VARIATION IN THE COLLIMATOR BEAM SIZE OF ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY FOR IMPROVED MEASUREMENT OF GOLD PURITY

A. A. M. Mazuki [1,2*], M. M. Mahat [1], R. Ramli [1], S. Abdullah [1]

[1] Universiti Teknologi MARA, Faculty of Applied Science,
40450 Shah Alam, Selangor, Malaysia; e-mail: mmuzamir@uitm.edu.my, adlan@sirim.my
[2] National Metrology Institute of Malaysia, SIRIM Berhad 43900 Sepang, Malaysia

The demand to improve the efficiency of precious metal trade has been increasing of late. Due to its non-destructive nature, energy-dispersive X-ray fluorescence has the potential to supplant the fire assay procedure. Improved accuracy in the measurement of gold purity can be achieved by optimizing the X-ray fluorescent signal by selecting a suitable collimator beam size. Four homogenous materials with different alloy matrix of gold-certified reference were investigated. The effects of collimator beam sizes on the accuracy of gold purity evaluation were observed. The findings can be treated as the foundation to improve the accuracy of gold purity measurement with X-ray fluorescence.

Keywords: *gold, X-ray fluorescence, collimator beam.*

ВАРЬИРОВАНИЕ РАЗМЕРА ПУЧКА КОЛЛИМАТОРА ПРИ ЭНЕРГОДИСПЕРСИОННОЙ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ ДЛЯ БОЛЕЕ ТОЧНОГО ИЗМЕРЕНИЯ ЧИСТОТЫ ЗОЛОТА

A. A. M. Mazuki [1,2*], M. M. Mahat [1], R. Ramli [1], S. Abdullah [1]

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[1] Технологический университет МАРА,
40450 Шах-Алам, Селангор, Малайзия; e-mail: mmuzamir@uitm.edu.my, adlan@sirim.my
[2] Национальный метрологический институт Малайзии, 43900 Сепанг, Малайзия

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Для повышения точности измерения чистоты золота применена энергодисперсионная рентгеновская флуоресценция как неразрушающий метод анализа. Повышенная точность может быть достигнута за счет оптимизации рентгеновского флуоресцентного сигнала путем выбора подходящего размера луча коллиматора. Исследованы четыре однородных материала с различными матрицами из сплава сертифицированного золота. Изучено влияние размеров луча коллиматора на точность оценки чистоты золота. Полученные результаты можно рассматривать как основу для повышения точности измерения чистоты золота с помощью рентгеновской флуоресценции.

Ключевые слова: *золото, рентгеновская флуоресценция, коллимированный пучок.*

Introduction. The purity of gold (Au) and other precious metals can be evaluated with several chemical and spectroscopic methods [1–4]. However, the most common method to measure gold content is the traditional fire assay. The assay chemically separates gold content through cupellation from the whole material. The second step requires the application of a high-accuracy weighing scale to determine the percentage of gold content. The fire assay conforms to the ISO 11426 standard, which guarantees accuracy and repeatability [4–6]. For instance, Jotanovic et al. reported a deviation of less than 0.03% after performing a fire assay (cupellation) method on 14-carat jewellery [4]. Due to its unparalleled accuracy, Artyukh et al. stated that the fire assay method is popular among the member countries of the International Convention [5]. Battaini et al. echoed the same statement, adding that the fire assay method is still practised among goldsmiths [6].

However, despite its widespread use, the fire assay method entails a few inherent disadvantages, such as its destructive nature [4, 5], reliance on chemicals [6], and time-consuming process [7]. Several spectrometry techniques have been developed to fulfill the needs of quality assurance of alloys and assaying of final products. These novel techniques include inductively coupled plasma (ICP) [8, 9], atomic absorption spectrometry (AAS) [9], laser-induced breakdown spectrometry-partial least squares (LIBS-PLS) [10], and X-ray fluorescence spectroscopy [11, 12].

Among the techniques stated above, energy-dispersive X-ray fluorescence spectroscopy (EDXRF) has gained immense popularity in recent years. It is a superior alternative to the standard fire assay method due to its nondestructive method, rapid test results, and easier sample preparation [13–15]. Nevertheless, the size and shape of the precious metal sample are factors for EDXRF's accuracy. The dimension of the sample can influence the accuracy of the measurement through the detected outbound fluorescent signal (X-Ray out) as the beam diameter changes [16, 17]. The effectiveness of the collimator beam to narrow the X-Ray beam on the target sample is shown in Fig. 1. Selecting a suitable collimator beam size that is relevant to the area of the target sample can optimize the X-ray fluorescent signal that contributes to measurement accuracy.

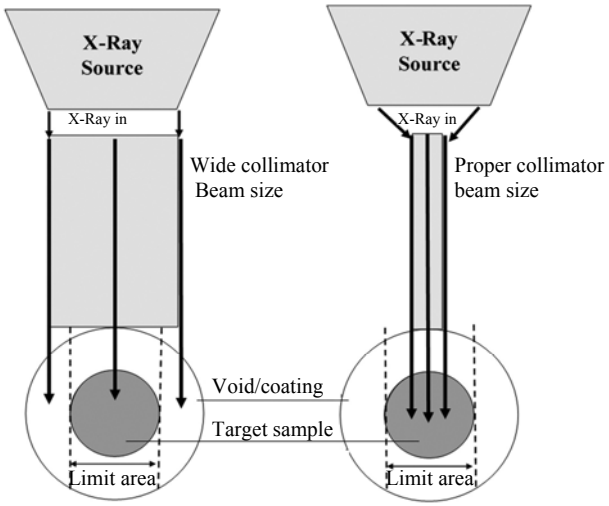

Fig. 1. Effectiveness of collimator beam on narrowing the X-ray beam to the target samples.

The collimator, some researchers have claimed, should be selected based on the sample's dimension and the objective of generating excitation of elements of interest [18]. The selection of the best collimator is crucial for the nondestructive analysis of nonhomogenous samples, including jewelry [14, 19–21]. It is important to note that the outbound fluoresced X-rays should come from the gold instead of the adjacent solder joint [22, 23]. This paper aims to ascertain the relationship between the diameter of the collimator beam and the accuracy of the gold measurement.

Experimental. *Instrumentation setup.* The condition parameters of the Thermo ARL Quant EDXRF were set up according to the suitable energy (keV) of the selected elements as shown in Table 1. The selection of filters was based on a recommendation from the manufacturer to improve the peak to background ratios. The counting rate was based on an excellent calibration fit. The fundamental parameter (FP-Theoretical) with an appropriate calibration standard was applied to compensate for the matrix effects of complex precious metal [24]. In this study, the correction was performed with the least-squares best fitting to several reference materials such as Au, Ag, Cu, Zn, and Ni. Four collimator beams with different diameters were designed to investigate their effects on the accuracy of the EDXRF measurement (Table 2).

TABLE 1. Setup Parameter of Energy Dispersive X-Ray Fluorescence

Filter	Condition	Selected element	Counting rate, s	Method
Palladium Medium	20 kV, vacuum medium	Au, Cu, Zn, Ni	60	Fundamental parameter with calibration standard
Copper Thick	50 kV, vacuum medium	Ag	60	Fundamental parameter with calibration standard

TABLE 2. Effectiveness of Surface Area Based on the Size of the Collimator Beams

Type	Diameter of collimator beam, mm	Effective diameter, mm	Effective spot area, mm^2
Collimator 1	1.00	2.06	3.33
Collimator 2	2.00	3.10	7.55
Collimator 3	3.50	5.60	24.63
Collimator 4	8.80	13.00	132.73

Materials. Four certified reference materials (CRM) with various circular surface area and gold purity content were used in this study, as shown in Fig. 2. The selection of CRM is essential to ensure the homogeneous distribution of gold in the samples.

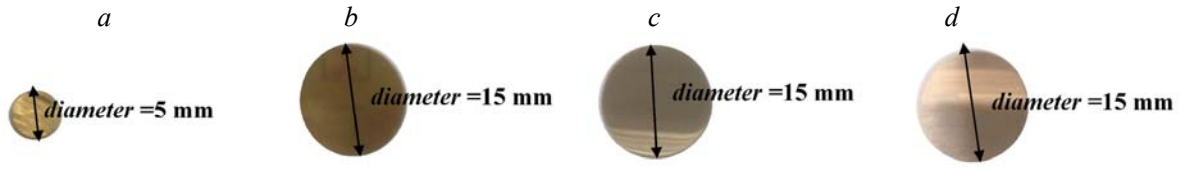

Fig. 2. Certified reference materials with different types and surface area:
a) SRM 685R; b) ERM 508, c) ERM 507; d) ERM 506.

TABLE 3. The Gold Purity Content with the Surface Area of Certified Reference Materials

Certified reference materials	Alloy mixture	Certified gold purity, %	Sample diameter (d, mm)	Calculated area, mm^2
SRM 685R	Au	99.99	5.00	19.64
ERM 508	Au-Ag	75.12	15.00	176.72
ERM 507	Au-Ag-Cu-Zn-Ni	75.1	15.00	176.72
ERM 506	Au-Ag-Cu-Zn	58.56	15.00	176.72

The gold purity content and surface area are shown in Table 3. ERM 508, ERM 507, and ERM 506 were purchased from Bundesanstalt fur Materialforschung und Prufung (BAM), Germany, while SRM 685 was purchased from the National Institute of Science and Technology (NIST), USA.

Results and discussion. *Effect of collimator beam size on the fluorescent signal.* The X-ray spectrum of the fluorescent signal of the four certified reference materials (CRMs) with the unit of counts per second (cps) against the collimator beam size is displayed in Fig. 3. The spectrum of CRMs based on the matrix elements in the samples is shown as Fig. 3, which represent SRM 685R, ERM 508, ERM 507, and ERM 506, respectively. The changes in the gold element peak at 9.72 keV for AuL_α and 11.44 keV for AuL_β were observed. As the collimator beam size increases, the fluorescent signal was discovered to increase in tandem. The increase in the Au peak fluorescent signal was due to the height of the solid angle, which was subtended by the detector as the opening of the collimator increased. Thus, the detection of the Au XRF peak was achieved by increasing the diameter of the collimator beam, indicating the increase in the acceptance angle of the detector's face. However, a low fluorescent signal was recorded when an 8.8 mm collimator was used.

A similar observation was recorded when a 3.5 mm collimator was used on the SRM 685R sample. Although their X-ray fluorescent signal was higher compared to the obtained signal with the 2.00 and 1.00 mm, collimator, the 'void' due to the discrepancies between the measured area and the size of the targeted sample led to the loss of fluorescent signal. However, smaller collimators are not without flaws. With smaller collimators, the XRF detector could only capture a low fluorescent signal due to the narrower X-ray beam on the sample target. This minimal fluorescent signal led to poor spectral distribution. Furthermore, the presence of more dominant elements in the sample could have contributed to this low signal observation [16–18, 22].

Effect of collimator beam sizes on accuracy of X-ray fluorescent. The differences in gold purity percentage against the certified values are summarized in Table 4. These disparities came about due to the range of applied collimator beam sizes.

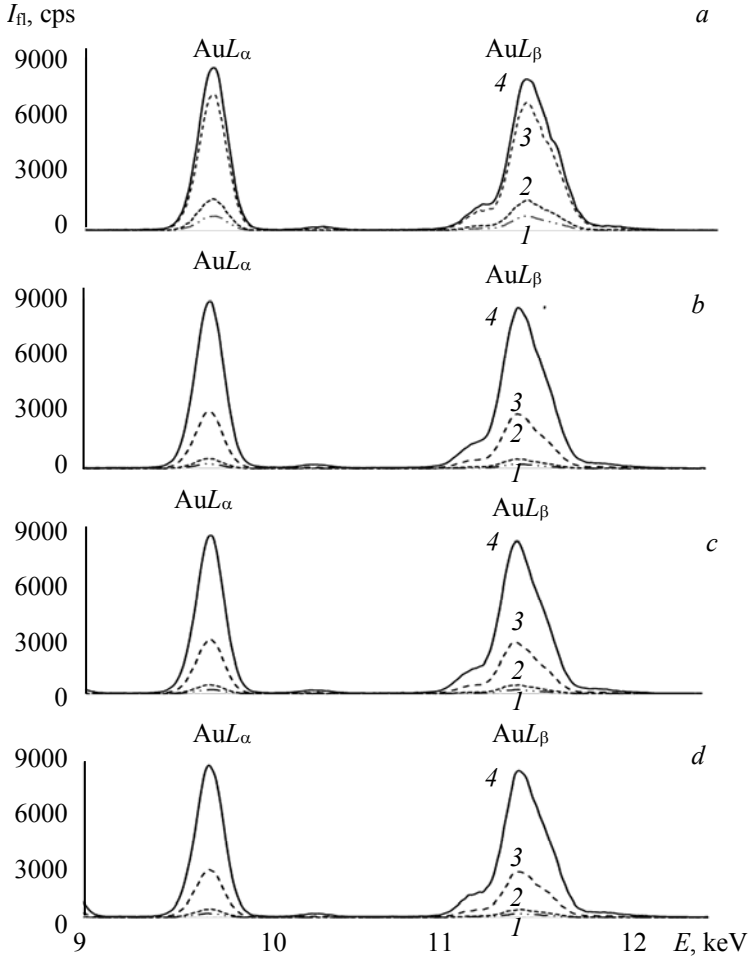

Fig. 3. X-ray spectrum of four certified reference materials: a) SRM 685R, b) ERM 508, c) ERM 507, d) ERM 506 against collimator beams of 1.0 (1), 2.0 (2), 3.5 (3), and 8.8 mm (4).

For SRM 685R, the collimator beam of sizes 8.8, 3.5, and 1.00 mm recorded differences of 1.98, 0.21, and 0.09%, respectively. The 2.00 mm collimator beam had the smallest difference at 0.05%. The loss in fluorescent signal was caused by the application of a collimator beam that was larger than the target sample. This phenomenon compromised measurement accuracy. Minimizing the loss in fluorescent signal and improving measurement accuracy can be achieved by utilizing a smaller collimator beam [17].

TABLE 4. The EDXRF Experimental Result of Gold Purity (%) Compared with the Certified Value

Sample	Certified	Experimental, %							
		8.8 mm	*d*	3.5 mm	*d*	2.0 mm	*d*	1.0 mm	*d*
SRM 685R	99.99	98.06	1.93	99.78	0.21	99.94	0.05	99.90	0.09
ERM 508	75.12	74.59	0.53	75.01	0.11	75.28	–0.16	74.84	0.28
ERM 507	75.1	74.25	0.85	75.13	–0.03	75.27	–0.17	74.92	0.18
ERM 506	58.56	57.70	0.86	58.48	0.08	58.89	–0.33	58.16	0.40

N o t e. *d* = differences.

For ERM 508, the collimator beams of sizes of 8.8, 2.00, 1.0, and 3.5 mm recorded the differences of 0.53, 0.16, 0.28, and 0.11%, respectively. This improvement in accuracy in measurements was possible due to the higher detection of fluorescent signals. The sizes of the collimator beam matched the area of the target samples and, thus, contributed to better measurement accuracy. Even though the 1.0 and 3.5 mm, collimator beam were not significantly different in terms of size, the recorded differences between the experimental

value and the certified value were remarkable. The low fluorescent signal caused the rest of the elements in the sample to assert their dominance over gold, which subsequently compromised the measurement accuracy [17, 18]. A similar theory was observed with ERM 507 and ERM 508. The difference was greater when an 8.8 mm collimator beam was used instead of the 3.5 mm collimator beam. Overall, the results proved that the collimator beam size affects the accuracy of XRF analysis [17, 18, 22].

Conclusions. The application of a suitable collimator beam gave positive impacts on the X-ray fluorescent signal and measurement accuracy. A minimum multiple scattering background was detected when a narrow detector collimator was used. This process can be capitalized to improve the measurement focus on a sample subjected to EDXRF analysis. Besides, increasing the diameter of the collimator beam will increase the number of counts (fluorescent signal), thus improving the accuracy. However, the size and shape of the precious metal sample can influence the accuracy of the measurement as it affects the amount of outbound fluorescent signal captured by the detector as the beam diameter changes. An appropriate selection of the collimator beam size suitable with the area of the target sample is important to optimize EDXRF analysis. Furthermore, this study could add value to the precious metal industry by instilling confidence in the accuracy of the X-ray fluorescence measurement.

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REFERENCES

1. S. Caporali, S. Bellandi, M. Innocenti, O. Lopilato, L. Romualdi, G. Pezzatini, *Gold Bull.*, **43**, No. 2, 122–130 (2010).
2. M. I. Dzyubenko, S. N. Kolpakov, D. F. Kulishenko, A. A. Priyomko, *J. Appl. Spectrosc.*, **77**, No. 2, 279–284 (2010).
3. A. P. M. Content, *Platinum Met. Rev.*, **55**, No. 4, 281–283 (2011).
4. A. Jotanović, M. Memić, Š. Suljagić, J. Huremović, *Bull. Chem. Technol. Bosnia Herzegovina*, **38**, 13–18 (2012).
5. T. Artyukh, I. Hryhorenko, A. Ternova, S. Yaheliuk, M. Cernavca, *Eastern-European J. Enterprise*, **5**, No. 12, 6–18 (2018).
6. P. Battaini, E. Bemporad, D. De Felicis, *Gold Bull.*, **47**, No. 1-2, 9–20 (2014).
7. H. Li, S. J. Shi, X. Wang, Y. Zhu, N. Yu, Y. J. Wang, *Adv. Mater. Res.,* **1120**, 1350–1355 (2015).
8. A. P. M. Content, *Platinum Met. Rev.*, **55**, No. 4, 281–283 (2011).
9. M. Balcerzak, *Anal. Sci.*, **18**, No. 7, 737–750 (2002).
10. D. Díaz, D. W. Hahn, A. Molina, *Spectrochim. Acta B: At. Spectrosc.*, **136**, 106–115 (2017).
11. A. Buccolieri, A. Castellano, E. Degl'Innocenti, R. Cesareo, R. Casciaro, G. Buccolieri, *X-Ray Spectrom.*, **46**, No. 5, 421–426 (2017).
12. I. Tissot, M. Tissot, M. Manso, L. C. Alves, M. A. Barreiros, T. Marcelo, M. F. Guerra, *Nucl. Instrum. Methods Phys. Res. B: Beam Interact. Mater. At.*, **306**, 236–240 (2013).
13. M. Ghosh, K. K. Swain, T. A. Chavan, D. N. Wagh, R. Verma, *X-Ray Spectrom.*, **44**, No. 1, 13–15 (2015).
14. A. Jurado-López, L. De Castro, R. Pérez-Morales, *Gold Bull.*, **39**, No. 1, 16–21 (2006).
15. Z. Sándor, S.Tölgyesi, I. Gresits, M. Káplán-Juhász, *J. Radioanal. Nucl. Chem.*, **246**, No. 2, 385–389 (2000).
16. M. W. Marashdeh, *Heliyon*, **4**, No. 8, E00724 (2018).
17. M. Singh, G. Singh, B. S. Sandhu, B. Singh, *Appl. Rad. Isotop.*, **64**, No. 3, 373–378 (2006).
18. R. Sitko, B. Zawisza, E. Malicka, *Spectrochim. Acta B: At. Spectrosc.*, **64**, No. 5, 436–441 (2009).
19. A. Pitarch, I. Queralt, *Nuclear Instr. Methods Phys. Res. B: Beam Interact. Mater. At.*, **268**, No. 10, 1682–1685 (2010).
20. F. M. Nor, A. R. Tamuri, A. K. Ismail, *Int. J. Eng. Technol.*, **8**, No. 1, 165–172 (2019).
21. M. J. Navas, A. G. Asuero, A. M. Jiménez, *Appl. Spectrosc.*, **70**, No. 1, 207–221 (2016).
22. S. Scrivano, B. Gómez-Tubío, I. Ortega-Feliu, F. J. Ager, A. I. Moreno-Suárez, M. A. Respaldiza, A. Marmolejo, *X-Ray Spectrom.*, **42**, No. 4, 251–255 (2013).
23. K. O. Emeriewen, F. E. Oladugbagbe, *Int. J. Conserv. Sci.*, **5**, No. 3, 321–328 (2014).
24. R. M. Conrey, M. Goodman-Elgar, N. Bettencourt, A. Seyfarth, A. Van Hoose, J. A. Wolff, *Geochem.: Exp., Environ., Anal.*, **14**, No. 3, 291–301 (2014).