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Determination of trace elements in refined gold samples by inductively coupled plasma atomic emission spectrometry

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Abstract: This paper presents a method for the determination of trace contents of silver, copper, iron, palladium, zinc and platinum in refined gold samples. A simultaneous inductively coupled plasma atomic emission spectrometer in the radial torch position and with a cross flow nebulizer was used for the determinations. In order to compare the different calibration strategies, two sets of calibration standards were prepared. The first set was based on matrix matched calibration standards and the second was prepared without the addition of matrix material. The detection limits for the matrix-matched calibrations were higher for some elements than those without matrix matching. In addition, the internal standardization method was applied and experiments indicated that indium was the best option as the internal standard. The obtained results for gold samples with matrix matched and matrix free calibrations were compared with the results obtained by the standard addition method. The accuracy of the methods was tested by performing a recovery test. The recoveries for the spiked sample were in the range of 90–115 %. The accuracy of the methods was also tested by analysis of a certified reference material of high purity gold AuGHP1. The best results were achieved by matrix free calibration and standard addition method using indium as the internal standard at a wavelength of 230 nm.

Keywords: refined gold samples; trace elements; ICP-AES; certified reference material of high purity gold AuGHP1.

INTRODUCTION

Gold, one of the most important precious metals, is widely used in different fields of science, mostly in microelectronic and medicine. During the last few years, gold has found extensive application in diagnostics and therapy of diffe-

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rent types of cancer. The application of gold mostly depends on its purity. The presence of trace impurities could significantly affect its physical and chemical properties. Therefore, it is very important to find a rapid and accurate technique for the determination of trace elements in refined gold samples. In the Mining and Metallurgy Institute Bor, high purity gold is produced from different materials, mostly from anode slime and electrical waste by a long process of purification and finally by reduction of gold with SO₂ gas or by electrolytic separation of gold. The American Society for Testing and Materials established the maximum allowed concentrations of some elements in 99.99 % purity gold (ASTM B562-95) standard,¹ as shown in Table I.

TABLE I. Maximum allowed concentrations of the investigated elements according to the requirements ASTM B562-95 standard¹ for 99.99 % purity gold

Element	Concentration, mg kg ⁻¹
Ag	90
Cu	50
Pd	50
Fe	20

A detailed study of the literature revealed that there are not many published papers that present results for the determination of trace elements in pure gold. The determination of major constituents in precious metals is mostly realized by fire assay and trace elements are determined using different spectrometric methods. During the 1960s and 1970s, the determination of trace elements in pure gold was performed by the emission spectrographic technique with different excitation sources, such as arc and glow discharge lamp.^{2,3} Atomic absorption spectrophotometry with a graphite furnace (ETAAS) or flame (FAAS) was used for the determinations of some elements in pure gold during 1990s.⁴⁻¹¹ In the last few years, inductively coupled plasma atomic emission spectrometry (ICP-AES)^{12,13} and especially inductively coupled plasma mass spectrometry (ICP-MS)¹⁴⁻²¹ and laser ablation inductively coupled plasma mass spectrometry (laser ablation-ICP-MS)²² have been extensively applied. Electrochemical techniques were also used for the determination of some trace elements in pure gold, in particular, stripping voltammetry was used for the determination of arsenic(III) and silver.^{23,24} Trace elements in gold and its alloys samples were determined by synchrotron radiation X-ray fluorescence spectrometry (SR-XRF)^{25,26} and energy dispersive X-ray spectrometry (EDXRF).²⁷

In order to improve the sensitivity and to reduce matrix effects, many researchers used a combination of different pre-concentration methods or matrix separation with instrumental analysis, mostly by FAAS, ETAAS, AES-ICP or ICP-MS for the determination of trace elements in pure materials. Procedures that involve separation steps for the complete removal of the matrix are often

tedious and complicated, thereby increasing the risk of contamination with the resulting worsening of the detection limits. On the other hand, the direct determination of trace elements has some advantages, such as minimizing sample preparation, reducing the potential risk of sample contamination, simplicity of use and rapidity.

In this paper, a direct determination of silver, copper, iron, palladium, zinc and platinum in refined gold samples was realized by application of simultaneous inductively coupled plasma atomic emission spectrometry.

EXPERIMENTAL

Apparatus

All measurements were performed using a Spectro Ciros Vision simultaneous inductively coupled plasma atomic emission spectrometer (Germany) and controlled by Smart Analyser Vision software. This device is provided with a radial torch position and a cross flow nebulizer, a double grating spectrometer with 22 linear CCDs as detectors situated on a Rowland circle, allowing a spectral range of 125–770 nm. The energy for the plasma was obtained by a free-running 27.12 MHz generator.

In the present investigations, the most sensitive and recommended wavelengths²⁸ of the analyzed elements were selected as much as possible free from spectral interferences from the gold matrix and other elements present in the samples (Table II). Emission peaks of analytes were symmetrical and well resolved from the gold peaks. The appropriate spline or polynomial corrections were applied for subtraction of background intensities from the analytical line of calibration standards and unknown samples.

TABLE II. Wavelengths used for the determination of the trace elements in refined gold

Element	Wavelength, nm
Ag	328.068
Cu	324.754
Pd	340.458
Fe	259.941
Pt	214.423
Zn	213.856

Preparation of calibration standard solutions

All chemicals and acids were of analytical grade. Calibration solutions of the elements Ag, Cu, Pd, Fe, Pt and Zn were prepared. They were prepared from the corresponding 1 g L⁻¹ stock solutions (Accu Standards, USA). Ultra pure deionized water was used for the dilution and preparation of the calibration standards at the desired concentration.

Two sets of calibration standards were prepared, *i.e.*, matrix-matched with and without internal standard and aqueous calibration standards also with and without internal standard. Fresh calibration standards were prepared before each analysis. This procedure was applied to reduce the possibility of precipitation the analyte elements that could occur if the diluted solutions were kept for some time.

Matrix-matched calibration standards were prepared so that all the calibration standards had the same concentration of matrix as the unknown samples. To this aim, 0.1000 g of pure gold powder, obtained from the laboratory of the Mining and Metallurgy Institute Bor, was

weighed and dissolved in 8 mL *aqua regia*. After complete dissolution, the gold solution was cooled and quantitatively transferred into a 10 mL volumetric flask. Then 1 mL of a solution containing all the mentioned trace elements at a concentration of 10 mg L⁻¹ was added and diluted with ultra pure deionized water to the final volume (10 mL); hence, the individual concentration of each element was 1 mg L⁻¹. This procedure was repeated for lower concentrations of the calibration samples. Indium was used as the internal standard at a concentration of 1 mg L⁻¹.

The concentration of the elements both with the internal standard and with standard additions were calculated according to Skoog.²⁹

In order to compare the obtained results by different calibration strategies and to conclude which is the best, different sets of calibration standard solutions were made. All six strategies are present in Table III.

TABLE III. Name of the analytical program, type of calibration standard and wavelength of the internal standard

Analytical program name	Type of calibration standard	Internal standard, nm
Au-H ₂ O	Matrix free	None
Au-Au	Matrix matching	None
Au-In230-H ₂ O	Matrix free	In II 230.606
Au-In230	Matrix matching	In II 230.606
Au-In325-H ₂ O	Matrix free	In I 325.609
Au-In325	Matrix matching	In I 325.609

Preparation of the samples and the certified reference material

Refined gold samples of unknown composition were weighed (0.5000 g) and dissolved in 40 mL *aqua regia*. After complete dissolution, the gold solutions were cooled, quantitatively transferred into 50 mL volumetric flasks. Indium was added as the internal standard in a concentration of 1 mg L⁻¹.

The certified reference material of high pure gold AuGHP1 (Order No. IA/7075/10, Rand Refinery Ltd., South Africa) was prepared in the same manner.

For the standard addition method, the gold samples and certified reference material were prepared as follows: after weighing (0.5000 g), they were dissolved in 40 mL *aqua regia*. After complete dissolution, the gold solutions were evaporated to a smaller volume, cooled, and quantitatively transferred into 25 mL volumetric flasks. Three aliquots of gold solution of 5 ml were transferred into 10 mL volumetric flasks. The first was diluted to the final volume with ultra pure deionized water. The appropriate volumes of standard solution from 10 mg L⁻¹ of analyzed elements were added to the second and third volumetric flask. Indium was added as the internal standard to all prepared solutions. The final concentration of indium was 1 mg L⁻¹.

RESULTS AND DISCUSSION

It is a well-known fact that a matrix element can change the intensities of the analytical lines of impurity elements in different matrix materials. A matrix element modifies almost all steps the sample undergoes, from its introduction into the system to light emission. Easily and non-easily ionized elements are responsible for changes in the analytical signals because they modify the state in which the analyte is introduced into the plasma, the plasma thermal characteristics, the

excitation efficiency of an analyte and the spatial distribution of the emitting species.^{30–32}

Matrix effects can be reduced using robust operating conditions that lead to efficient energy transfer between the plasma and sample.^{33,34} The ideal robust conditions would result in the absence of variation in the signal intensities of analytes for any change in the matrix or reagent composition.³⁵ Under robust conditions, an increase in the matrix concentration or acid leads to signal depression for ionic lines. Usually, this depression is similar for every line, regardless of the ionization energy and the line excitation energy. The use of robust conditions results in a flat response for all elements, contrary to non-robust conditions when the response is element dependent.³⁶ Under non-robust conditions, the plasma is more sensitive to any small change in the forward power or the amount of aerosol delivered to the plasma. Therefore, non-robust conditions should be avoided for analytical application; they can be useful to enhance the matrix effects.^{37–40}

The most effective way to eliminate matrix effects is the separation of the matrix element but this is not practical in daily work, as it is time consuming and demands working with ultra pure chemicals in order to avoid contamination of the samples. Direct analysis has the advantages of minimizing the sample preparation procedure and reducing the potential risk of sample contamination. Thus, the possibility for direct determination of trace elements in pure gold was investigated with and without matrix matching and with internal standardization methods. Such results were compared with those obtained by the standard addition method.

Choice of the internal standard

In order to apply the internal standardization method, some potential internal standard elements were investigated. Preliminary experiments indicated that most of the commonly investigated elements (Sc, Mo, Y, Ge, Sr, V and Zr) had significant spectral overlap with some of the sensitive analytical lines of the analyzed elements. However, as indium did not show spectral interferences with the analyzed elements, it was employed as the internal standard in further experiments. The most sensitive wavelengths of indium, *i.e.*, 230 nm and 325 nm, were tested as the internal standard. Internal standardization is effective if the characteristics of the internal standard and analyte elements are similar in the plasma and they strongly depend on the operating conditions.^{41–43}

Selection of the optimal experimental parameters

The optimal experimental parameters for all analyzed elements and internal standard were obtained by pumping a working solution containing 0.5 mg L⁻¹ of the analytes through the carrier line and optimizing one parameter while fixing

all the other parameters. The optimal experimental parameters were selected as a compromise for multi-element analysis and they are given in Table IV.

TABLE IV. Optimal experimental parameters for ICP-AES

Parameter	Value
Generator power, W	1450
Relative torch position, mm	5
Diameter of injector bore, mm	1.8
Coolant flow rate, L min ⁻¹	12
Auxiliary flow rate, L min ⁻¹	0.6
Nebulizer flow rate, L min ⁻¹	0.75
Sample uptake rate, mL min ⁻¹	1.5
Measurement processing mode	Peak height
Background correction	Manual selection

Investigation the influence of relative torch position on the intensity of all analytical and internal standard lines showed that the maximum intensities were achieved by observation 5 mm above the induction coil. In particular, satisfactory results could be obtained under robust operating conditions when a high generator power (Figs. 1 and 2) is combined with a long residence time, which could be achieved with lower carrier gas flow rates (Figs. 3 and 4). It may be seen in Figs. 1–4 that indium could be an adequate internal standard for the efficient compensation of changes in the amount of formed aerosol and analyte residence time at a carrier gas flow rate of 0.75 L min⁻¹ and a high generator power of 1450 W.

The change in the behavior of the ionization and excitation conditions of plasma as a function of operating conditions was monitored through the MgII280/MgI285 intensity ratio in order to obtain its highest value.^{33,35,36,38} An increase in the generator power from 1000 to 1500 W led to an increase in the values of MgII280/MgI285 ratio. Generator power of 1500 W had slightly higher value for this ratio, but *RSD* value of the measurements was higher under this condition. The effect of nebulizer flow rate on the MgII280/MgI285 ratio from 0.5 to 1 L min⁻¹ showed that the highest values for MgII280/MgI285 ratio were obtained for a nebulizer flow rate in the range from 0.7 to 0.85 L min⁻¹, but the lowest *RSD* value of the measurements was obtained with a nebulizer flow rate of 0.75 L min⁻¹.

Determination of trace elements in gold samples

Using the establish experimental conditions, as given in Table IV, the achievable detection limits for the investigated elements, defined as the analyte concentration giving a signal that is three times the standard deviation ($n = 6$) of the blank, are given in Table V.

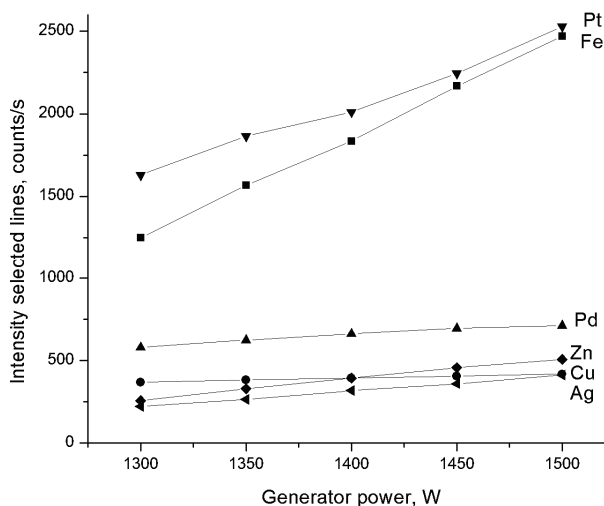


Fig. 1. The effect of the generator power on the intensity of the analytical lines.

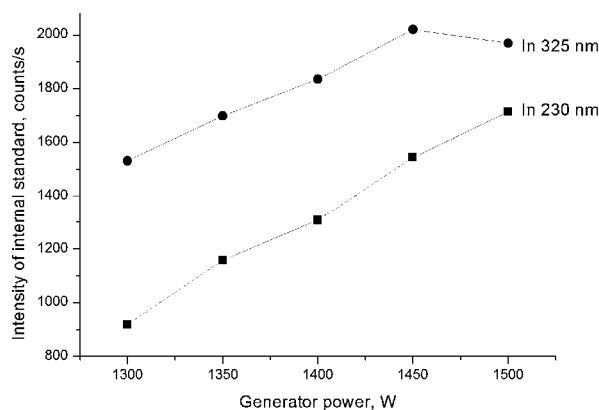


Fig. 2. The effect of the generator power on the intensity of the internal standard lines.

A refined gold sample of unknown composition was analyzed using the previously defined analytical programs and experimental parameters. The obtained results for different calibration strategies are presented in Table VI. Since the detection limits for most of the analyzed elements were slightly higher with the matrix matching calibrations than without matrix matching, especially for copper and iron, the contents of such elements could not be quantified with the former technique. Similar results for a decrease in sensitivity for matrix matching calibration were obtained by Hinds,⁹ Baucells¹³ and Kogan.²² These results could be explained by the fact that high purity gold free from all the analyzed elements, which should be used for the preparation of calibration solutions as the matrix material, is not readily available. Inhomogeneous distributions of these trace elements present in the matrix material lead to higher standard deviation of blank and higher detection limits. Therefore, matrix free calibration and standard addi-

tion methods are more convenient for analyte contents lower than 10 mg kg^{-1} in solid samples.

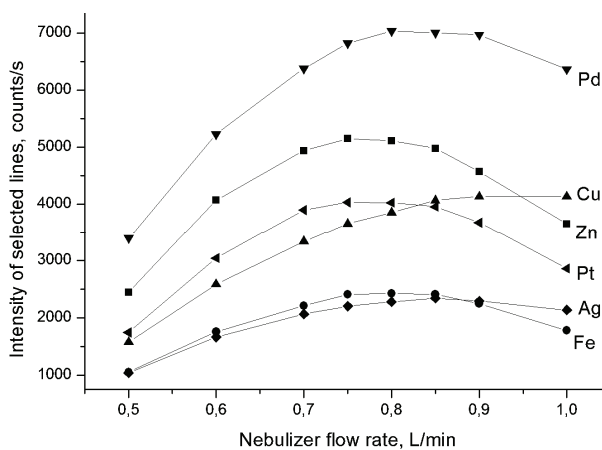


Fig. 3. The effect of the nebulizer flow rate on the intensity of the analytical lines.

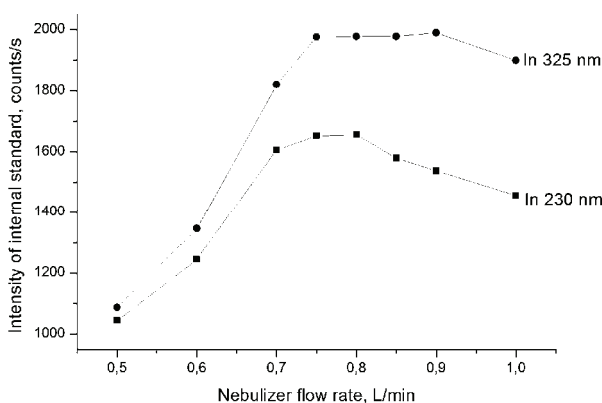


Fig. 4. The effect of the nebulizer flow rate on the intensity of the internal standard lines.

TABLE V. Detection limits for the determination of trace elements in gold

Analyte	Matrix matching calibration, mg/L			Matrix free calibration, mg/L		
	No IS	In 230 nm	In 325 nm	No IS	In 230 nm	In 325 nm
Ag	0.006	0.006	0.009	0.006	0.004	0.007
Cu	0.014	0.019	0.014	0.007	0.004	0.006
Fe	0.020	0.022	0.020	0.005	0.003	0.004
Pd	0.017	0.018	0.018	0.017	0.018	0.016
Pt	0.039	0.027	0.035	0.016	0.010	0.014
Zn	0.004	0.008	0.008	0.003	0.001	0.002

In general, matrix matching is certainly a better way to overcome matrix effects. However, this matching requires perfect knowledge of the sample composition, which is not always possible. In the case of analysis of ultra pure materials, matrix-matching calibration requires using a matrix material with as low

possible concentrations of the investigated elements. The gold matrix used in the present investigation did not contain significant amounts of Ag, Pt and Pd but involved some contents of Cu, Fe and Zn. Therefore, the results for Cu, Fe and Zn were better using internal standardization without the addition of the matrix material and standard addition methods, while, the results for Ag, Pt and Pd were in accordance with all calibration strategies and standard addition methods.

TABLE VI. The results of the analysis of the gold sample (mean \pm SD, mg kg⁻¹); the results for zinc were lower than the limit of quantification of the employed ICP-AES

Analytical program	Ag	Pd	Pt	Cu	Fe
Au-H ₂ O	88.80 \pm 1.30	10.84 \pm 0.22	13.70 \pm 0.34	2.80 \pm 0.17	6.52 \pm 0.31
Au-Au	91.55 \pm 2.14	12.06 \pm 0.62	12.27 \pm 0.55	ND	ND
Au-In230-H ₂ O	91.97 \pm 1.13	13.06 \pm 0.28	14.64 \pm 0.28	3.57 \pm 0.20	6.60 \pm 0.22
Au-In230	83.05 \pm 3.12	11.93 \pm 0.53	12.45 \pm 0.51	ND	ND
Au-In325-H ₂ O	102.17 \pm 2.34	12.38 \pm 0.26	14.90 \pm 0.55	3.57 \pm 0.35	7.05 \pm 0.57
Au-In325	85.60 \pm 3.31	11.47 \pm 0.66	12.07 \pm 0.73	ND	ND
Standard addition method					
No-Is	79.02 \pm 2.30	12.79 \pm 0.52	12.79 \pm 0.53	3.01 \pm 0.03	7.23 \pm 0.41
Is-In230	82.78 \pm 3.67	11.29 \pm 0.28	13.55 \pm 0.63	3.39 \pm 0.18	6.77 \pm 0.25
Is-In325	82.78 \pm 4.99	12.04 \pm 0.61	13.55 \pm 0.75	3.76 \pm 0.13	8.28 \pm 0.81

The precision of the methods, expressed as *RSD* values for four replicate determinations from the same sample solution, was apparently better using matrix free calibration standards, especially when indium at wavelength of 230 nm was used as the internal standard. The obtained *RSD* values were within 5 % for all analyzed elements, except for copper. The main reason for higher *RSD* values for copper compared to other investigated elements was its lower concentration, which is close to the limit of quantification. The precision of the obtained results by matrix matching and matrix free calibration for silver, palladium and platinum was also compared through the *F* test. As the ratios of the variances $F_{\text{experiment}}$ were smaller than F_{table} , this indicated that there were no significant differences in precision of the methods at the 95 % confidence level.

As no pure gold certified reference material containing all analyzed elements was available, the accuracy of the methods was realized by performing the recovery test for all the analyzed elements. The recoveries were evaluated by analysis of trace elements in unspiked and spiked samples using the described methods. The results from Table VII indicated spike recoveries in the range 90–115 % and there was no evidence of interferences of the gold matrix in the described AES-ICP analysis. The accuracy expressed as the percent of the spike recoveries shows good agreement for all calibration strategies.

TABLE VII. Spike recoveries, %, of the trace elements in the pure gold sample

Analytical program	Ag	Pd	Pt	Cu	Fe	Zn
Au-H ₂ O	109.8	93.6	103.2	95.3	93.5	93.2
Au-Au	115.3	90.9	99.3	92.2	98.3	93.5
Au-In230-H ₂ O	102.2	101.0	109.7	99.6	99.0	99.2
Au-In230	112.1	89.8	100.3	92.2	94.0	95.7
Au-In325-H ₂ O	108.2	100.1	107.0	97.0	99.2	99.9
Au-In325	110.8	91.3	102.0	95.4	101.1	95.6

Analysis of certified reference material of high purity gold

The internal standardization and the standard addition method were further validated by analyzing a certified reference material of high purity gold AuGHP1. The determination results of the certified reference material by the internal standardization and the standard addition methods, together with the certified values, are given in Table VIII.

TABLE VIII. The results of analysis the certified reference material of highly pure gold AuGHP1 (mean \pm SD, mg/kg)

Analytical program	Fe	Cu	Zn	Pt
Au-H ₂ O	8.62 \pm 0.30	4.67 \pm 0.07	4.30 \pm 0.08	ND
Au-In230-H ₂ O	10.27 \pm 0.26	4.78 \pm 0.21	5.01 \pm 0.19	ND
Au-In325-H ₂ O	10.74 \pm 0.27	4.43 \pm 0.10	5.25 \pm 0.33	ND
Certified value	8.90	4.40	4.30	1.80
Standard addition method				
No-Is	8.13 \pm 0.26	4.69 \pm 0.25	4.69 \pm 0.26	1.56 \pm 0.39
Is-In230	8.75 \pm 0.40	4.38 \pm 0.09	4.69 \pm 0.11	1.56 \pm 0.29
Is-In325	10.31 \pm 0.56	4.38 \pm 0.29	5.00 \pm 0.41	2.50 \pm 0.50

The results of the analysis of the certified reference material obtained by the internal standardization and the standard addition methods were in accordance with certified values, with the exception of platinum. The obtained results for platinum using matrix-matching and matrix free calibrations with and without internal standard were lower than the limit of quantification, but the recoveries obtained by standard addition methods were in the range from 86.67 to 138.89 %. Thus sensitivity enhancement is essential for the determination of low concentrations of platinum by inductively coupled plasma atomic emission spectrometry. This can be achieved using a more efficient sample introduction technique, such as ultrasonic nebulizer or electrothermal vaporizer, as well as using more sensitive techniques such as inductively coupled plasma mass spectrometry or electrothermal atomizer atomic absorption spectrophotometry. The internal standardization and standard addition method were proved effective ways of overcoming matrix effects. Comparison of the results obtained using the two

wavelengths for indium, employed as an internal standard, indicated better results were obtained using the 230 nm wavelength.

CONCLUSIONS

A rapid and simple method for the determination of trace contents of silver, copper, iron, palladium, zinc and platinum in refined gold samples was developed. Indium was used as the internal standard. Two sets of calibration standards were prepared. In the first set of matrix matched calibration standards, the concentration of the gold matrix was the same as in the samples, while in the second set, the matrix material was not present. The detection limits of some elements for matrix matching calibrations were higher than those obtained without the addition of matrix material. The precision of the methods, expressed through the RSD values, was better using matrix free calibration standards using the indium 230 nm line as the internal standard or without using the internal standard. The accuracy of methods was confirmed by performing the recovery test and by analysis of a certified reference material of high purity gold AuGHP1. Therefore, simultaneous inductively coupled plasma atomic emission spectrometry with a radial torch position and a cross flow nebulizer can be successfully applied for the determination the trace elements in refined gold samples. The best results were achieved by matrix free calibration and the standard addition method using the indium 230 nm line as an internal standard.

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ИЗВОД

ОДРЕЂИВАЊЕ ТРАГОВА ЕЛЕМЕНАТА У УЗОРЦИМА РАФИНИСАНОГ ЗЛАТА АТОМСКОМ ЕМИСИОНОМ СПЕКТРОМЕТРИЈОМ СА ИНДУКТИВНО КУПЛОВАНОМ ПЛАЗМОМ

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Овај рад приказује методу за одређивање ниских садржаја сребра, бакра, гвожђа, палладијума, цинка и платине у узорцима рафинисаног злата. За испитивања је коришћен атомски емисиони спектрометар са индуктивно куплованом плазмом, радијално постављеним пламеником са унакрсним распршивачем. Да би се упоредиле различите стратегије калибрације припремљена су два сета калибрационих стандарда. Први сет калибрационих стандарда са и други сет стандарда без додатка матрикса. Границе детекције добијене при коришћењу стандарда са додатком матрикса су више за неке елементе од калибрација без додатка матрикса. Такође, примењена је и метода унутрашње стандардизације, експерименти су показали да је индијум најбољи избор за унутрашњи стандард. Резултати анализа узорка злата добијених коришћењем стандарда са и без додатка

матрикса упоређени су са методом стандардног додатка. Тачност метода испитана је приносом стандардног додатка и добијене су вредности у опсегу од 90 до 115 %. Тачност методе, такође, је проверена коришћењем сертификованог референтног материјала високочистог злата AuGHP1. Најбољи резултати постигнути су употребом калибрационих стандарда без додатка матрикса и методом стандардног додатка употребом индијума као унутрашњег стандарда на таласној дужини од 230 nm.

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