

Contamination, Precision and Accuracy of pXRF Geochemistry: Case Study-Polymetals Resources Ltd., Mansala Gold Project, Siguiri Basin, Northeast Guinea

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How to cite this paper: Asante, N.Y. (2023) Contamination, Precision and Accuracy of pXRF Geochemistry: Case Study-Polymetals Resources Ltd., Mansala Gold Project, Siguiri Basin, Northeast Guinea. *International Journal of Geosciences*, 14, 677-688.

<https://doi.org/10.4236/ijg.2023.148036>

Received: May 6, 2023

Accepted: August 14, 2023

Published: August 17, 2023

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Abstract

Quality Assurance and Quality Control (QA/QC) is a critical component of all pXRF geochemistry processes. A properly constructed pXRF QA/QC programme identifies possible instrumental errors and provides a means of securing fit for purpose data from the pXRF programme. pXRF QA/QC programmes involve daily contamination, precision, and accuracy checks to ensure the generation of fit for purpose data. In the exploration field or mine-site, pXRF is capable of producing extremely valuable data that is fit for purpose if calibrated properly. However, it should not be used as a replacement for acquiring data from an accredited laboratory using established analytical techniques that produce high quality data. Contamination is the checking of the cleanliness of the analyser window or the presence of dust in the measuring environment. At Polymetals, using Olympus Vanta C-Series pXRF analyser with silver anode, contamination is assessed by measuring an instrumental blank (SiO_2), to identify any foreign matter on the analyser window. Assuming that the window film is new, and the fused silica disc is dust free, only Si should be detected. If any other significant element is detected, the film is replaced, and the test is re-run. Accuracy is a measure of how close the measured value is to the true value and is assessed by measuring the abundance of selected elements contained within a Certified Reference Material (CRM) or the NIST check standard sample supplied with the pXRF analyser. Elements of interest must report within $\pm 20\%$ of the standard value. Precision is a measure of how close repeat measurements are to one another and is assessed by taking multiple readings on a particular sample to determine the stability of the analyser. The Relative Standard Deviation (RSD) of the replicate measurements is then calculated. The RSD values should be less than 20% for

most analytes, except chromium, for which the value should be less than 30%. Once contamination, accuracy and precision are within accepted limits, the batch/daily measurements are considered to have passed the QA/QC protocol. The data is thus fit for purpose and transferred to the data file. Any batch/daily measurement reported to have failed due to instrumental errors is re-analysed. QA/QC protocols should be applied to each project. The QA/QC protocols instituted after the pXRF samples meeting the quality sample conditions thus pulverised dry samples in pXRF sample cup covered with thin pXRF films, are used to generate fit for purpose data from soils samples at Mansala which is used to generate pathfinder element(s) to delineate anomalous pathfinder trends for further exploration works.

Keywords

Contamination, Precision, Accuracy, pXRF, Polymetals, Mansala

1. Introduction

Generating fit for purpose data from a pXRF programme requires quality sample preparation, optimal sample irradiation interval, appropriate sample containers, films and QA/QC protocols [1]. Energy calibration check is done at the prior to the first analytical batch of the day and repeated after 4 hours of continuous measurements to ensure the analyser is still operating within resolution and stability tolerances (*i.e.* no shifts in energy line positions, regions of interest, or shift in gain control due to temperature changes) [2]. This should be carried out each day with the manufacturer's check ("coupon"), often an alloy or pure metal, or if drift is suspected.

Assay irradiation time has great impact on precision and limit of detection, with precision improving with increased testing time. This is particularly important when light elements are being measured [2]. For the Polymetals Mansala Auger pXRF programme, 45 seconds per beam was used as the optimum time in order to undertake enough measurement daily. This assay interval was based on test work which showed no significant variation in precision and accuracy for the standard suite of analytes when irradiated for 30, 45 and 60 seconds per beam. Refer to **Figure 1**.

Quality sample condition is necessary for all pXRF measurements. This means that:

- Samples are properly dried;
- Samples should be pulverised to 75% passing 150 μ mesh to ensure homogeneity; and
- Aliquots of sample transferred to assay cups covered with thin pXRF films.

Pulverised samples minimise effects of heterogeneity associated with varying grain-size and nuggety element distribution, and the precision of repeat analyses is significantly improved [1]. The level of sample preparation normally depends

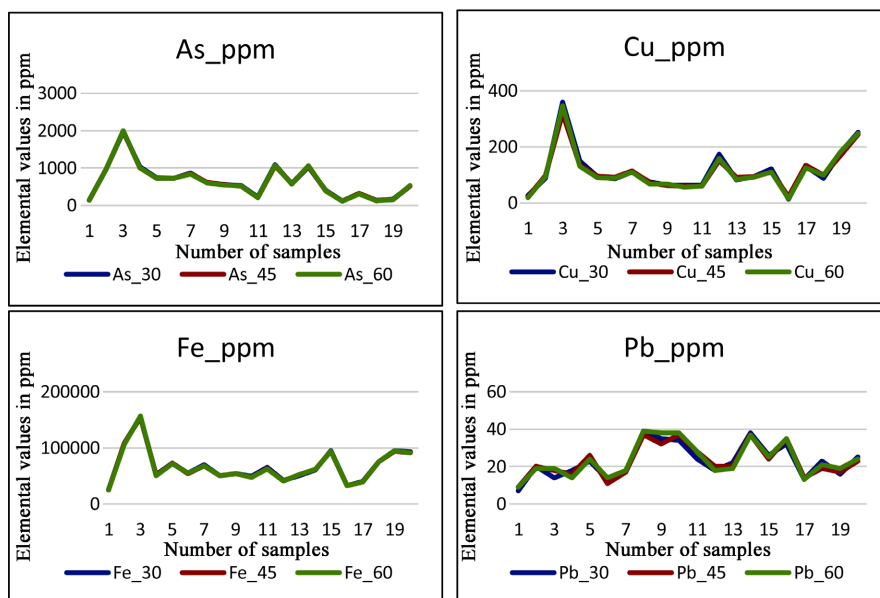


Figure 1. Optimum testing of assay intervals analysis using As, Cu, Fe and Pb.

on the objectives of the pXRF programme. It could be full sample preparation or partial sample preparation or no sample preparation.

Samples for the Mansala auger pXRF programme are pulp samples (grain size -75μ) from the laboratory, prepared in pXRF sample cups covered with thin polypropylene film. Sample condition is thus optimal. Note that polypropylene films have the best transmittance of fluorescence signal [2]. It is very important to always ensure that samples for pXRF measurement are always dry as moisture in the sample can absorb some of the X-rays, making some elements to be under reported and, the pXRF machine is also factory calibrated on dry samples and will always under report results on moist samples.

The standard operating procedure used comprises:

- optimum sample preparation;
- energy calibration check;
- optimum test time;
- contamination checks—first sample of the day should be a blank;
- accuracy checks;
- precision checks.

When these procedures are put in place, fit for purpose pXRF data will be generated and can be used profitably for sample screening and selection tasks. QA/QC monitoring of pXRF results should be done systematically especially if the pXRF field measurements are to be used as data by the project or if operational decisions are based on them. QA/QC protocols are the same as in the laboratory, with blanks, CRMs and standards, systematic and random duplicates, and careful performance monitoring of each instrument [2]. A good rule of thumb is to run QA/QC 1 out of every 20 samples in a pXRF programme. The first sample of the day should be the blank to ensure that there is no contamination on the detector window [3]. Monitoring the quality of analysis after good

sample preparation, testing time, appropriate sample cups and films, is fundamental to ensuring the generation of fit for purpose data and providing the necessary confidence to make informed decisions when interpreting all the available information. A comprehensive quality control system is necessary to monitor the sampling—preparation—analysis sequence in an effort to ensure the generation of fit for purpose data [4]. Companies are strongly encouraged to designate someone with technical acumen within their group to be their pXRF specialist, to undergo training, be responsible for the maintenance and calibrations of the pXRF instruments, and to train others in the operation of pXRF analysers.

2. Results and Discussion

2.1. Contamination

pXRF contamination is assessed by using the supplied fused silica disc to check the cleanliness of the analyser window. The analyser should only report silica (SiO₂) which is contained in the fused disc. The presence of other elements implies contamination of the analyser window with dust from the measurement environment. The contamination check is conducted on a daily basis.

A total of 11 analyses on 15th October 2022 were conducted on the silicon blank during the Mansala Auger pXRF programme. A plot of the readings as in **Figure 2** shows constant values measured during the day signifying.

- No loss in beam voltage

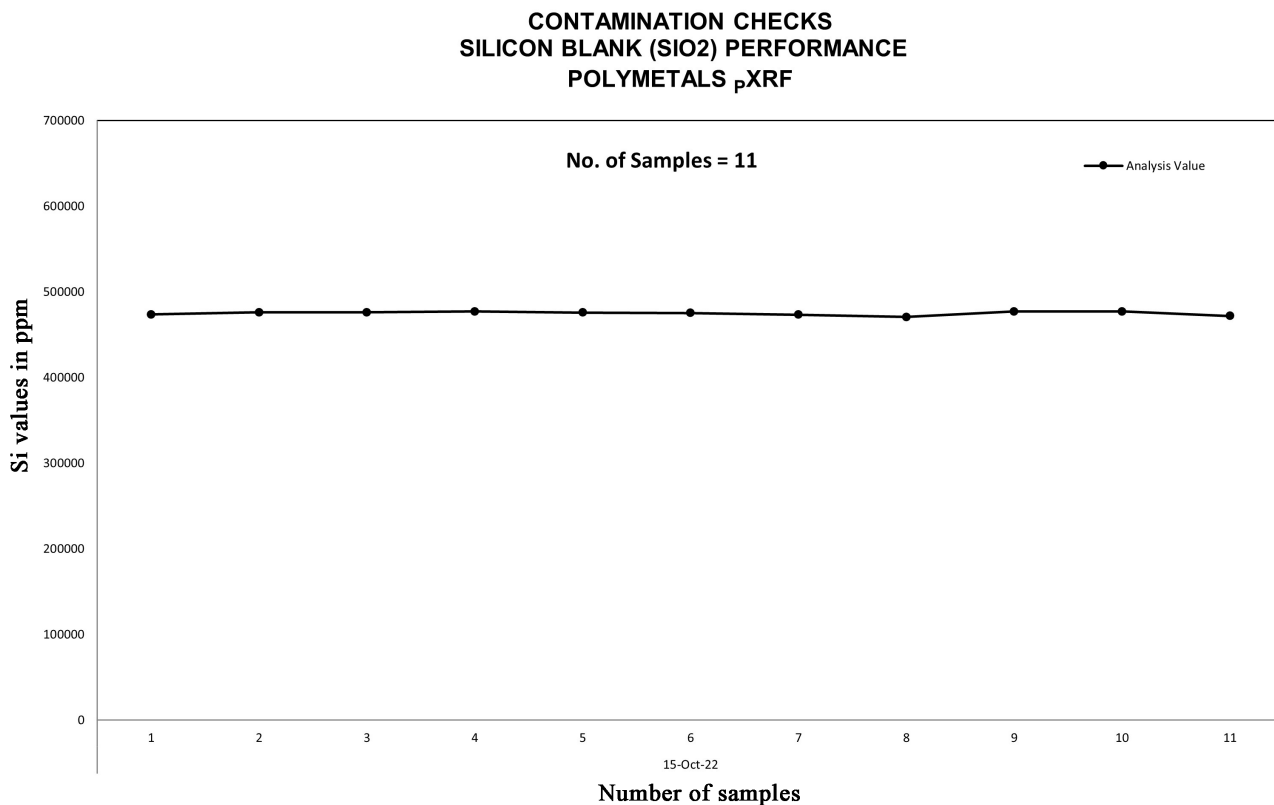


Figure 2. Representation plot of measurements on Silicon Blank (SiO₂).

- No drift in measure values.
- Good filtering of X-rays emissions by the polypropylene film.

2.2. Accuracy

Accuracy is a measure of how close the measured value is to the true value and is influenced by the quality of reference standard used in the calibration, the calibration procedure, and the duration of the measurement [5]. pXRF accuracy is assessed by measuring elements of interest in a certified reference material (CRM) that has been assayed repeatedly by the lab supplying the material. Alternatively, a NIST check standard sample supplied with the pXRF analyser may be used. Nearness of the pXRF data to the approved value for each element provides a measure of the instrument's accuracy. Measured values which fall within $\pm 20\%$ of the standard value are considered acceptable. Accuracy checks are conducted on a daily basis and will detect malfunctions of the pXRF instrument.

A total of 11 analyses were conducted on NIST 2711A for the Mansala Auger pXRF programme on 15th October 2022. Accepted values for As and Cu in NIST 2711A are 107 ppm and 140 ppm, respectively. Values for arsenic (As) and copper (Cu) as measured by an Olympus Vanta C-Series pXRF analyser are plotted in Figure 3 and Figure 4 respectively. The figures also contain two additional traces which define the extent of acceptable values measured by this pXRF

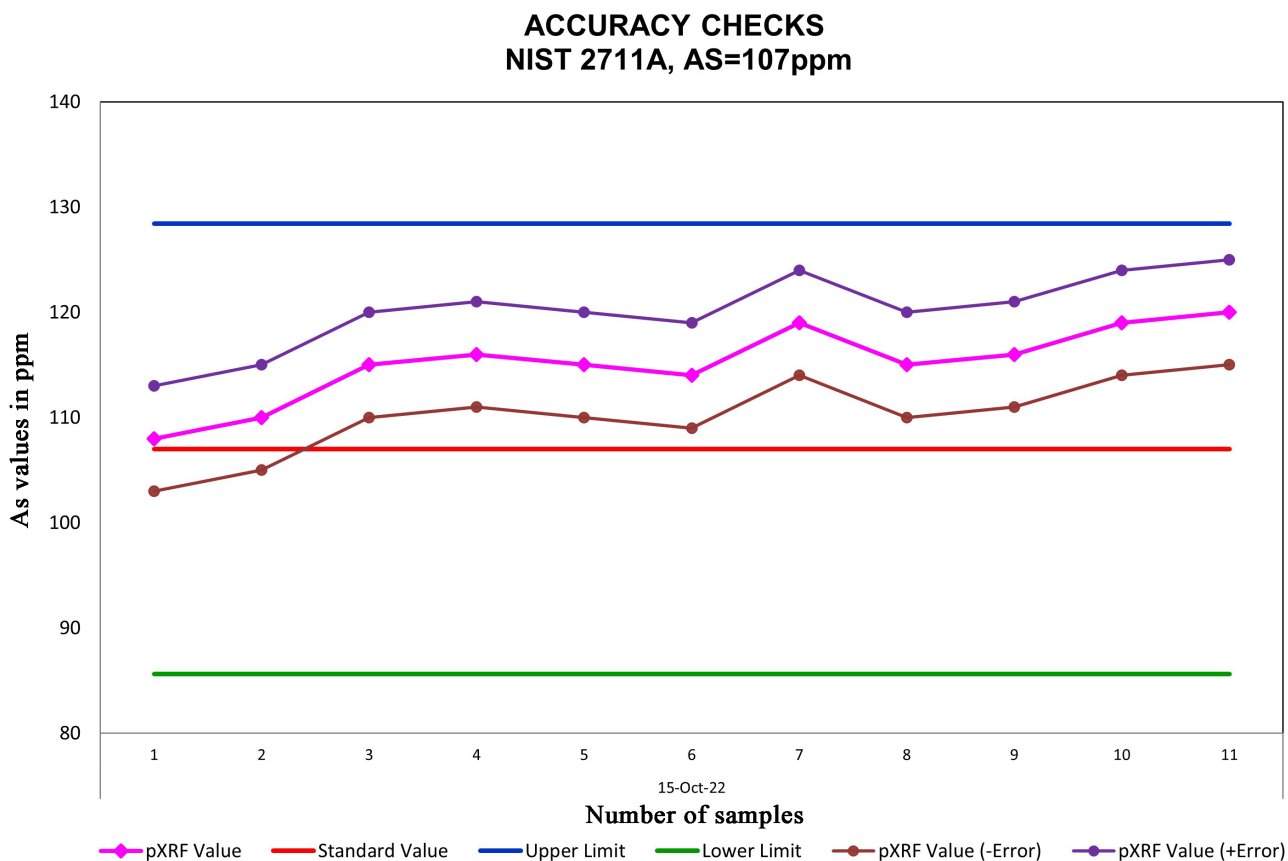


Figure 3. Plots of As measurements of NIST 2711A (As = 107 ppm) against $\pm 20\%$ As value.

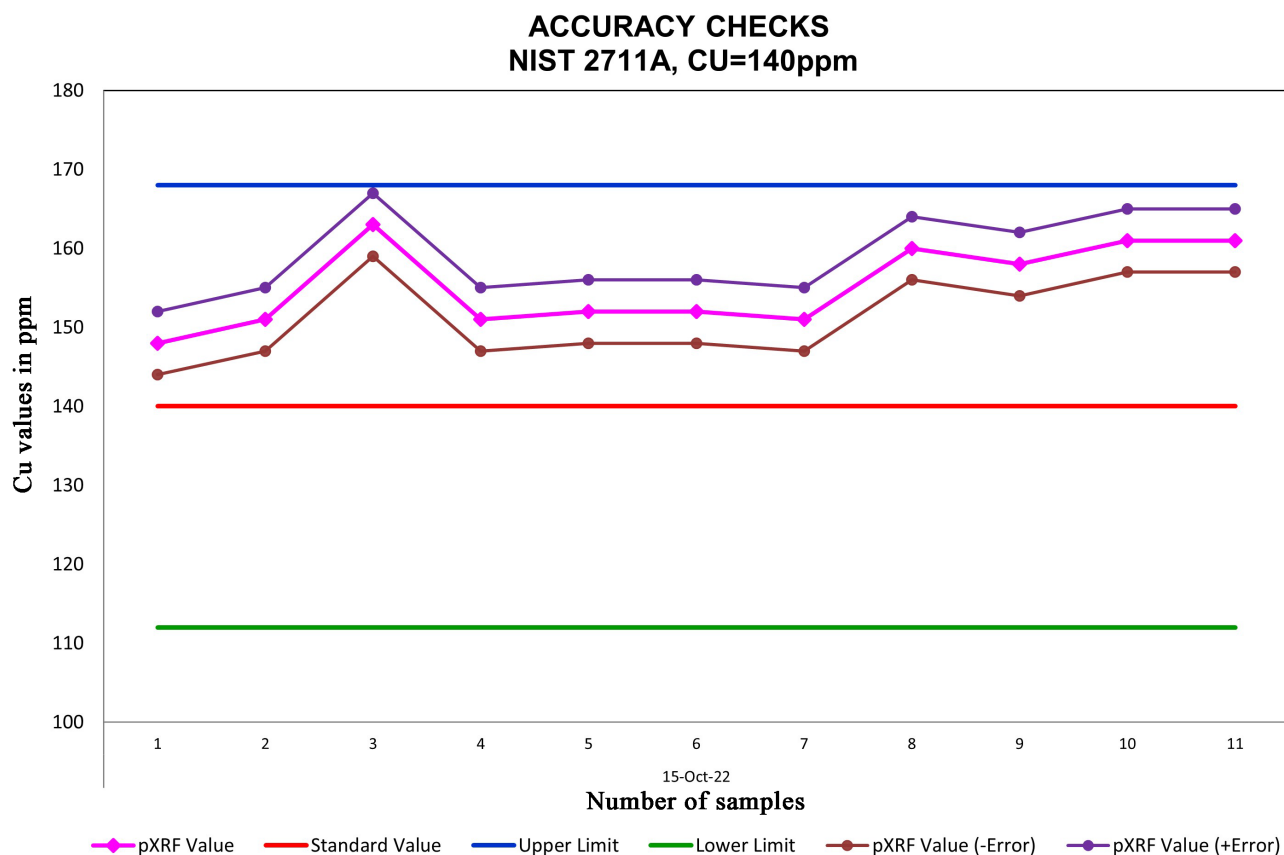


Figure 4. Plots of Cu measurements of NIST 2711A (Cu = 140 ppm) against $\pm 20\%$ Cu value.

instrument (*i.e.* $\pm 20\%$).

Figure 3 shows:

- All values plotted above the As value in the standard, NIST 2711A;
- No value fell above the maximum acceptable As value by 20%;
- No values fell below the minimum acceptable As value by 20%.

Figure 4 shows:

- All values plotted above the Cu value in the standard, NIST 2711A;
- No value fell above the maximum acceptable Cu value by 20%;
- No values fell below the minimum acceptable Cu value by 20%.

2.3. Precision

Precision is a measure of how close repeat measurements are to one another and is influenced by statistical nature of the x-ray tube emission process, statistical nature of the sample's x-ray absorption/emission process, statistical nature of detection process and unpredictable variations in substrate or matrix effects [5]. pXRF precision is assessed by calculating the Relative Standard Deviation (RSD) of the replicate measurements for the analytes. The RSD values should be less than 20% for most analytes, except chromium, for which the value should be less than 30% (Anon, No date). The smaller the RSD, the better the precision. pXRF precision determines the stability of the analyser in terms of measurement re-

peatability by doing multiple readings on a particular sample and looking at the variability of the data. Precision check is conducted on a daily basis with a different sample.

A total of 20 repeated analyses were conducted on 4 samples, 5 analyses per sample, for the entire Polymetals Mansala Auger pXRF programme on four (4) different days. A plot of the readings for Arsenic (As), Copper (Cu) and Lead (Pb) as in **Figure 5** indicates a very good repeatability signifying a good stability of the pXRF analyser.

2.4. Pathfinder Analysis

Pathfinder elements provide a means to evaluate large areas for their mineral potential by eliminating likely barren areas from the areas under consideration during exploration studies [6]. Nude *et al.*, in their gold exploration studies in the Wa-Lawra Belt, Northwest Ghana, using a multivariate statistical approach, found that Fe and Mn are strongly associated with gold, and alongside Pb, Ag, As, and Cu, these elements could be used as pathfinders for gold in the area, with ferruginous zones as targets [7].

With all QA/QC protocols being satisfied and generating fit for purpose data, the Mansala auger pXRF data is used to determine gold (Au) pathfinder elements(s) on the Mansala permit. Since the Mansala property lies in the Sigiri basin with expectation of a typical Orogenic gold deposit, Orogenic gold deposits

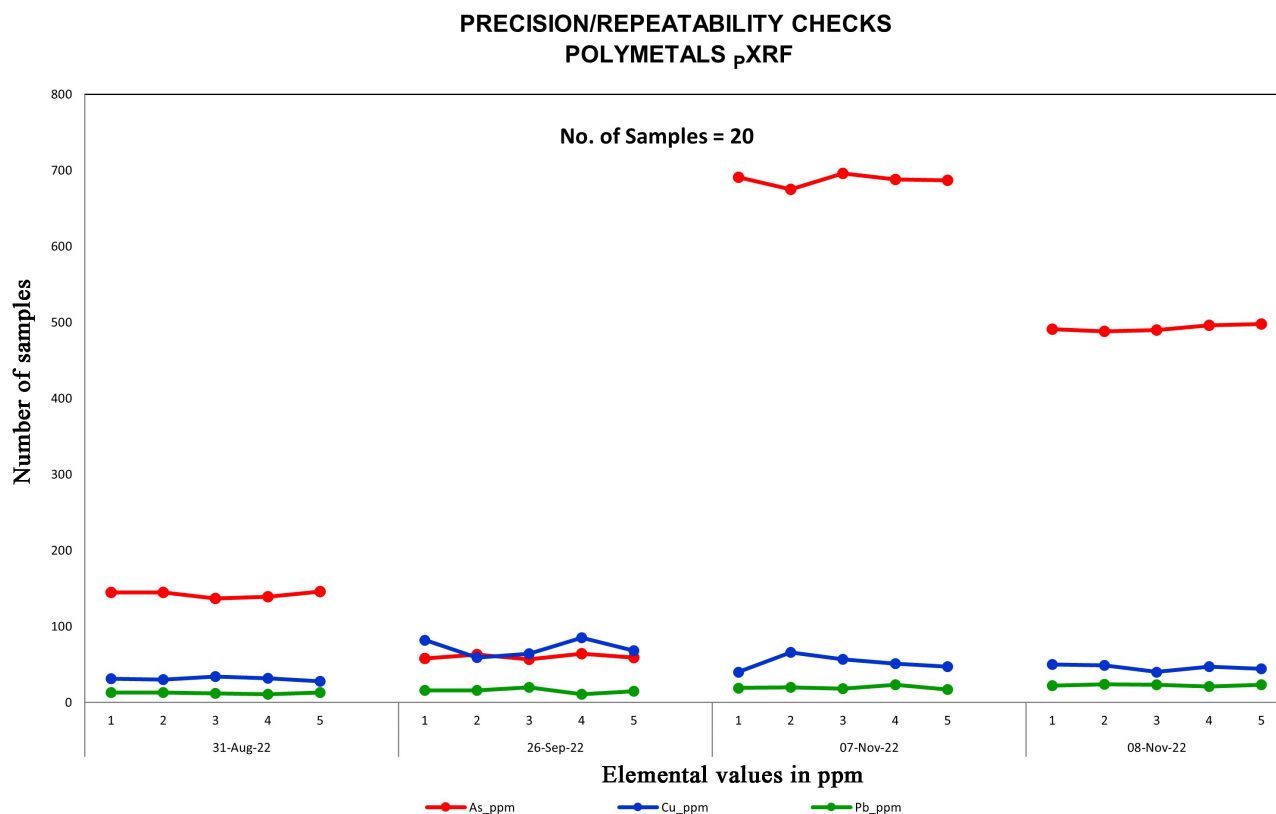


Figure 5. Repeatability plot of As, Cu and Pb.

geochemical signatures including sulphur (S), copper (Cu), zinc (Zn), arsenic (As), molybdenum (Mo), antimony (Sb), tungsten (W), mercury (Hg) and Lead (Pb) were used in the analysis.

Summary statistics as in **Table 1**, shows As, Cu, Pb, and Zn are likely to be abundantly available on the Mansala property as these elements were detected in almost all the 130 auger samples. S and Mo are likely to be moderately present on the Mansala property while W, Hg and Sb are likely to be less present on the Mansala property as these elements were not detected in most of the 130 samples

Table 1. Summary statistics of auger samples.

	<i>Au</i>	<i>S</i>	<i>Cu</i>	<i>Zn</i>	<i>As</i>	<i>Mo</i>	<i>Sb</i>	<i>W</i>	<i>Hg</i>	<i>Pb</i>
Count Numeric	130	105	130	123	130	76	21	19	6	128
Count Text	0	25	0	7	0	54	109	111	124	2
Count Null	0	0	0	0	0	0	0	0	0	0
Count Negative	0	0	0	0	0	0	0	0	0	0
Count Zero	0	0	0	0	0	0	0	0	0	0
Unique Values	95	76	85	61	122	12	18	13	5	33
Minimum	0.01	110.00	9.00	6.00	6.00	4.00	27.00	9.00	7.00	5.00
Maximum	16.30	466.00	321.00	340.00	2117.00	27.00	61.00	34.00	10.00	97.00
Mean	0.58	198.31	86.28	42.57	409.90	6.71	39.48	18.68	8.00	21.61
Median	0.08	193.00	70.50	19.00	258.50	6.00	36.00	18.00	7.50	20.00
Range	16.29	356.00	312.00	334.00	2111.00	23.00	34.00	25.00	3.00	92.00
Interquartile Range	0.28	80.50	61.50	39.00	486.25	3.00	12.50	6.00	2.25	8.00
Standard Deviation	1.94	56.78	60.96	52.53	413.81	3.33	9.82	6.25	1.26	10.75

Table 2. Correlation analysis using log 10 transformation.

<i>Correlation Log 10 Transformation</i>	<i>Au</i>	<i>S</i>	<i>Cu</i>	<i>Zn</i>	<i>As</i>	<i>Mo</i>	<i>Sb</i>	<i>W</i>	<i>Hg</i>	<i>Pb</i>
Au	1.00									
S	0.23	1.00								
Cu	-0.06	-0.01	1.00							
Zn	-0.37	-0.13	0.58	1.00						
As	0.50	0.20	0.14	-0.23	1.00					
Mo	0.22	-0.05	0.23	0.10	0.29	1.00				
Sb	-0.15	-0.35	0.33	0.49	-0.14	0.04	1.00			
W	-0.01	-0.03	0.47	0.30	0.47	-0.71	-0.61	1.00		
Hg	0.09	-0.55	-0.17	-0.24	0.49	0.34	NaN	NaN	1.00	
Pb	0.13	0.26	0.16	0.01	0.29	0.13	0.21	0.36	0.03	1.00

Table 3. Correlation analysis using power transformation.

<i>Correlation Power Transformation</i>	<i>Au</i>	<i>S</i>	<i>Cu</i>	<i>Zn</i>	<i>As</i>	<i>Mo</i>	<i>Sb</i>	<i>W</i>	<i>Hg</i>	<i>Pb</i>
Au	1.00									
S	0.24	1.00								
Cu	-0.05	-0.01	1.00							
Zn	-0.38	-0.12	0.60	1.00						
As	0.53	0.14	0.14	-0.22	1.00					
Mo	0.22	-0.06	0.24	0.17	0.35	1.00				
Sb	-0.09	NaN	0.35	0.54	0.01	0.26	1.00			
W	-0.01	NaN	0.28	0.24	0.34	NaN	NaN	1.00		
Hg	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	
Pb	0.13	0.24	0.12	0.05	0.24	0.07	0.26	0.56	NaN	1.00

used for the analysis. Correlation analysis using both log transformation and power transformation of the data as shown in **Table 2** and **Table 3** respectively, shows arsenic (As) to moderately correlate with gold (Au) whiles Sulphur (S) and Molybdenum (Mo) weakly correlate with Au.

2.5. Delineation of Pathfinder Trends

Correlation analysis from the initial 130 auger samples identified arsenic as good gold (Au) pathfinder on the Mansala property. With this in mind, a soil sampling programme consisting of 500 soil samples on 12 crosslines on a 100 × 25 m grid system was initiated to delineate arsenic (As) trends at the most prospective area of the Mansala property for further exploration works. The samples collected were subjected to the pXRF QA/QC protocols instituted to generate fit for purpose data. The samples were dried, pulverised and transferred to pXRF sample cups covered with polypropylene films.

pXRF measurements were undertaken on the 500 samples taking into consideration optimum sample preparation, energy calibration checks and optimum testing time. Contamination, precision, and accuracy checks were done to ensure the generation of fit for purpose results to delineate the arsenic (As) trends for further exploration works.

Arsenic (As), the main pathfinder element of interest, has 7 ppm and 2004 ppm as minimum and maximum values respectively as shown in **Table 4**. Threshold determination using the boxplot, cumulative distribution, [median ± 2 MAD] and [mean ± 2sdev] gave 100, 78, 80 and 487 respectively. Since statistical analysis using the boxplot is best for identifying geochemical data outliers, the threshold value from the boxplot was used for the class boundaries (0 - 100, 100 - 200, 200 - 300, 300 - 400, >400) for plotting and delineation of the arsenic trends.

Table 4. Summary statistics of Arsenic (As).

	<i>As</i>
Mean	106.99
Standard Error	8.52
Median	37.00
Mode	18.00
Standard Deviation	190.44
Sample Variance	36,265.75
Kurtosis	28.48
Skewness	4.41
Range	1997.00
Minimum	7.00
Maximum	2004.00
Sum	53,493.00
Count	500.00

Figure 6 shows delineated Arsenic (As) trend from the soil sampling programme superimposed on auger and pit samples and geophysical structures delineated from the aeromagnetic survey. Interpretation of the pXRF soils sampling results, delineated Arsenic (As) trend coincident with the delineated NNE trend from the pits and auger samples. Discrete Arsenic (As) anomalies also occur at the west of the main NNE trend. The delineated Arsenic (As) trends are open to the North and South. The Arsenic (As) trends also confirm the high prospectivity of the area sampled that is already delineated by the pit sampling, auger drilling and aeromagnetic survey.

3. Conclusion

This case report suggests that, with the right QA/QC protocols (contamination, precision, and accuracy) put in place after pXRF samples meeting the quality sample conditions thus pulverised dry samples in pXRF sample cup covered with thin pXRF films, fit for purpose data is expected to be generated. This data can then be used to make further decisions.

Acknowledgements

The author wishes to thank Mr. William Pountney, Exploration Manager, Polymetals Resources Ltd—Guinea, for his encouragement to publish this case study. Special thanks also go to Dr. Chris Johnston and Mr. Alex Hanly, formal Technical Director and CEO respectively, Polymetals Resources—Australia, for instituting this pXRF programme. I am again very grateful to Mr. David Sproule, Mr. Linden Sproule, and Mr. Aguibou BAH, executive chairman—Australia,

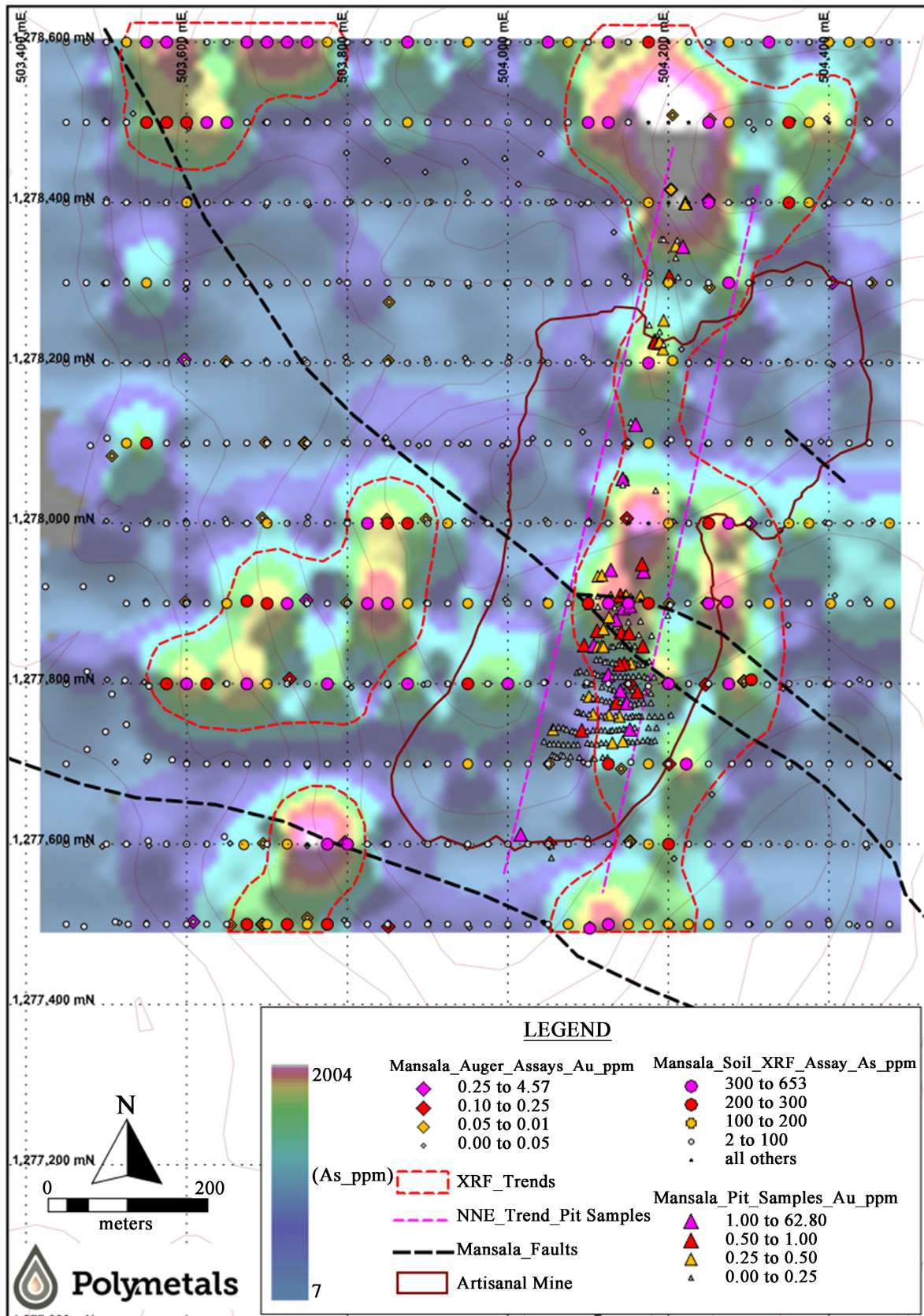


Figure 6. Delineated Arsenic (As) trend from pXRF soil samples.

executive director—Australia, and country manager—Guinea respectively of Polymetals Resources for accepting to publish this pXRF case report.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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