High Precision Analysis of Major Components in Precious Metals by ICP-OES

Determination of major components in jewelry alloys by ICP-OES and standard bracketing per ISO methods

Author

Ruby Bradford
Agilent Technologies, Inc.

Introduction

Accurate quantification of major components in precious metal alloys can be challenging due to high precision and accuracy requirements, often to stringent industry-specific standards. This challenge is particularly relevant for the precious metals industry, where the stoichiometric composition and purity of metal alloys define both product quality and commercial value. A technique for high-precision measurements developed specifically for the precious metals industry is standard bracketing. As described in ISO methods 11494 and 11495 for ICP-OES analysis,[1,2] this technique employs *standard–sample–standard* sequencing, which improves control over instrumental fluctuations and matrix effects, ensuring high levels of accuracy and precision.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is a powerful technique that is often used to analyze trace impurities in a broad range of samples. Both the Agilent 5800 and 5900 ICP-OES instruments are inherently precise, as discussed elsewhere.[3] However, precision is further improved when the instruments are operated with the ISO-compliant standard bracketing feature within the Agilent ICP Expert Pro software version 7.8 onwards. The software provides additional useful features for jewelry assaying, catalyst refining, and material recycling. These functions include built-in automated result summarization, reporting in fineness (‰), karat (k), or concentration units, and processing tools specifically for determining major components and purity analysis. Standard bracketing is also applicable to other demanding applications, such as semiconductors, fertilizers, and the emerging battery materials sector.

In this study, the Agilent 5800 Vertical Dual View (VDV) ICP-OES with Agilent SPS 4 autosampler and ICP Expert 7.8 Pro software[4] was used to determine the purity of gold (Au), palladium (Pd), and platinum (Pt) in three precious metal alloys. The analytical procedure was in accordance with ISO methods 11494 and 11495.

Experimental

Instrumentation

The Agilent 5800 VDV ICP-OES was configured with the Agilent SPS 4 autosampler, which provided automated sample delivery to the instrument (Figure 1). The 5800 ICP-OES was equipped with a SeaSpray nebulizer, double-pass cyclonic spray chamber, and Agilent one-piece VDV torch with a 1.8 mm internal diameter (id) injector. All components were controlled by Agilent ICP Expert Pro* 7.8 software. Instrument operating parameters are listed in Table 1.

Figure 1. Agilent 5800 VDV ICP-OES with Agilent SPS 4 autosampler and Agilent ICP Expert Pro software.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.3
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	12
Aux Flow (L/min)	1.0
Replicates	3
Rinse Time (s)	30
Read Time (s)	20
Stabilization Time (s)	30
Sample Pump Tubing	White-white
Waste Pump Tubing	Blue-blue
Internal Standard	Y 371.029 nm
Background Correction	Fitted

Standard preparation

Bracketing standards for analytes should be prepared at concentrations slightly below and above the expected sample concentration. Standards can be generated using either high-purity metals (≥99.95%), prepared in the same way as the samples, or certified aqueous stock solutions, depending on availability and analyte requirements.

In cases where the sample concentration is initially unknown, a preliminary external calibration can be performed across a broad range (for example, 0 to 100 mg/L, representing 0 to 1000‰ purity) to establish an approximate concentration. This approach enables the selection of bracketing standards within a narrow range, typically ±5 mg/L of the target value.

In this study, certified Agilent stock solutions for Au, Pd, and Pt were used to prepare all standards, with concentrations calculated based on the certificate of analysis (CoA) values, expressed in µg/g. The certified standards ensured traceability and accuracy in standard preparation.

An internal standard (IS) solution of yttrium (Y) at 6 mg/L in 5% nitric acid (HNO_3) was prepared and added to all standards and samples. The amount added was equivalent to 10% of the total volume, converted to grams. For example, for a 1000 mL flask, 100 g of IS solution was added. It is critical that the ratio of IS solution added to each standard and sample is recorded and kept consistent. The IS was used to correct for sample-to-sample fluctuations and matrix effects.

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*Standard bracketing requires ICP Expert Pro v7.8 or later.

Bracketing standards were prepared by accurately weighing a mass-corrected aliquot of a 10,000 mg/L calibration stock solution, adding the IS solution, adding hydrochloric acid (HCl) and HNO_3, and diluting to volume such that the final matrix consisted of 20% HCl and 3% HNO_3. The final concentrations of the standards were selected to bracket the expected sample concentration. For example, for the analysis of 18k gold (750‰), standards were prepared at 70 and 80 mg/L to bracket the anticipated sample concentration of approximately 75 mg/L.

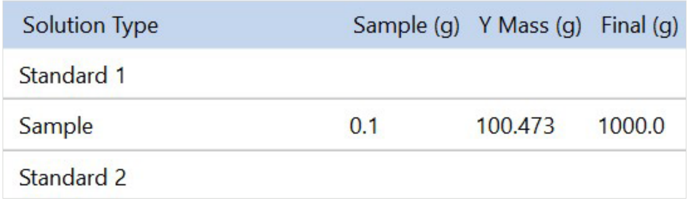
Sample preparation

The samples included a commercially available gold wire, palladium metal, and a platinum wire bought from a jewelry supplier in Australia. To ensure accurate and reproducible results, each metal sample was prepared twice, in accordance with ISO 11494 and 11495. Two portions of each sample, each weighing exactly or close to 0.1000 g, were measured using an analytical balance. The weighed samples were transferred into separate glass beakers in a fume hood.

Aqua regia was freshly prepared in each beaker by adding a total of 100 mL of HCl and 30 mL of HNO_3. The beakers were covered with watch glasses and placed on a hot plate at 100 °C. As aqua regia is prone to decomposition, especially when heated, smaller batches of aqua regia were freshly prepared and heated until fuming ceased. Then fresh aqua regia was added again, repeating the process until the total amount of acid was added. Higher hot plate temperatures can be used to reduce the metal dissolution time as long as the solution does not exceed the aqua regia boiling point of 108 °C. A handheld infrared thermometer can be used to monitor the temperature. Once all the acid was added and complete dissolution of the metal was achieved, the heat was turned off and the solutions were allowed to cool.

After cooling, each solution was quantitatively transferred into separate 1000 mL volumetric flasks and the glassware was thoroughly rinsed into each flask with deionized water to ensure complete transfer. To each flask, 100 g of the yttrium IS solution (6 mg/L in 5% HNO_3) was accurately weighed and added. An additional 100 mL of HCl was introduced and the solutions were diluted to volume with deionized water. The final matrices were 20% HCl and 3% HNO_3.

The prepared solutions were transferred into 50 mL centrifuge tubes and placed into racks on the SPS 4 autosampler ready for analysis by the 5800 ICP-OES. To enhance the accuracy and precision of the quantitative results, the exact masses of the metal samples and the IS solution were recorded in the instrument software, as shown in Figure 2.



Solution Type	Sample (g)	Y Mass (g)	Final (g)
Standard 1			
Sample	0.1	100.473	1000.0
Standard 2			

Figure 2. Inputs of sample, internal standard, and final masses into the Agilent ICP Expert 7.8 Pro software.

Enhanced precision and accuracy

ICP-OES analyses using external calibration methods provide great precision for most applications. However, an even higher degree of precision is required for major component and purity analyses. ICP-OES standard bracketing is a high-precision calibration technique that alternates the measurement of calibration standards and samples throughout a run (Figure 3). The method compensates for instrument variability and matrix effects, delivering exceptional accuracy, precision, and traceability.

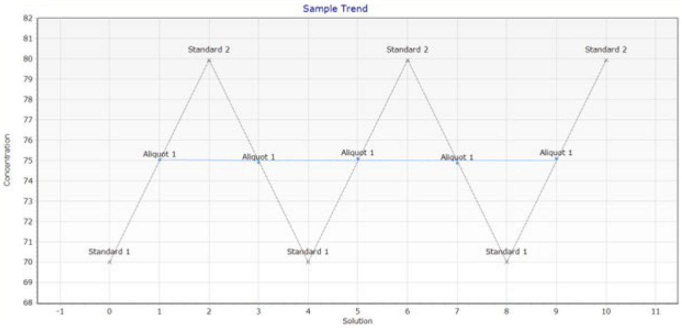


Figure 3. Example of a bracketing sequence, consisting of five bracketing cycles (sample measurements).

To evaluate the precision of the external and standard bracketing calibration methods, a comparison was performed using a single aliquot of the Pd metal sample. The sample aliquot was measured five times using a three-point external calibration method and the five cycle standard bracketing method.

The precision of each calibration method was assessed using relative standard deviation (RSD) and the reproducibility between duplicate measurements was evaluated using relative percent difference (RPD). As shown in Table 2, standard bracketing improved the %RSD values by more than 3× compared to external calibration. While both calibration methods yielded acceptable precision (RSD), standard bracketing demonstrated superior reproducibility between duplicate measurements, with an average RPD of 0.00056 compared to 0.225 for external calibration, a >400× improvement.

The results highlight the effectiveness of standard bracketing in mitigating measurement fluctuations and matrix effects, leading to more precise quantitation.

Table 2. Average concentration (fineness), RSD, and RPD between duplicate measurements of a Pd metal sample determined by the Agilent 5800 ICP-OES using external calibration and standard bracketing, n=5.

		Pd 342.122		
Calibration Method		**Average Fineness (‰)**	**RSD (%)**	**RPD* (%)**
Standard Bracketing	Aliquot 2	999.22	0.033	0.00056
	Aliquot 2_2	999.23	0.028	
External Calibration	Aliquot 2	993.75	0.089	0.225
	Aliquot 2_2	995.99	0.098	

**Reflects the agreement between duplicates. A lower RPD value indicates better agreement.*

New QC type for real-time reporting

ICP Expert includes the Sample Aggregate feature, also known as SSUM, a statistical tool that helps summarize data and enhance data transparency during ICP-OES workflows and QC evaluation. It can be added as a new row into a worksheet. Once added, SSUM enables the analyst to define custom result calculations and reporting metrics that update dynamically as the run progresses. It works across multiple measurements in real time, making it easy to track data across different sample preparations. In the example shown for aliquot 1 of the Pd metal (Figure 4), three distinct SSUM (purple) rows were added separately to serve different analytical purposes.

SSUM uses the values generated from the preceding bracketing sequences to calculate metrics that summarize sample performance. It can be used to display real-time %RSD and RPD values and be configured to stop a run if user-defined thresholds (for example, maximum allowable %RSD) are exceeded. Integrating SSUM into the workflow allows analysts to identify and address issues in real time, reducing the likelihood of generating unusable data and avoiding reruns.

SSUM also allows for persistent display of results in the preferred unit of measurement, independent of the global display settings of the analysis page. This flexibility provides greater control for analysts, particularly when comparing results across different datasets or reporting formats.

Solution Label	Timestamp	Pd 1 340.458 nm ppm
Aliquot 1	10/16/2025 1:38:59 PM	96.6845
Standard 2	10/16/2025 1:41:23 PM	99.9509
Conc (mg/L)		96.7024
Sample RSD		0.0482
Fineness		996.9319

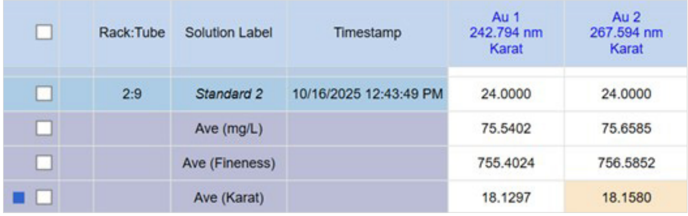
Figure 4. Sample aggregate (or SSUM) QC rows (purple) allow user-defined labels and calculations to auto-populate as the run progresses, displayed in persistent units regardless of global analysis page display settings.

Enhanced result display capabilities

To meet the specific requirements of the precious metals industry, the ICP Expert software can convert analytical results into purity and report them as fineness (‰) and karats (k), rather than just concentration units such as mg/L. Extra rows can be added into the worksheet for this purpose (Figure 5). This flexibility enables direct interpretation of sample purity in industry-standard terms.

Purity calculations are automatically performed using the user-input gravimetric data obtained during sample preparation. By integrating these values directly into the worksheet, the purity of each sample can be automatically calculated and displayed without the need for additional post-processing or manual conversion steps.

This streamlined workflow enhances efficiency and ensures consistency in reporting and is particularly useful for applications involving Au, Pt, Pd, and other high-value metals where purity is a critical specification.



☐	Rack:Tube	Solution Label	Timestamp	Au 1 242.794 nm Karat	Au 2 267.594 nm Karat
☐	2:9	*Standard 2*	10/16/2025 12:43:49 PM	24.0000	24.0000
☐		Ave (mg/L)		75.5402	75.6585
☐		Ave (Fineness)		755.4024	756.5852
■ ☐		Ave (Karat)		18.1297	18.1580

Figure 5. Setting user-defined units to display in mg/L, fineness, and karats in the Agilent ICP Expert software by inserting extra rows (shown in purple) into the worksheet.

Results and discussion

Sample analysis

Two replicate preparations (aliquots) of the three precious metal samples were analyzed by the 5800 VDV ICP-OES using the standard bracketing method (five measurements). The second aliquot was measured again as a duplicate. The calculated fineness (‰) values, RSD for individual measurements, and RPD for duplicate samples are shown in Table 3.

All RSD values, both for individual bracketing cycles and across the full bracketing sequence, were below 0.18%, significantly lower than the 0.3% threshold specified in the ISO methods (Table 4). This level of precision confirms the robustness of the 5800 ICP-OES bracketing approach for high-purity metal determinations.

The results demonstrate excellent reproducibility, not only within individual measurements but also across duplicate samples. This high level of precision highlights the method's ability to effectively compensate for sample-to-sample variability over the course of an analytical day, ensuring consistent quantitation of major elements for demanding applications.

Table 3. Sample fineness and relative standard deviation (RSD) of bracketing sequence and relative percent difference (RPD) of duplicate measurements of three precious metal samples, n=5.

		Fineness (‰)	RSD (%)	RPD* (%)
Au 267.594	Aliquot 1	755.40	0.052	
	Aliquot 2	756.59	0.071	0.0036
	Aliquot 2-2	756.56	0.073	
Pd 342.122	Aliquot 1	997.21	0.055	
	Aliquot 2	999.22	0.033	0.00056
	Aliquot 2-2	999.23	0.028	
Pt 224.552	Aliquot 1	944.86	0.048	
	Aliquot 2	941.36	0.044	0.017
	Aliquot 2-2	941.52	0.072	

**Reflects the agreement between duplicates. A lower RPD value indicates better agreement.*

Table 4. Relative standard deviation (RSD) of individual bracketing cycle measurements.

		RSD (%)				
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Au 267.594	Aliquot 1	0.086	0.018	0.025	0.058	0.069
	Aliquot 2	0.133	0.032	0.028	0.091	0.062
	Aliquot 2-2	0.101	0.071	0.154	0.023	0.052
Pd 342.122	Aliquot 1	0.014	0.065	0.019	0.038	0.077
	Aliquot 2	0.034	0.101	0.020	0.067	0.066
	Aliquot 2-2	0.051	0.025	0.063	0.066	0.077
Pt 224.552	Aliquot 1	0.084	0.058	0.011	0.180	0.032
	Aliquot 2	0.085	0.037	0.029	0.044	0.056
	Aliquot 2-2	0.065	0.030	0.088	0.092	0.046

Conclusion

This application demonstrates the effectiveness of high-precision standard bracketing calibration for the quantification of major components in gold, palladium, and platinum alloys using the Agilent 5800 VDV ICP-OES.

By employing gravimetrically prepared standards and integrating internal standard correction, the method improves analytical precision (RSD) more than threefold compared to conventional external calibration. It also reduces sample-to-sample fluctuations, resulting in a 400× improvement in RPD values between duplicate measurements.

The high precision and reproducibility of the standard bracketing method enable accurate assaying of precious-metal samples, making it ideal for quality control of high-value materials where composition control is often required within ±0.1%.

The latest version of Agilent ICP Expert Pro software facilitates the standard bracketing method and includes tools for in-worksheet calculations and custom result displays. This approach simplifies metal-alloy purity testing, enables direct interpretation of sample purity in industry-standard terms, and provides confident, traceable quantification in accordance with ISO methods.

The method is useful in other applications that require tight composition control, such as battery materials, catalysts, semiconductors, and fertilizers.

References

1. ISO 11494:2019 Jewellery and precious metals — Determination of platinum in platinum alloys — ICP-OES method using an internal standard element, https://www.iso.org/standard/75285.html
2. ISO 11495:2019 Jewellery and precious metals — Determination of palladium in palladium alloys — ICP-OES method using an internal standard element, https://www.iso.org/standard/75284.html
3. Integrated Design: Accuracy and Precision of Agilent ICP-OES Instruments, Agilent publication, 5994-8853EN
4. Agilent ICP Expert Software: Powerful software with smart tools for ICP-OES, Agilent publication, 5994-1517EN

Products used in this application

Agilent products

Easy-fit 1.8 mm one-piece torch for 5000 series VDV/SVDV ICP-OES

Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet

SeaSpray concentric glass nebulizer for 5000 series ICP-OES

Peristaltic pump tubing, white/white, 12/pack

Peristaltic pump tubing, blue/blue, 12/pack

Diluent/carrier bottle kit for ADS 2 and Autosampler (6 L HDPE)

Waste container kit, 10 L with Stay Safe cap and filter

Gold (Au) standard, 10,000 µg/mL, in 20% HCl, 100 mL

Palladium (Pd) standard, 10,000 µg/mL, in 10% HNO_3, 100 mL

Platinum (Pt) standard, 10,000 µg/mL, in 20% HCl, 100 mL

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DE-011159

Published in the USA, December 24, 2025
5994-8849EN

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