling pattern permutations were compared with the overall mean assays for each element over the whole cycle. The results are shown in Figure 6. The results indicated no significant variances between the means of the various sub-sampling permutations with the overall mean for the whole cathode blade. The diagonal pattern (as shown in Figure 7) was found to be the most cost-effective due to reduced turnaround time.

Determination of Number of Cathode Pieces to be Sampled per Section Pulled

The number of cathode pieces per section was determined by using the online sample size calculator (Creative Research Systems, 2012) at 95% confidence level as per illustration in Figure 8. Based on the established quality consistency of MCM2 copper cathodes, a population size of 2880 copper cathode pieces per section and working at a confidence interval of 25, the sample size calculated was 15 cathode pieces.

It was established that 15 cathode pieces selected at random, using the random generation system, was a representative sample of the whole section pulled; therefore, a change from 24 pieces per section pulled to 15 pieces per section was implemented.

Determination of Number of Points to be Punched per Cathode Piece

The number of points to be punched per cathode piece was determined by statistical evaluation of a variety of permutations along the established diagonal sub-sampling pattern, i.e., 15, 10, 7 and 5 points. The means assays of the various permutations were then compared with the overall means for each of the elements of interest.

The chemical test results in Figure 9 showed no significant variances between the means of the various permutations, with the overall mean for the whole cathode blade. The most cost-effective of five points per cathode piece was therefore established and implemented.

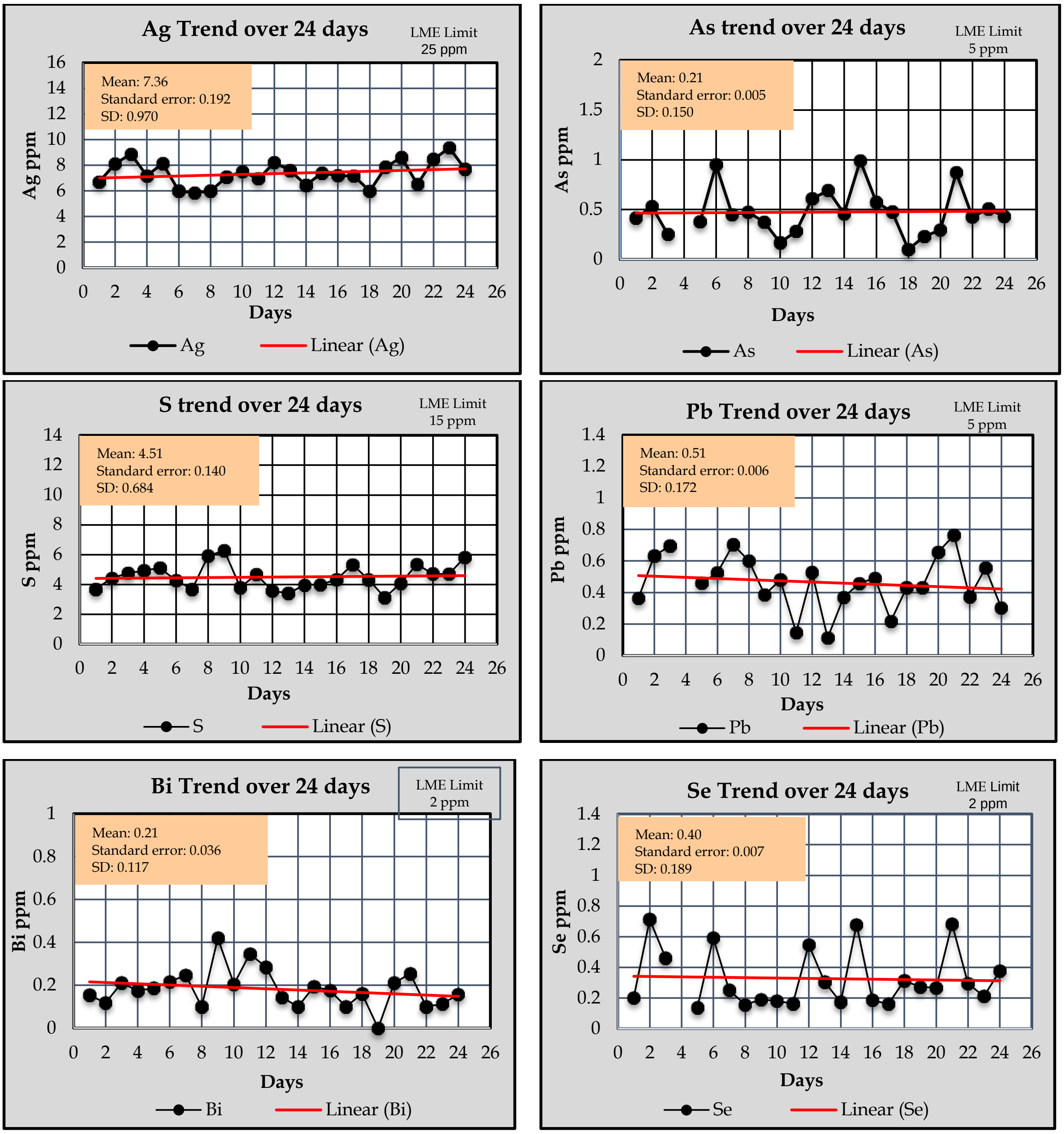
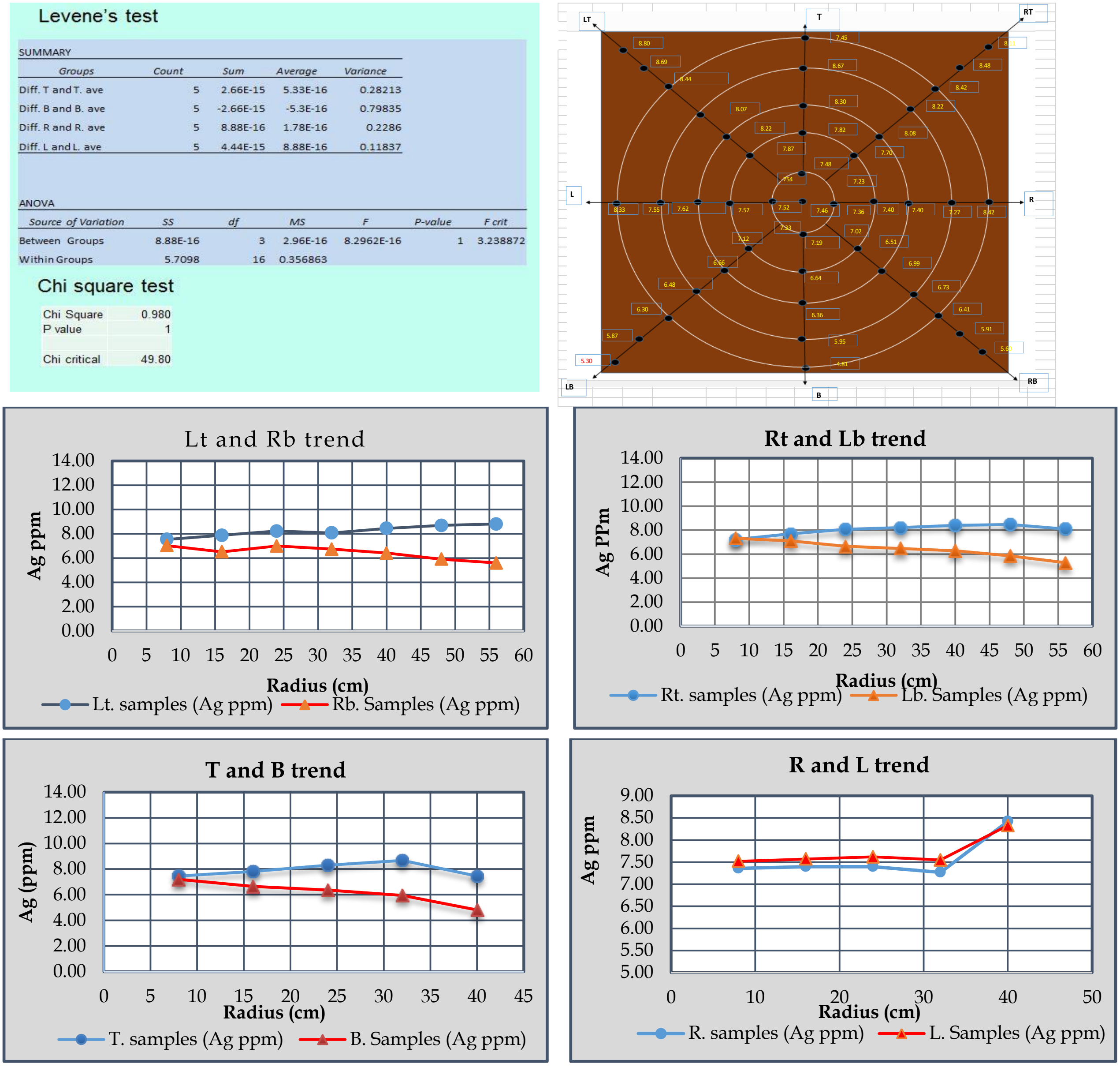


Figure 3: Cathode quality (impurity content) consistency over 24 days production cycle.



Levene's test

SUMMARY

Groups	Count	Sum	Average	Variance
Diff. T and T. ave	5	2.66E-15	5.33E-16	0.28213
Diff. B and B. ave	5	-2.66E-15	-5.3E-16	0.79835
Diff. R and R. ave	5	8.88E-16	1.78E-16	0.2286
Diff. L and L. ave	5	4.44E-15	8.88E-16	0.11837

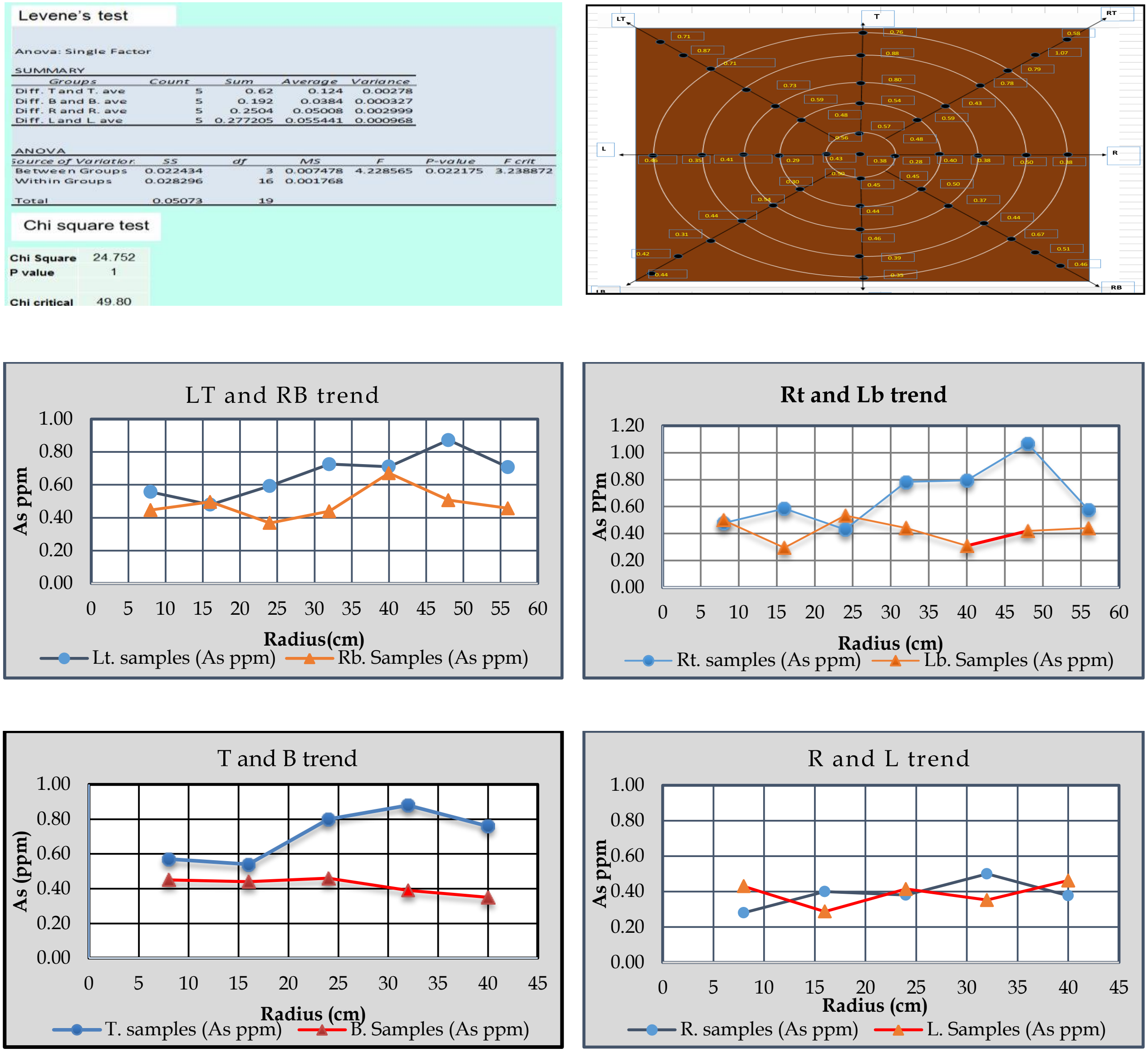
ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	8.88E-16	3	2.96E-16	8.2962E-16	1	3.238872
Within Groups	5.7098	16	0.356863			

Chi square test

Chi Square	0.980
P value	1
Chi critical	49.80

Figure 4: Results for silver distributions in MCM2 copper cathodes.



Levene's test

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Diff. T and T. ave	5	0.62	0.124	0.00278
Diff. B and B. ave	5	0.192	0.0384	0.000327
Diff. R and R. ave	5	0.2504	0.05008	0.002999
Diff. L and L ave	5	0.277205	0.055441	0.000968

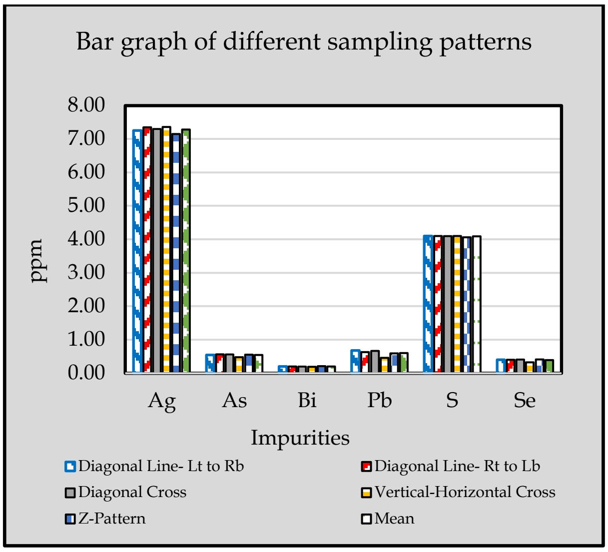
ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.022434	3	0.007478	4.228565	0.022175	3.238872
Within Groups	0.028296	16	0.001768			
Total	0.05073	19				

Chi square test

Chi Square	24.752
P value	1
Chi critical	49.80

Figure 5: Results for arsenic distributions in MCM2 copper cathodes.



Pattern	Ag	As	Bi	Pb	S	Se
Diagonal Lt to Rb	7.25	0.54	0.20	0.67	4.10	0.40
Diagonal Rt to Lb	7.35	0.56	0.20	0.63	4.10	0.40
Diagonal cross	7.30	0.56	0.20	0.66	0.40	0.41
Vertical-horizontal cross	7.36	0.47	0.19	0.45	0.41	0.32
Z-Pattern	7.15	0.55	0.21	0.59	4.06	0.41
Mean	7.28	0.54	0.20	0.60	4.09	0.39
SD	0.0848	0.0373	0.0057	0.0905	0.0201	0.0391
2SD	0.1696	0.0747	0.0115	0.1810	0.0403	0.0782
S.E	0.0068	0.0030	0.0005	0.0072	0.0016	0.0031

Comment: no significant variance between the means of the various patterns and the overall mean.
Key: Lt = Left to Top; Lb = Left to Bottom; Rb = Right to Bottom; Rt= Right to Top

Figure 6: Results of various sub-sampling pattern permutations.

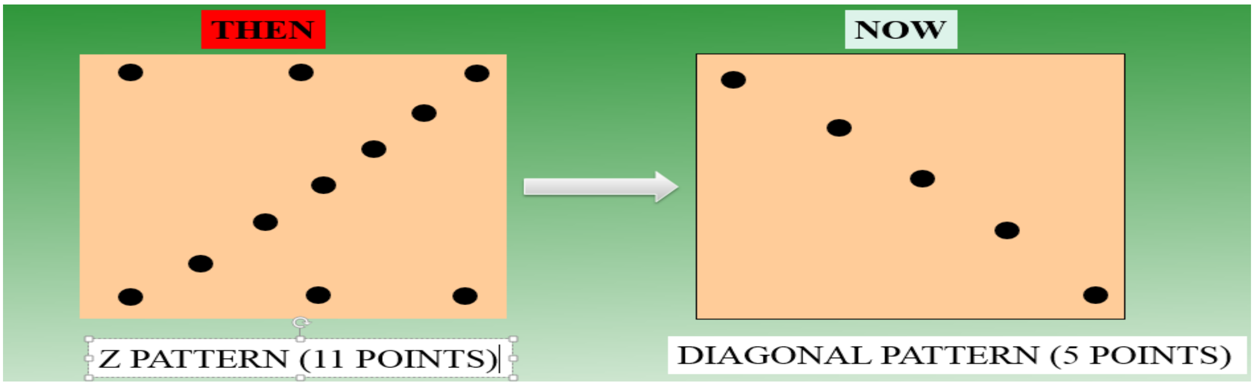


Figure 7: Established MCM2 copper cathode sub-sampling pattern.

DISCUSSION

The importance of analytical chemistry in the mining industry, particularly in defining an internationally acceptable analytical regime for electrorefined copper cathodes as a precursor to the LME Grade A copper registration process, has proved to be very critical. Copper is a major contributor to the Zambian economy; therefore, the analytical regime applied must reflect, as accurately as possible, the quality consistency of copper produced from refinery operations. The copper produced is released onto the international commodity market under very stringent LME Grade A copper metal listing requirements. LME listing is important for sustainable economic development because it attracts a significant premium on the world commodity market.

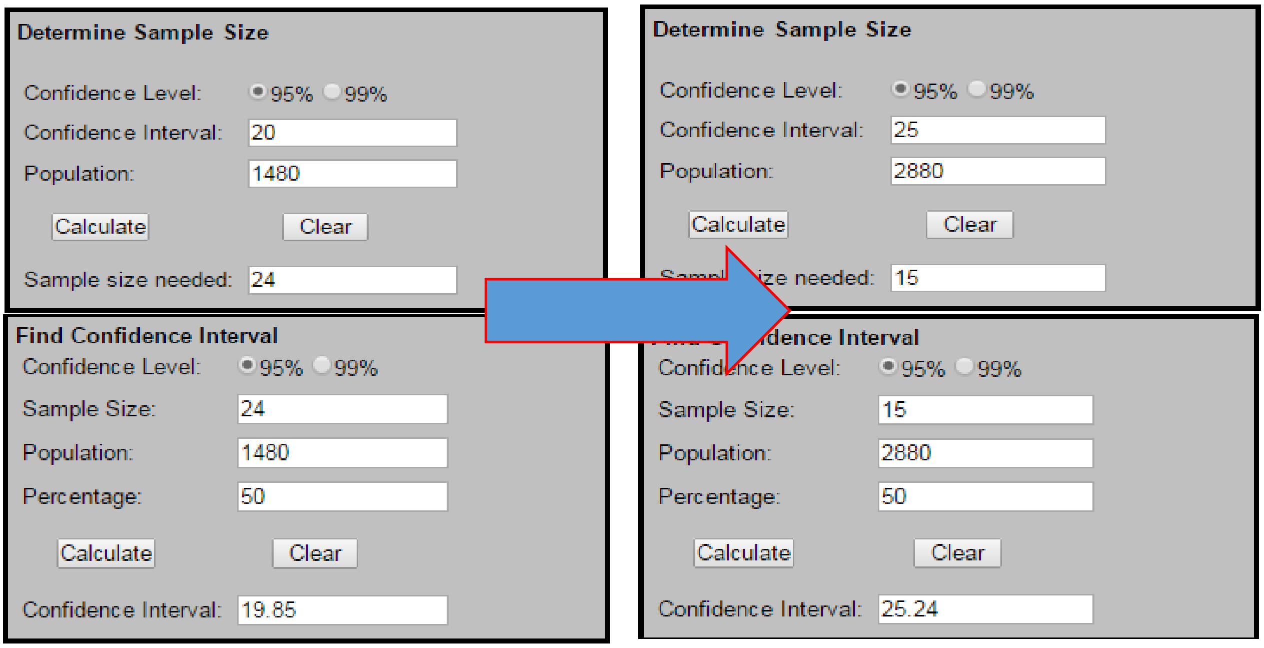
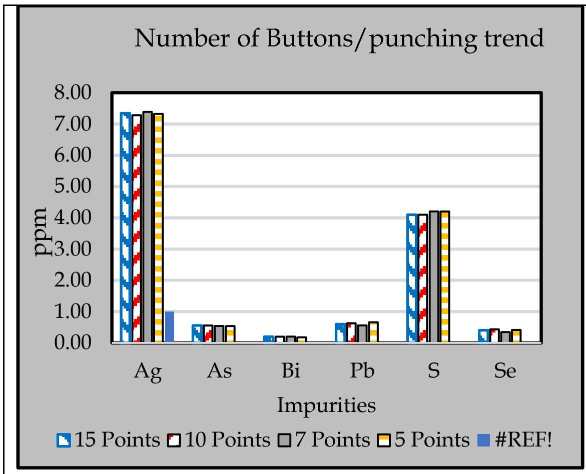


Figure 8: Sample size calculator based on consistency of ISA new Confidence Interval estimated at 25.



- Minimum 5 points selected, close to mean
- Minimum 5 points statistically coherent and economical
- Decision based on current good quality

No of Points	Ag	As	Bi	Pb	S	Se
15	7.35	0.56	0.20	0.60	4.10	0.40
10	7.29	0.56	0.20	0.63	4.10	0.44
7	7.39	0.54	0.20	0.56	4.20	0.34
5	7.33	0.54	0.18	0.66	4.20	0.42
Mean	7.34	0.55	0.20	0.61	4.15	0.40
SD	0.04	0.01	0.01	0.04	0.06	0.04
2SD	0.080	.020	0.03	0.080	0.110	0.080

Figure 9: Established of number of points to be punched per cathode piece.

CONCLUSION

The quality of MCM2 copper cathodes produced using the ISA process was found to be of good consistency and with low level and homogeneously distributed impurities. From evaluation of the analytical data, a sampling protocol of 15 pieces per section, diagonal sampling pattern and a five-point sub-sampling regime was determined and validated. This sampling protocol is in line with LME analytical criteria for copper exporters.

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