OPTIMIZING EDXRF METHODS FOR ACCURATE GOLD ALLOY PURITY ASSESSMENT

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ABSTRACT

The need for quicker and more effective methods for using gold in transactions is increasing. Gold has always been a valuable investment and carries cultural importance. Accurately assessing the purity of gold in items such as jewelry is crucial. Conventional techniques, like fire assay and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), are precise but are often slow and costly. Energy Dispersive X-ray Fluorescence (EDXRF) offers a non-destructive approach that can easily analyze gold purity without destroying the sample. However, various factors can influence its accuracy. This research explores methods to enhance the accuracy of EDXRF in measuring gold purity. It involves tweaking the machine settings, using specific calibration materials, and understanding how the presence of other metals mixed with gold can impact the results. The study indicated that EDXRF can achieve accuracy comparable to traditional techniques for measuring gold purity with appropriate adjustments and calibration. The findings showed regression results (R^2) of about 0.9999 for the targeted gold calibration curve across all metals, indicating a strong correlation between certified values and EDXRF measurements. Furthermore, the relative error of the measured gold value was less than 0.1 rel % across all matrices. The relative standard deviation was minimized to less than 0.11 % rsd for pure Au, 0.16 % rsd for Au-Ag, and Au-Cu alloys, and below 0.20 % rsd for Au-Ag-Cu alloys with matrix correction. This enhanced technique could accelerate and reduce the cost of analysing gold alloys, benefiting the precious metals sector and encouraging fair trade.

ABSTRAK

Keperluan untuk kaedah yang lebih cepat dan berkesan untuk menggunakan emas dalam urus niaga semakin meningkat. Emas sentiasa menjadi pelaburan yang bernilai dan membawa kepentingan budaya. Menilai ketulenan emas dengan tepat dalam barangan seperti perhiasan adalah penting. Teknik konvensional, seperti ujian kebakaran dan Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), adalah tepat tetapi selalunya lambat dan mahal. Energy Dispersive X-ray Fluorescence (EDXRF) menawarkan pendekatan tidak merosakkan yang boleh menganalisis ketulenan emas dengan mudah tanpa memusnahkan sampel. Walau bagaimanapun, pelbagai faktor boleh mempengaruhi ketepatannya. Penyelidikan ini meneroka kaedah untuk meningkatkan ketepatan EDXRF dalam mengukur ketulenan emas. Ia melibatkan pengubahsuaian tetapan mesin, menggunakan bahan penentukuran khusus, dan memahami bagaimana kehadiran logam lain yang dicampur dengan emas boleh memberi kesan kepada keputusan. Kajian menunjukkan bahawa EDXRF boleh mencapai ketepatan setanding dengan teknik tradisional untuk mengukur ketulenan emas dengan pelarasan dan penentukuran yang sesuai. Penemuan menunjukkan keputusan regresi (R2) kira-kira 0.9999 untuk keluk penentukuran emas yang disasarkan

merentas semua logam, menunjukkan korelasi yang kuat antara nilai yang diperakui dan pengukuran EDXRF. Tambahan pula, ralat relatif bagi nilai emas yang diukur adalah kurang daripada 0.1 rel% merentas semua matriks. Sisihan piawai relatif telah diminimumkan kepada kurang daripada 0.11 % rsd untuk Au tulen, 0.16 % rsd untuk aloi Au-Ag, dan Au-Cu, dan di bawah 0.20 % rsd untuk aloi Au-Ag-Cu dengan pembetulan matriks. Teknik yang dipertingkatkan ini boleh mempercepatkan dan mengurangkan kos menganalisis aloi emas, memanfaatkan sektor logam berharga dan menggalakkan perdagangan yang adil.

Keywords: Energy Dispersive X-ray Fluorescence (EDXRF), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), gold and gold alloy

INTRODUCTION

The Energy Dispersive X-ray Fluorescence (EDXRF) method shows promise as an alternative to fire assay, but it has limitations. Existing calibrations don't fully utilize commercial EDXRF capabilities due to manufacturer restrictions [1-4]. This default calibration is not well-suited for analysing complex precious metals [1,5]. Additionally, EDXRF analysis of jewellery with gold alloys can be affected by matrix effects [6-8]. As a result, EDXRF analysis results are often used as supplementary data. In contrast, fire assay has been the benchmark method with up to 0.05 wt% accuracy [5,9-12]. Calibration curves are crucial for accurately analysing components like gold in jewellery [13-15]. Factors such as the presence of other alloying components and the matrix effect should be considered. Using fundamental parameter modelling (FP) can provide reliable results by accounting for all elements in the matrix, improving measurement accuracy for atypical samples such as a gold ornament or heritage items [16-17].

However, the use of FP modelling, despite its notable accuracy, poses difficulties in analysing precious metals. In a prior study, an absolute error between 0.5 wt% and 1.5 wt% was observed in the gold assay of a ternary matrix of gold-silver-copper (Au-Ag-Cu) alloy when FP was utilised without calibration materials [5]. In contrast, using appropriate calibration materials and software led to an enhanced absolute error of below 0.27 wt% in the gold assay of jewelry alloys. This research addressed the systematic error associated with the standardless FP method for the Au-Ag-Cu alloy by implementing both standardless (FP) and empirical calibration with specific matrix materials. The study also aimed to explore the effects of matrix-specific materials on EDXRF gold measurements for a chosen alloy. By integrating the FP and standard empirical techniques, the investigation successfully reduced the matrix influence from silver and copper in the gold alloy [17-18]. Figure 1 displays the research roadmap for implementing the method and ensuring quality management in this EDXRF study. The findings indicated that EDXRF delivered analytical results that were either comparable to or superior to those of traditional techniques, making it beneficial for various professionals in the industry.

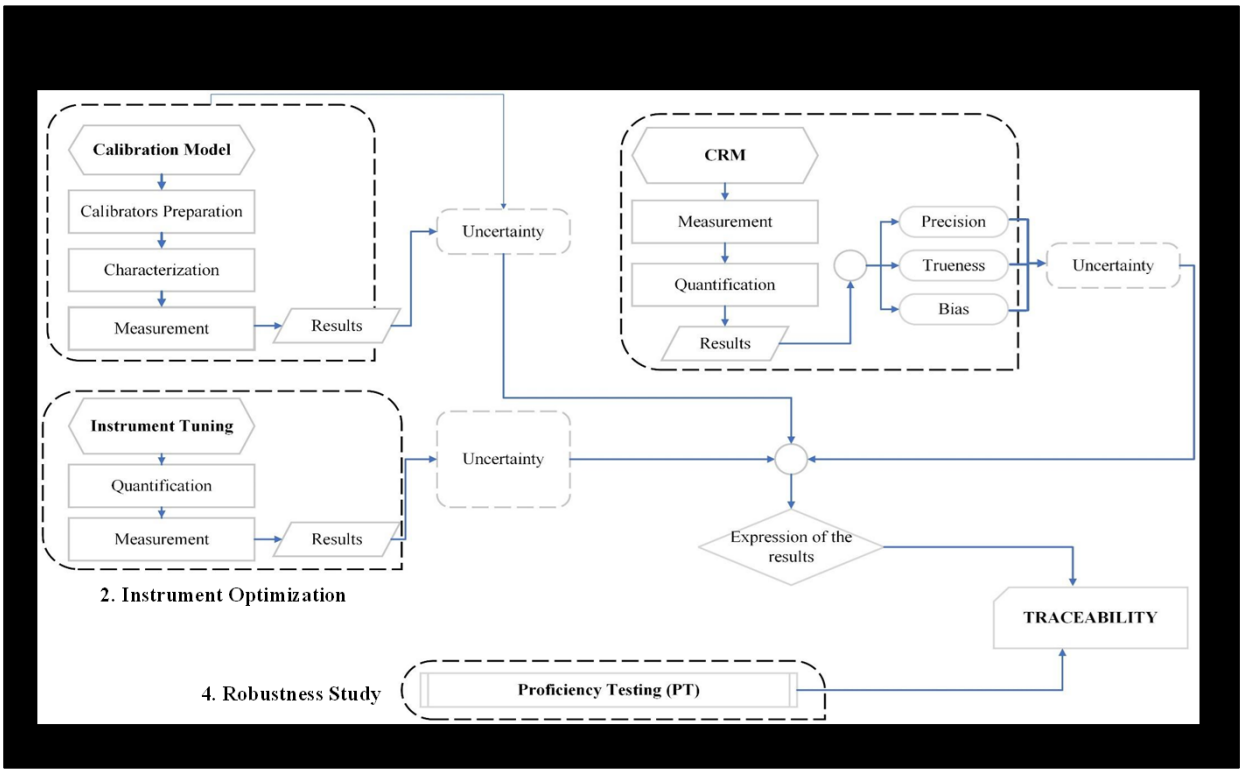

Figure 1. Research roadmap for implementation and quality management in the EDXRF method

EXPERIMENTAL

Matrix Effect Correction

Non-destructive analytical techniques like EDXRF require calibration tailored to the specific matrix. Calibration materials (CM) designed to enhance EDXRF matrix adjustment were created to imitate actual samples using uniform gold. Figure 2 depicts the development of seven unique gold matrix calibration materials. These calibration materials were made up of mixtures of gold, silver, and copper that simulated the full range of yellow gold alloys, with weight percentages varying from 75.00% to 99.99%. The materials were shaped into discs with a diameter of 12 mm and thickness between 0.25 mm and 0.30 mm.

The uniformity of the calibration materials was evaluated using an ARL OPTIM'X Wavelength Dispersive X-ray Fluorescent (WDXRF) Spectrometer. Following ASTM E826-81 [19], random measurements were performed on the surface of each disc to assess the distribution of gold content. A statistical evaluation was carried out to verify the consistency of the materials. The results were obtained by measuring the XRF radiation intensity in 10 chosen areas on both sides of each calibration material using a 1.0 mm collimator beam. The analysis of element purity indicated that the alloying elements were evenly distributed throughout all calibration materials.

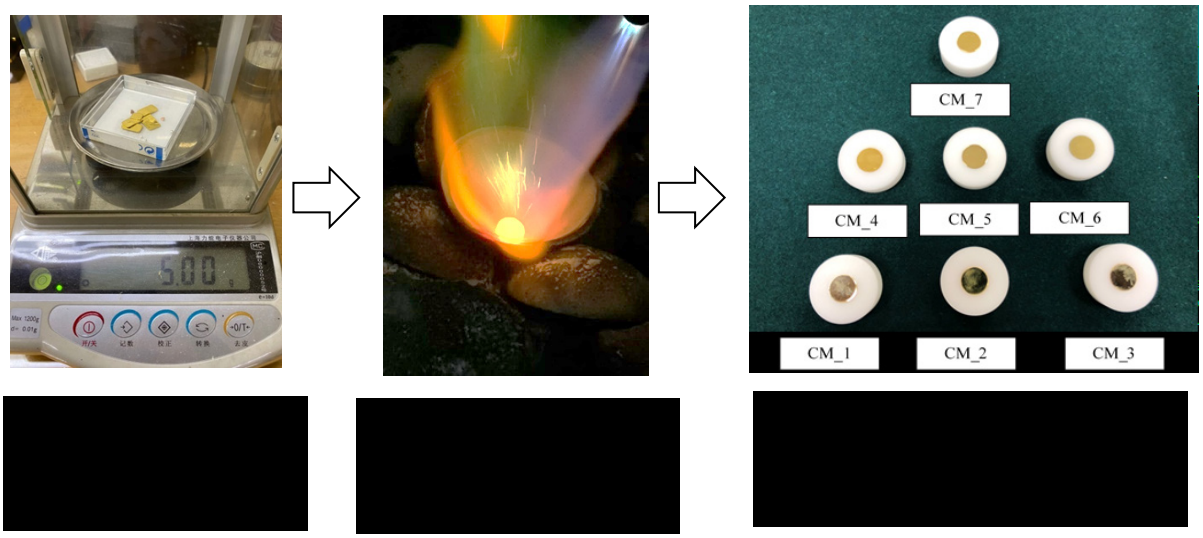

Figure 2. Preparation of calibration materials for yellow gold.

The purity of gold (Au) was evaluated through fire assay following ISO 11426 [20], a technique that utilises fusion extraction alongside dry chemical reagents. This method provides an accurate measurement of gold content with a measurement uncertainty of 0.05 wt%. The purity of silver (Ag) and copper (Cu) was determined using WDXRF in line with ISO 9516 [21]. Table 1 presents the calibration materials containing gold alloy.

Table 1. The gold matrix composed of Au-Ag-Cu in range 75.00 wt % to 99.99 wt%

Calibration Materials Code	Composition in weight fraction of percent (%)		
	Au[a]	Ag[b]	Cu[b]
CM (1)	76.34 ± 0.05	23.66 ± 0.08	0.00 ± 0.00
CM (2)	75.85 ± 0.05	0.00 ± 0.00	24.15 ± 0.10
CM (3)	74.00 ± 0.05	15.00 ± 0.07	11.00 ± 0.07
CM (4)	91.89 ± 0.05	8.11 ± 0.0.5	0.00 ± 0.00
CM (5)	91.67 ± 0.05	4.72 ± 0.04	3.61 ± 0.04
CM (6)	92.02 ± 0.05	0.00 ± 0.00	7.98 ± 0.05
CM (7)	99.90 ± 0.04	0.00 ± 0.00	0.00 ± 0.00

[a] *Purity was evaluated with the cupellation method*

[b] *Purity was evaluated by Wavelength Dispersive X-ray fluorescent (WDXRF)*

Instrument Optimization

The primary analytical instrument for this study is the Thermo ARL Quant EDXRF spectrometer located at the National Metrology Institute of Malaysia (NMIM), as illustrated in Figure 3. It features a high flux 50 W rhodium anode X-ray tube that operates within an excitation voltage range of 4 to 50 kV and has an anode current of 0.8 mA. The instrument is fitted with a Silicon Drift Detector (SDD) that includes a narrow window, which can manage high count rates while achieving resolutions of less than 165 eV FWHM (Full Width at Half Maximum) at the Mn K-alpha line. This capability provides outstanding performance across the entire periodic table, from light to heavy elements.

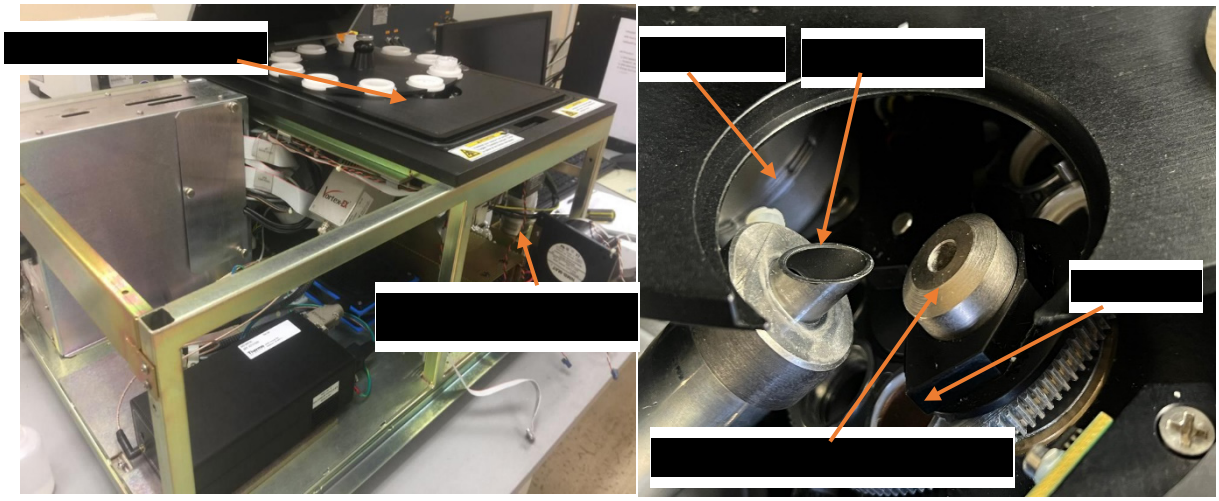

Figure 3. A Thermo ARL QUANT'X EDXRF equipped with an SDD. (The instrument is configured with a 1.0 mm collimator beam size.)

The excitation of electrons from the K-shell of silver and copper, as well as from the L-shell of gold, was achieved using voltages of 50kV and 20kV, respectively. To remove the dominant x-rays from the tube that could interfere with the element of interest, filters made of copper and palladium were utilized. To enhance the accuracy of the peak spectra for silver, gold, and copper, thick copper and palladium filters were implemented. An X-ray collimator with a diameter of 1.0 mm was employed to analyse the area of the sample and optimize the assessment. In this research, the FP model was integrated with an empirical calibration approach. A summary of the setup parameters is provided in Table 2.

Table 2. Set-up parameter of EDXRF analysis with the combined calibration method

Filter	Condition	Selected Element(s)	Counting Rate (seconds)	Method
Pd Medium,	20 kV, Vacuum medium	**Au, Cu,** Zn, Pt, Ni, W, Fe, Cr, Ti, Co, Si, Hg	120	Combination of FP model with empirical calibration materials
Cu Thick	50 kV, Vacuum medium	**Ag**, Pd, Mo, Sn, Pb, Cd, Rh, In,	120	Combination of FP model with empirical calibration materials

Method Validation

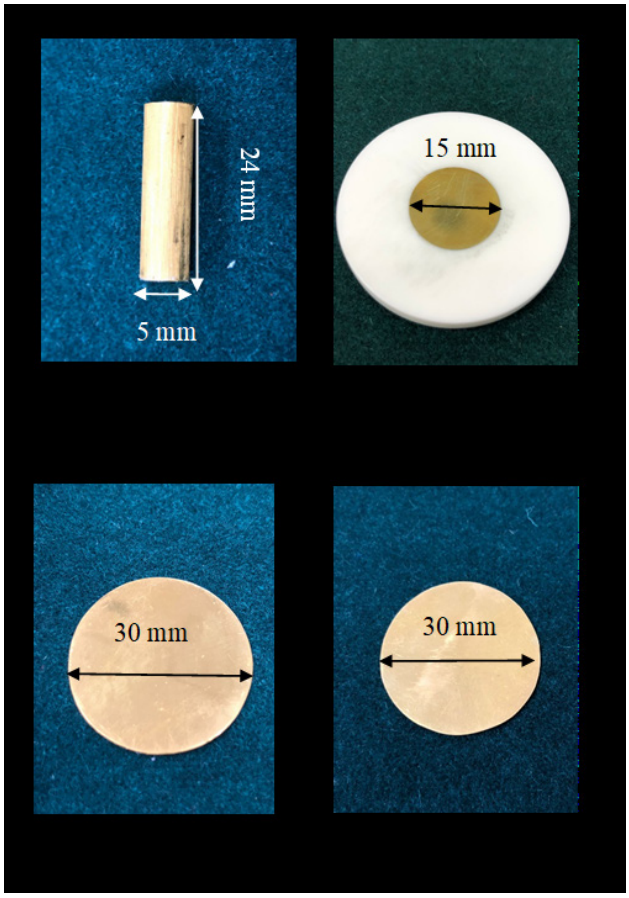

Figure 4. Four series of gold standard certified reference materials (CRMs).

In Figure 4, a selection of gold certified reference materials (CRMs) was made based on their compositions, which closely match those of the actual samples. As shown in Table 3, gold and its alloys were evaluated using fire assay and WDXRF with a 95% confidence interval expanded uncertainty. The careful choice of CRMs ensured that the gold was evenly distributed throughout the samples, adhering to ISO 17034 standards. The gold purity of ERM 508 was sourced from the Bundesanstalt für Materialforschung und Prüfung (BAM) in Germany. SRM 685R was purchased from the National Institute of Standards and Technology (NIST) in the United States. The compositions of MyRM 5.102 and MyRM 22K were certified by the National Metrology Institute of Malaysia.

Table 3. Gold alloy composition for certified reference materials (CRMs)

Mixture	Code of CRMs	Composition in mass fraction of percent (wt%)		
		Au	Ag	Cu
Au	SRM 685R	99.99 ± 0.05	-	-
Au-Ag	ERM 508	75.12 ± 0.11	24.90 ± 0.05	-
Au-Cu	MyRM 22K	91.80 ± 0.15	-	8.20 ± 0.05
Au-Ag-Cu	MyRM 5.102	92.14 ± 0.16	1.93 ± 0.05	5.96 0.04

The correction *K-factor* values for each alloy combination were modified to recalibrate the EDXRF measurements. The series CRMs were employed to validate and establish the correction *K-factor* values. These *K-factor* values were then utilised in the calculations for each analysed sample, considering the similarities of the elements in the

gold mixture. The correction *K-factor* is derived by comparing the gold value certified through the gravimetric method with the value obtained through EDXRF. The ratio of the validated gold value established the corrective *K-factor* by using the fire assay method (gravimetric) in comparison to the gold value obtained via EDXRF (Equation 1) [22].

$$K = \frac{m(Au, CRM^{grav})}{m(Au, CRM_{obs}^{XRF})} \qquad (Eq.\ 1)$$

where,

$m(Au, CRM^{grav})$ The purity of CRM gold was measured by the fire assay

$m(Au, CRM_{obs}^{XRF})$ The purity of CRM gold was measured by the XRF method

Robustness Study

The illustration in Figure 5 shows 16 gold alloy specimens (Carbon Worldwide Sdn Bhd) that possess properties akin to the gold matrix materials to assess the reliability of EDXRF measurements. Of the samples, eight were circular disks measuring 30 mm in diameter, while the remaining ones were rectangular with 10 mm x 5 mm dimensions. Each sample had a thickness of approximately 1 mm. The EDXRF analysis was performed on each sample surface five times using a 1.0 mm collimator beam. The commercial samples had compositions that appeared to be a mixture of Au, Au-Ag, Au-Cu, and Au-Ag-Cu matrices. In Table 4, a sample code demonstrates the purity determined through the fire assay.

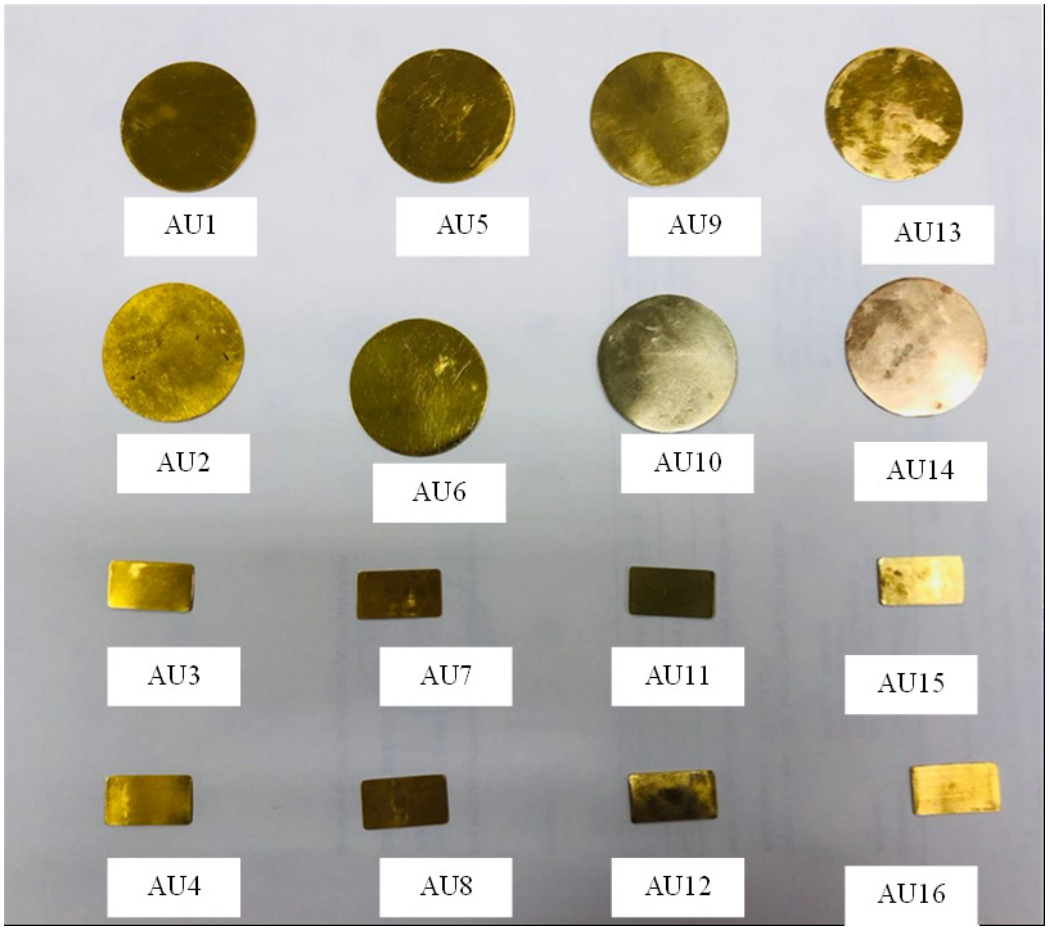

Figure 5. 16 items made of gold alloy exhibit characteristics like those of the gold matrix-specific materials.

The unknown composition of gold $m(Au, X_{obs})$ in the gold alloy sample was rectified with the factor K, which led to the value of $m(Au, X)$ as shown in *Equation 2* [23]:

$$m(Au, X) = K\ x\ m(Au, X_{obs}) \qquad (Eq.\ 2)$$

where,

$m(Au, X_{obs})$ EDXRF measurement of gold in the sample (before correction)

$m(Au, X)$ Composition of gold in the sample (after correction)

Table 4: The series of commercial gold alloy samples

Mixture	Sample code	Gold Purity (wt%)	Expanded Uncertainty, 95% confidence interval
Au	AU (1)	99.9187	0.0459
	AU (2)	99.9902	0.0452
	AU (3)	99.9903	0.0450
	AU (4)	99.9901	0.0451
Au-Ag	AU (5)	83.5013	0.0482
	AU (6)	91.7019	0.0473
	AU (7)	87.5007	0.0484
	AU (8)	75.1002	0.0491
Au-Cu	AU (9)	91.8821	0.0480
	AU (10)	91.9002	0.0471
	AU (11)	76.1203	0.0492
	AU (12)	83.5801	0.0484
Au-Ag-Cu	AU (13)	91.8901	0.0490
	AU (14)	76.3401	0.0494
	AU (15)	75.1002	0.0489
	AU (16)	74.5500	0.0498

The gold's purity was determined by using the fire assay according to ISO 11426.

RESULTS AND DISCUSSION

Correlation study of EDXRF with Fire Assay and WDXRF Method

The EDXRF spectrum displayed peaks corresponding to all the elements present in the gold alloy, as illustrated in Figure 6. The observed peaks comprised Cu Kα at 8.041 keV, Cu Kβ at 8.907 keV, Au Lα at 9.711 keV, Au Lβ at 11.439 keV, Au Lg at 13.733 keV, Ag Kα at 22.104 keV, and Ag Kβ at 24.987 keV. The purity of the alloy was evaluated by measuring the areas of the spectrum peaks for each element and applying "matrix-matching" analysis with calibration materials that had known compositions. Purity calculation was performed using Equation 1. The XRF measurements that relied on calibration materials are detailed in Table 5.

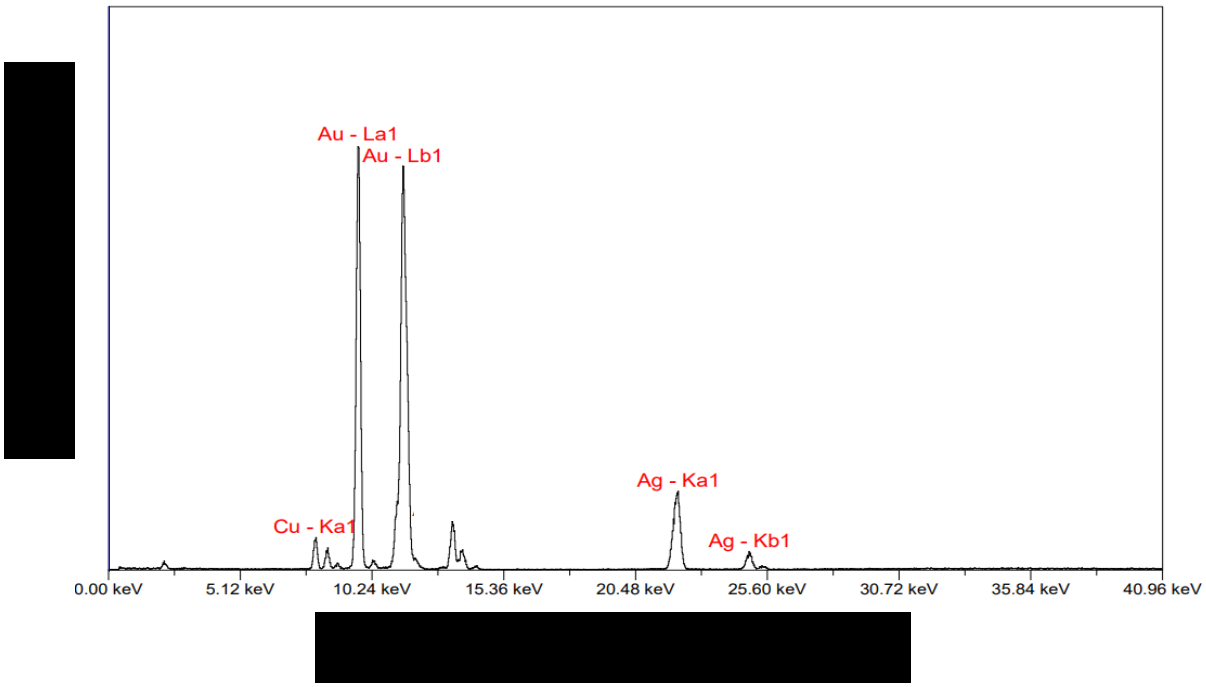

Figure 6. EDXRF Spectrum of Au–Ag–Cu alloy. The peak at lower energy was tagged as the Cu Kα peak with an energy of 8.041 keV and Cu Kβ at 8.907 keV. Au Lα and Au Lβ peaks were visible at 9.711 keV and 11.439 keV, respectively. Meanwhile, the peak at 22.104 keV was identified as the Ag Kα peak, and the Ag Kβ peak was assigned to 24.987 keV

Table 5. The purity measurement is based on a series of calibration materials (CM). The precision is expressed as an expanded standard deviation at a 95% confidence interval

Cal. sample code	Composition in mass fraction of percent (wt%)								
	Fire Assay	WDXRF		Corrected [a]			Non-Corrected [b]		
	Au	Ag	Cu	Au	Ag	Cu	Au	Ag	Cu
CM (1)	76.34 ± 0.05	23.66 ± 0.08	0.00 ± 0.00	76.30 ± 0.15	23.70 ± 0.09	0.00 ± 0.00	77.89 ± 0.32	21.74 ± 0.16	0.21 ± 0.15
CM (2)	75.85 ± 0.05	0.00 ± 0.00	24.15 ± 0.10	75.70 ± 0.15	0.00 ± 0.00	24.30 ± 0.10	74.20 ± 0.30	0.14 ± 0.15	21.82 ± 0.19
CM (3)	74.00 ± 0.05	15.00 ± 0.07	11.00 ± 0.07	74.15 ± 0.16	14.88 ± 0.08	10.97 ± 0.09	77.56 ± 0.41	12.56 ± 0.18	8.90 ± 0.18
CM (4)	91.89 ± 0.05	8.11 ± 0.05	0.00 ± 0.00	91.79 ± 0.15	8.21 ± 0.06	0.00 ± 0.00	94.45 ± 0.28	9.03 ± 0.15	0.23 ± 0.15
CM (5)	91.67 ± 0.05	4.72 ± 0.04	3.61 ± 0.04	91.60 ± 0.15	4.78 ± 0.05	3.65 ± 0.05	93.10 ± 0.27	3.28 ± 0.15	5.23 ± 0.17
CM (6)	92.02 ± 0.05	0.00 ± 0.00	7.98 ± 0.05	91.88 ± 0.17	0.00 ± 0.00	8.12 ± 0.06	90.89 ± 0.28	0.15 ± 0.05	6.15 ± 0.17

CM (7)	99.90 ± 0.04	0.00 ± 0.00	0.00 ± 0.00	99.90 ± 0.15	0.00 ± 0.00	0.00 ± 0.00	99.60 ± 0.20	0.10 ± 0.15	0.20 ± 0.15

[a] *The element composition was determined by combining fundamental parameters (FP) and an empirical standard calibration approach.*

[b] *The element composition was determined by fundamental parameters (FP) only.*

The data were then plotted to form a correlation graph between the fire assay and WDXRF as the reference with the EDXRF experimental values in mass fraction (wt%), as shown in Figures 4.4 to 7a, 7b, and 7c presents a comparative analysis of gold (Au) content determined using the EDXRF method and fire assay in the range of in 75.00 wt% to 99.99 wt%. The results are shown under two conditions: corrected and non-corrected data. This graph highlights how correction protocols impact the accuracy and consistency of the EDXRF measurements when compared to the fire assay method.

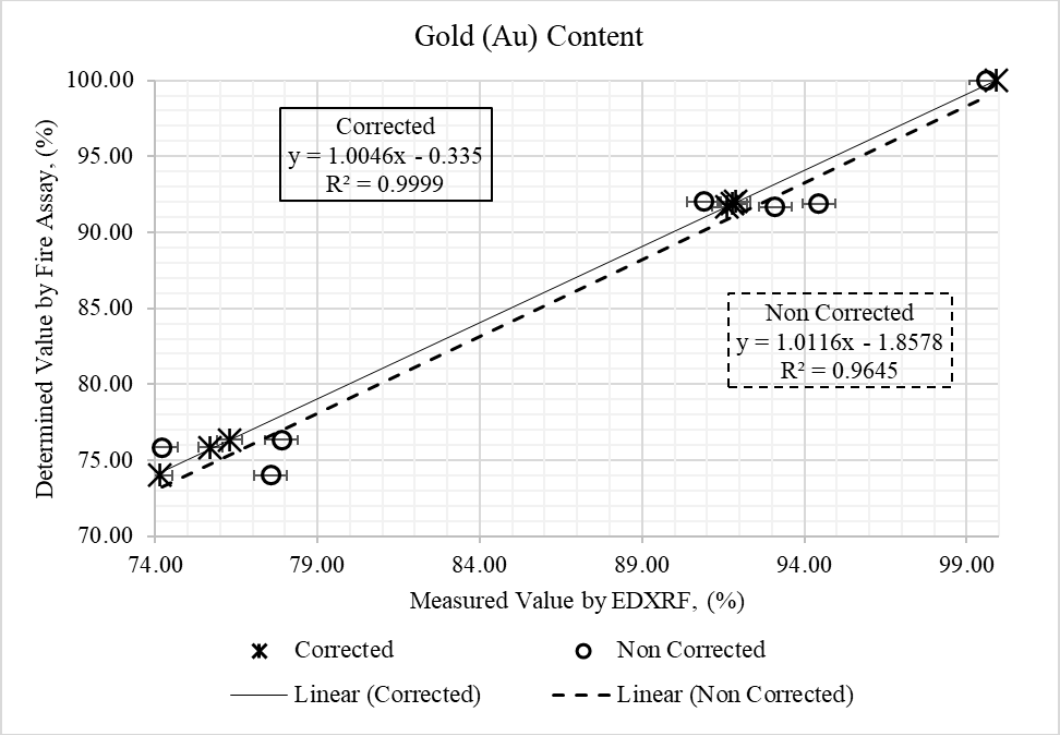

Figure 7a. Correlation graph between fire assay and EDXRF measurement (matrix corrected and non-corrected) on gold (Au) content

The corrected data, represented by the solid line, follows the regression equation y = 1.0046x - 0.335, with an R^2 value of 0.9999, indicating a nearly perfect linear relationship between EDXRF and fire assay values. The minimal intercept suggests negligible deviation, while the high R^2 confirms the reliability of the corrected EDXRF results, validating the effectiveness of the implemented correction protocols. In contrast, the non-corrected data, represented by the dashed line, follows the regression equation y = 1.0116x - 1.8578, with an R^2 value of 0.9645. Although still strong, this linear relationship shows greater deviation from 1, indicating systematic bias and increased variability, which diminishes the reliability of elemental analysis.

The differences in R^2 values emphasize the importance of correction protocols to mitigate matrix effects, instrumental biases, and calibration errors. With these corrections, EDXRF closely aligns with fire assay results, establishing it as an efficient and accurate alternative for routine gold content analysis, especially in industrial

and research settings. Non-corrected data, while indicative of trends, lack the precision needed for critical applications.

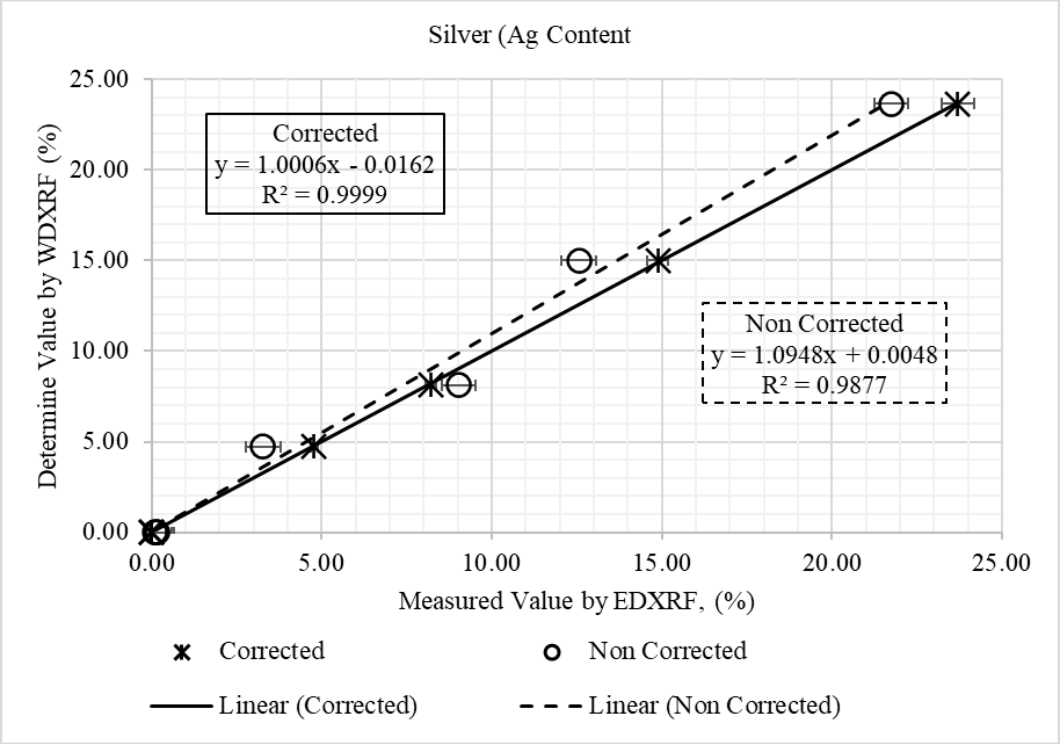

Figure 7b. Correlation graph between WDXRF value and EDXRF measurement (matrix corrected and non-corrected) on silver (Ag) content

Figure 7b illustrates the correlation between silver (Ag) content measured by the EDXRF method and WDXRF methods, the latter serving as the reference standard. The corrected data, represented by a solid line with the equation y = 1.0006x - 0.0162 and an R^2 value of 0.9999, show a nearly perfect linear relationship and negligible intercept, indicating close alignment with WDXRF. In contrast, the non-corrected data, shown by a dashed line with the equation y = 1.0948x + 0.0048 and an R^2 value of 0.9877, demonstrate a systematic overestimation and greater variability. This analysis underscores the importance of data correction in EDXRF measurements, which minimizes systematic errors and enhances accuracy. Corrected EDXRF data offer greater consistency and reliability, making it a practical, faster, and cost-effective alternative to WDXRF for silver content analysis, particularly in high-accuracy applications. Non-corrected data may suffice for preliminary assessments but lack the accuracy needed for detailed analysis.

Meanwhile, Figure 7c presents a comparative analysis of copper (Cu) content measured using EDXRF and WDXRF methods, focusing on both corrected and non-corrected data. The corrected data follow the regression equation y = 0.9946x - 0.0062 with a perfect R^2 value of 1, indicating a highly accurate alignment with WDXRF. The slope is close to 1, and the negligible intercept shows minimal deviation. In contrast, non-corrected data (dashed line) follow y = 1.1328x - 0.2392 with an R^2 value of 0.9844, indicating a systematic overestimation of copper content and significant bias. This comparison highlights the importance of correction protocols in EDXRF measurements, as corrected data demonstrate exceptional accuracy and consistency, making it a reliable analytical tool for copper content analysis when proper corrections are applied. Overall, the findings reinforce the need for robust correction techniques to achieve reliable results in elemental analysis.

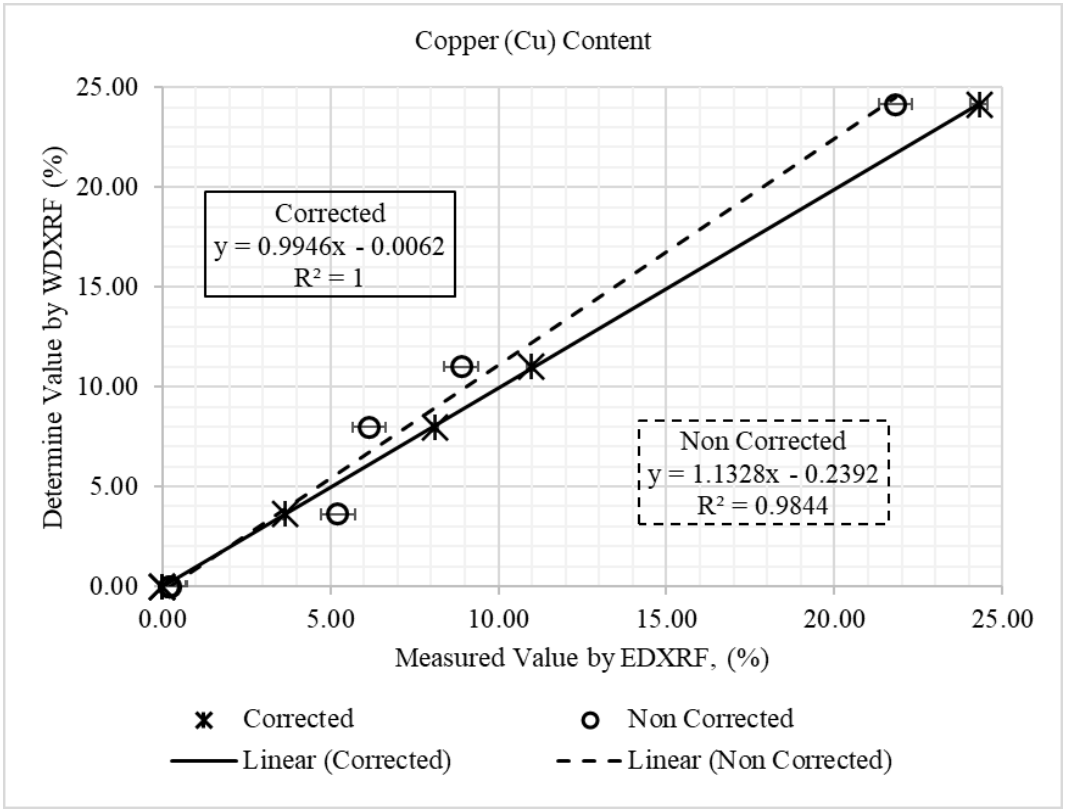

Figure 7c. Correlation graph between WDXRF value and EDXRF measurement (matrix corrected and no corrected) on copper (Cu) content

Calculation of Corrective K-Factor values

Table 6. presents a comparison of certified values and measurements obtained through EDXRF for various alloy mixtures, highlighting the effect of using a corrective *K-factor* to enhance the precision of EDXRF results. The corrective *K-factor* is determined by taking the ratio of the certified value to the experimental EDXRF measurement, as shown in *Equation 2*. This corrective *K-factor* is crucial for adjusting EDXRF measurements to align with the certified reference values.

Table 6. Corrective *K-factor* based on the compositions of gold certified reference materials.

Mixture	CRM Code	Certified Value, wt% $m(Au, X^{grav})$	XRF Measurement, wt% $m(Au, RM_{obs}^{XRF})$	Correction Factor, $k = \frac{m(Au, X^{grav})}{m(Au, RM_{obs}^{XRF})}$
Au	NIST -SRM 685R	99.99 ± 0.05	99.95 ± 0.15	1.0004 ± 0.0005
Au-Ag	BAM ERM 508	75.12 ± 0.11	75.19 ± 0.18	0.9991 ± 0.0011
Au-Cu	MyRM 22K	91.80 ± 0.15	91.95 ±0.17	0.9985 ± 0.0014
Au-Ag-Cu	MyRM 5.102	92.14 ± 0.16	92.26 ±0.18	0.9987 ± 0.0016

The corrective *K-factor* plays a vital role in addressing systematic biases that are inherent in the EDXRF measurement process. Such biases may occur due to variations in detector sensitivity, inconsistencies in calibration, or differences in the surrounding composition of alloy samples, all of which can influence fluorescence signal intensities. By utilising the corrective *K-factor,* the EDXRF measurements are modified to closely match the certified values, which is evidenced by the enhanced accuracy across the various samples.

As indicated in *Equation 2*, the corrective *K-factor* is applied to the raw EDXRF measurements to rectify the deviations noted in the experimental results. For each analysed sample, the corrective *K-factor* is determined based on the specific composition of the alloy mixture. The table illustrates how the corrected EDXRF values show greater alignment with the certified values, especially in complex mixtures containing gold (Au), silver (Ag), and copper (Cu). In a gold alloy mixture with a significant percentage of silver, the corrective *K-factor* modifies the EDXRF measurement to compensate for the fluorescence signal contributions from both gold and silver, thereby providing a more precise representation of the actual composition. Conversely, in the case of pure gold, the corrective *K-factor* addresses overestimations in the experimental ratio, which may stem from calibration difficulties associated with pure elements. These results highlight the significance of including correction protocols in EDXRF workflows to improve their accuracy and reliability for elemental analysis.

Application of corrective K-factor to unknown gold samples

Table 7. Comparison of EDXRF measurements pre and post-corrective *K-factors* against fire assay method results

Mix	Sample Code	Composition of gold in mass fraction of percent (%)						
		Fire Assay (wt%) **A**	**XRF result *pre* K-*factor* (wt%) B**	***%rsd***	***rel%* (AB) /A*100**	**XRF result post *K- factor* (wt%) C**	***%rsd***	***rel%* (AC) /A*100**
Corrective *K-factor* 1.0004 ± 0.0005								
Au	AU (1)	99.92 ± 0.05	99.88 ± 0.16	0.16	0.04	99.92 ± 0.11	0.11	0.00
	AU (2)	99.99 ± 0.05	99.94 ± 0.15	0.15	0.05	99.98 ± 0.10	0.10	0.01
	AU (3)	99.99 ± 0.05	99.93 ± 0.15	0.15	0.06	99.97 ± 0.10	0.10	0.02
	AU (4)	99.99 ± 0.05	99.93 ± 0.16	0.16	0.06	99.97 ± 0.11	0.11	0.02
Corrective *K-factor* 0.9991 ± 0.0011								
Au-Ag	AU (5)	83.50 ± 0.05	83.63 ± 0.18	0.22	-0.13	83.52 ± 0.13	0.16	-0.02
	AU (6)	91.70 ± 0.05	91.86 ± 0.16	0.17	-0.16	91.74 ± 0.11	0.12	-0.04
	AU (7)	87.50 ± 0.05	87.70 ± 0.17	0.19	-0.2	87.59 ± 0.12	0.14	-0.09
	AU (8)	75.10 ± 0.05	75.25 ± 0.17	0.23	-0.15	75.15 ± 0.12	0.16	-0.05
Corrective *K-factor* 0.9985 ± 0.0014								
Au-Cu	AU (9)	91.88 ± 0.05	92.02 ± 0.16	0.17	-0.14	91.94 ± 0.11	0.12	-0.06
	AU (10)	91.90 ± 0.05	92.03 ± 0.15	0.16	-0.13	91.95 ± 0.10	0.11	-0.05
	AU (11)	76.12 ± 0.05	76.27± 0.16	0.21	-0.15	76.20 ± 0.11	0.14	-0.08
	AU (12)	83.58 ± 0.05	83.70 ± 0.18	0.22	-0.12	83.62 ± 0.13	0.16	-0.04
Corrective *K-factor* 0.9987 ± 0.0016								
Au-Ag-Cu	AU (13)	91.89 ± 0.05	92.03 ± 0.19	0.21	-0.14	91.95 ± 0.14	0.15	-0.06
	AU (14)	76.34 ± 0.05	76.50 ± 0.18	0.24	-0.16	76.43 ± 0.13	0.17	-0.09
	AU (15)	75.10 ± 0.05	75.24 ± 0.19	0.25	-0.14	75.17± 0.14	0.19	-0.07
	AU (16)	74.55 ± 0.05	74.70 ± 0.20	0.27	-0.15	74.63 ± 0.15	0.20	-0.08

Table 7 shows a comparison of fire assay measurements and EDXRF results, presented with two decimal places. Additionally, the table outlines the values of different elements in the gold mixture both with and without the application of the corrective *K-factor values*. The relative error was determined by dividing the absolute error of the measurement by the actual measurement value. The relative error implied EDXRF's accuracy concerning fire assay values. The relative error (*rel%*) was calculated with the formula, $rel\% = (|x_1 - x_0|)/x_0) * 100$, where x_0 is the measured value from the fire assay method and x_1 refers to the measured value from EDXRF. The relative error for the method consistently improved and aligned closely with fire assay values, reaching below 0.1 *rel%* after implementing the K-factor across all analysed metals.

To assess the reproducibility of the measurements, the relative standard deviation (%rsd) was calculated. This was expressed as a percentage by dividing the standard deviation by the EDXRF measurement and then multiplying the result by 100. The findings demonstrated that the measurements showed improvement with less than 0.11 *%rsd* for pure Au, 0.16 %rsd for Au-Ag and Au-Ag-Cu mixtures, and below 0.20 *%rsd* for Au-Ag-Cu mixtures when the measurement was done with K-factor correction, in contrast to 0.16 *%rsd*, 0.23 *%rsd*, 0.22 *%rsd*, and 0.27 *%rsd* for measurements without correction, respectively. This could be attributed to the enhanced accuracy of results and decreased bias when compared to the fire assay. The corrective K-factor has been utilized for several commercial gold mixtures.

Interlaboratory Comparison (Proficiency Testing)

The NMIM laboratory has successfully participated an Interlaboratory comparison with the Institute of Metrology of Bosnia and Herzegovina (IMBIH). To evaluate the technical competence of the NMIM laboratory method, IMBIH organized the Bilateral Proficiency Testing Scheme – IMBIH.LH-B01.PT/20 on gold alloy by the international standard ISO/IEC 17043 – Conformity Assessment – general requirements for proficiency testing [24]. IMBIH prepared and distributed an unknown gold sample, with the gold purity being determined using the fire assay method. Then, NMIM analysed the sample using the improvised EDXRF method. The comparison result, displayed in Figure 8, unequivocally demonstrates the traceability of the EDXRF method to the fire assay, validating the gold purity results.

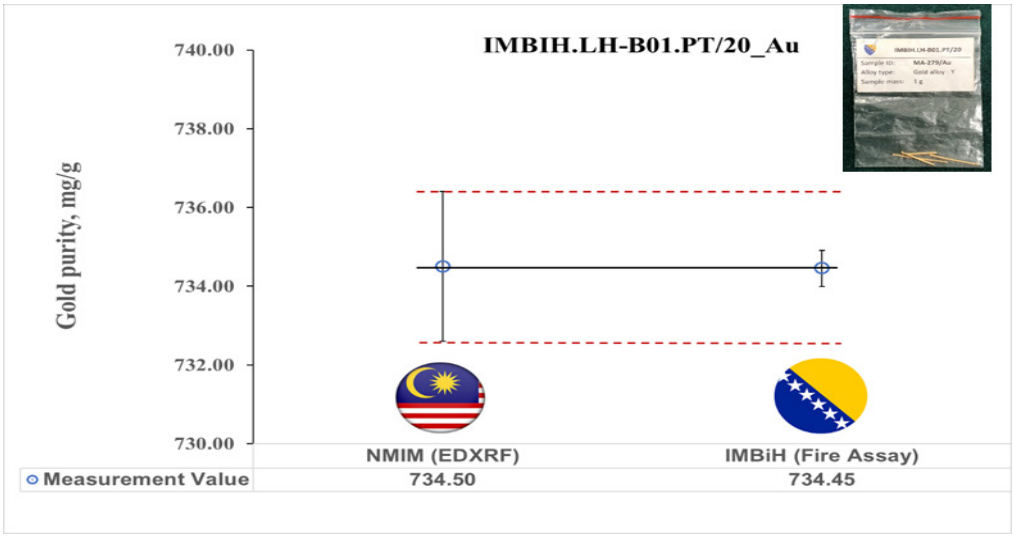

Figure 8. Comparison of improvised EDXRF method with fire assay through proficiency testing (PT)

Table 8 summarizes the results of proficiency testing (PT) for the MA-279/Au sample, comparing the measured value by NMIM EDXRF of gold purity with an assigned value by reference lab, IMBIH. The table also includes the z'-score, which evaluates the laboratory's performance relative to the reference. The measured value reported

by the laboratory (lab) is 734.50 with an associated uncertainty ($u$lab) of 0.95 mg/g. The reference value (ref) is 734.45 mg/g with a reference uncertainty (uref) of 0.23 mg/g. A z'-score of 0.09 is well within the acceptable range ($|z'| \leq 2$ indicating that the laboratory's result is consistent with the reference value and falls within acceptable performance limits.

A conclusion, the proficiency testing results for the MA-279/Au sample demonstrate a high degree of accuracy and reliability in the laboratory's measurements. The close alignment between the measured value and the reference value confirms the laboratory's strong performance and adherence to quality standards. These findings support the validity of the reported gold concentration and highlight the robustness of the analytical methods employed.

Table 8 Results of proficiency testing (PT) for the MA-279/Au sample, comparing the measured value by NMIM EDXRF of gold purity with an assigned value by reference lab, IMBIH

PT sample Code	Measured Value (%)					
	Ref (IMBIH)	u_{REF}	Lab (NMIM	u_{LAB}	Lab - Ref	z' score
MA 279/Au	734.45	0.23	734.50	0.95	0.05	0.09

CONCLUSION

The integration of FP with materials specific to the matrix offers a highly dependable approach for assessing the purity of precious metals through EDXRF. This reliable technique was effectively utilised to examine various gold alloys, such as Au-Ag, Au-Cu, and Au-Ag-Cu. Employing calibration materials tailored to the matrix significantly improved the precision of the EDXRF readings. An exceptional correlation ($R^2 = 0.9999$) was found between the certified reference values and the EDXRF readings for all metals. The method's validation using certified reference materials allowed for the determination of the corrective *K-factor*, leading to an unprecedented enhancement in accuracy, with a consistent relative error of under 0.1*%rel* for all metals in comparison to fire assay values. Furthermore, the relative standard deviation *(%rsd)* demonstrated notable improvement alongside the *K-factor* adjustment. These results highlight the substantial influence of gold alloy compositions on the precision of EDXRF measurements. Although this research aimed to introduce a non-destructive method for gold assaying as an alternative to the conventional fire assay, the thorough methodology and solid results obtained provide a strong argument for ongoing investigation into non-destructive EDXRF techniques for gold evaluation.

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