



SPECTRO ARCOS

Analysis of Impurities in High-Purity Precious Metals by ICP-OES With Axial Plasma Observation

Introduction

The purity of precious metals is the main factor for their monetary value. Therefore, it needs to be most accurately determined when trading precious metals or precious metal products whereby contents of up to 99 % are determined with ICP-OES following the bracketing method (EN ISO 11494, 11495). For high-purity gold and platinum, the determination of the precious metal content is done with a difference method. Here the impurities are measured, and the purity of the precious metal is calculated by a subtraction of all measured impurities.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) can be perfectly used for the analysis of impurities in precious metals. Due to its multi-element capability — large linear dynamic range and high sensitivity — it is the recommended analytical procedure for the analysis of contamination traces in high-purity gold and platinum. The application is described in the ISO standard 15093 [1]. This report describes the principle methodology for the analysis of trace elements in precious metals. It presents typical detection limits for a wide range of elements as well as studies on accuracy.



Experimental

Instrumentation

All measurements were performed with the SPECTRO ARCOS inductively coupled plasma-optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with true axial as well as true radial plasma observation. The SPECTRO ARCOS features a Paschen-Runge spectrometer mount, employing the Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 32 linear CCD detectors, the wavelength range between 130 and 770 nm can be simultaneously analysed.

Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later date. The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the VUV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region.

Instrumentation Parameters

For sample introduction, a Crossflow nebulizer, a Scott spray chamber and an argon humidifier were used. The ICP operating conditions for all precious metal matrices are given in Table 1 to Table 2.

Table 1: Typical ICP operating conditions for 50 g/l Au samples

Plasma Power	1250 W
Observation Mode	Axial
Coolant flow	13.0 l/min
Auxiliary flow	1.40 l/min
Nebulizer flow	0.75 l/min
Plasma Torch	Quartz, 2.0 mm Injector tube
Spray Chamber	Scott type
Nebulizer	Crossflow
Sample aspiration rate	2 ml/min
Replicate read time	30 s per replicate

Table 2: Typical ICP operating conditions for 10 g/l Pt samples

Plasma Power	1250 W
Observation Mode	Axial
Coolant flow	13.0 l/min
Auxiliary flow	0.80 l/min
Nebulizer flow	0.85 l/min
Plasma Torch	Quartz, fixed, 2.0 mm Injector tube
Spray Chamber	Scott type
Nebulizer	Crossflow
Sample aspiration rate	2 ml/min
Replicate read time	30 s per replicate

Sample Preparation

Before the digestion, each sample should be washed and dried to remove all contaminations on the surface. The clean sample was weighed into a beaker and aqua regia [2,3] was added. The solution was heated until the sample was completely dissolved. After the cooling to room temperature, the sample was transferred into a volumetric flask and diluted to the total volume. Depending on the purity of the precious metal the matrix concentration can be adjusted between 10 g/L (99.0 – 99.99) and 50 g/L (> 99.99).

Calibration Standards

For the preparation of calibration solutions, a high-purity reference material was dissolved using aqua regia [2,3] to match the matrix of the samples. Commercially available multi-element standards [4,5] were added to the dissolved precious metal solution to obtain matrix-matched calibration solutions for all analytes.

Results and Discussion

In the following section, the selected wavelengths for each matrix are shown together with the limits of detection (LOD) achieved. The LODs were calculated according to the equation [6]:

$$\text{LOD} = 3 \text{ RSD}_b \cdot c / 100 \cdot \text{SBR}$$

Where:

- RSD_b – relative standard deviation of 10 replicates of the blank (in %)
- c – concentration of the standard
- SBR – signal to background ratio

The LODs were calculated considering the dilution factor for the digested sample, referring to the original concentration in the solid material.

Impurities in gold

The impurities in gold were measured in a 50g/L Au matrix with axial plasma observation. Table 3 displays the achieved limits of detection in the solid gold material.

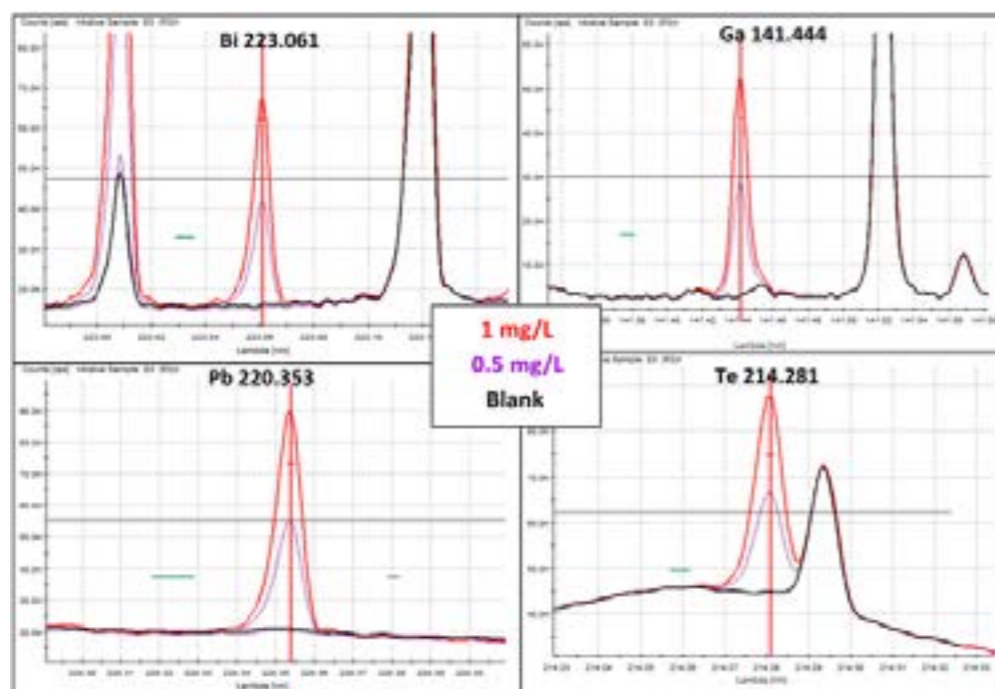
Table 3: Typical Limits of Detection (LOD) in the original gold material

Element	λ [nm]	LOD [mg/kg]	Element	λ [nm]	LOD [mg/kg]
Ag	328.068	*	Mn	259.373	0.006
Al	167.078	0.01	Ni	221.648	0.04
As	189.042	0.11	Pb	220.353	0.10
Ba	455.404	0.002	Pd	340.458	--*
Be	313.042	0.001	Pt	177.708	0.04
Bi	223.061	0.11	Rh	343.489	0.05
Cd	214.438	0.006	Ru	240.272	0.03
Co	238.892	0.01	Sb	206.833	0.06
Cr	205.618	0.01	Se	204.050	0.52
Cu	327.396	0.03	Si	251.612	0.06
Fe	259.941	0.05	Sn	147.516	0.05
Ga	141.444	0.05	Sr	421.552	0.001
Hg	194.227	0.05	Te	214.281	0.27
In	230.606	0.02	Tl	190.864	0.08
Ir	183.250	1.3	Zn	202.613	0.004
Mg	280.270	0.008	Zr	339.198	0.02

*Contaminated blank standard

The following Figure 1 shows the calibration spectra of the blank and standards with a concentration of 0.5 mg/L and 1 mg/L for a selection of elements. It demonstrates the sensitivity of these challenging elements in a 50 g/L gold matrix.

Figure 1: Spectra of the Blank, 0.5 mg/l and 1 mg/l calibration standards in 50 g/L gold matrix



Impurities in platinum

For the measurements of impurities in platinum, 10 g/L platinum solutions were prepared and measured with axial plasma observation. The limits of detection achieved in the solid platinum material are displayed in Table 4.

Table 4: Typical Limits of Detection (LOD) in the original platinum material

Element	λ [nm]	LOD [mg/kg]	Element	λ [nm]	LOD [mg/kg]
Ag	328.068	0.10	Mn	257.611	0.008
Al	167.078	0.07	Mo	281.615	0.16
As	197.262	1.1	Ni	231.604	0.50
Au	267.595	0.28	P	213.618	1.5
Ba	455.404	0.04	Pb	220.353	0.62
Be	313.042	0.004	Pd	324.270	0.66
Cd	226.502	0.02	Rh	233.477	0.42
Co	228.616	0.04	Ru	245.553	0.58
Cr	283.563	0.07	Sb	217.581	0.77
Cu	324.754	0.07	Sn	147.516	0.37
Fe	259.941	0.18	Sr	407.771	0.01
Ir	212.681	0.12	Tl	190.864	0.31
Li	670.780	0.02	V	292.402	0.07
Mg	280.270	0.04	Zn	213.856	0.02

The accuracy of the method was investigated by analyzing a spiked platinum sample. The measured concentrations of the original sample solution and the spiked solution are displayed in Table 5. For better comparison, the given and the measured spiked concentrations are listed, too. The recoveries are in perfect agreement with the given values for all elements.

Table 5: Recovery of a spiked platinum sample

Element/ Line	Measured Unspiked Sample Concentration [mg/kg]	Given Sample Spike [mg/kg]	Measured Sample + Spike Concentration [mg/kg]	Measured Spike Concentration [mg/kg]	Spike Recovery [%]
Ag 328.068	< LOD	25	25.0	25.0	100.2%
Al 167.078	< LOD	100	100.7	100.7	100.7%
As 197.262	< LOD	100	102.0	102.0	102.0%
Cd 226.502	< LOD	100	100.3	100.3	100.3%
Co 228.616	< LOD	100	101.4	101.4	101.4%
Cr 283.563	< LOD	100	99.6	99.6	99.6%
Cu 324.754	< LOD	100	100.2	100.2	100.2%
Fe 259.941	191.2	100	291.0	99.8	99.8%
Mg 280.270	6.0	100	105.2	99.1	99.1%
Mn 257.611	1.3	100	99.9	98.6	98.6%
Mo 281.615	55.8	100	155.9	100.1	100.1%
Ni 231.604	< LOD	100	96.9	96.9	96.9%
P 213.618	< LOD	500	514.7	514.7	102.9%
Pb 220.353	< LOD	100	103.8	103.8	103.8%
Sb 217.581	< LOD	100	103.8	103.8	103.8%
Sn 147.516	< LOD	100	98.4	98.4	98.4%
Tl 190.864	< LOD	100	101.0	101.0	101.0%
Zn 213.856	1.9	100	102.5	100.6	100.6%

Conclusions

This study demonstrates that the SPECTRO ARCOS with direct light path axial plasma observation is perfectly suited for the analysis of impurities in high-purity precious metals according to ISO 15093 [1]. The axial plasma observation offers highest sensitivity with excellent limits of detection, even with a high matrix load like 50 g/l gold. Depending on the requirements, the SPECTRO ARCOS Multiview can also be operated with a true radial plasma observation; another option for the analysis of impurities in precious metals. The radial mode offers an excellent long-term stability and very easy handling with only a minor loss in sensitivity.

In conjunction with an autosampler, the SPECTRO ARCOS can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates, pre-flush and method rinse) can be performed in less than three minutes.

References

- [1] ISO 15093:2020-02; Jewellery and precious metals – Determination of high purity gold, platinum and palladium – Difference method using ICP-OES
- [2] HNO₃ Suprapur[®], 65%, Merck, Darmstadt, Germany
- [3] HCl Suprapur[®], 30%, Merck, Darmstadt, Germany
- [4] Bernd Kraft GmbH Duisburg, Germany
- [5] Inorganic Ventures, Christiansburg, Virginia
- [6] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

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