Ingeniatrics
Nebulizers and Nozzles

Application Note

MultiNeb®: Precision and reproducibility in gold determination in geological samples using ICP-OES after fire assay procedure.

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1. Introduction

Accurate analyses of exploration data and ore reserves are two of the most important functions of professional geologists and engineers in a mine development. These analysis become quite challenging because of precious metal values and the analytical methodology employed, frequently based on ICP-OES techniques. A high sensitivity, precision and reproducibility are required. In this sense, nebulizer selection is a critical but often overlooked aspect of ICP-OES analyses.

It is well known that fire assay is the most common technique for precious metals determination in rock and ore samples, and it is generally accurate for the determination of gold, based on techniques such as ICP-OES and ICP-MS. Alternative methods are also available, offering the advantages of a faster determination of small concentrations of gold in a number of samples, but only for preliminary exploration studies.
One basic reason for the continued use of the fire assay technique is its ability to analyze relatively large sample size that can be treated by this technique; another reason is that fire assay is relatively free of interferences. In contrast, the samples

resulting from aqua regia digestion are saturated in Ag^+ and Cl^- ions, generating AgCl precipitates and high TDS in matrix samples which perturbs the analysis and the nebulization mechanism itself (clogging). For this reason, an internal standard quantification is required.

In this study, we compare the performance of OneNeb® and MultiNeb® inert, robust and durable nebulizers (designed and manufactured by Ingeniatrics Technologies) for analytical methodologies based on ICP-OES for gold determination after fire assay sample preparation and aqua regia digestion, using internal standard quantification.

2. Experimental

Reagents and solutions

The aqueous calibration standards of 0.25, 0.5, 1, 5 and 10 µg g^{-1} were prepared by appropriate dilution of a mono-elemental stock solution of 1000 mg L^{-1} of Au (ICP CetriPUR, Merck, Darmstadt, Germany) in deionized water (18 MΩ cm resistivity). All aqueous solutions are acidified by adding up to 5% nitric acid and 15% high purity hydrochloric acid (Merck, Darmstadt, Germany). A solution containing internal standard is prepared by appropriate dilution of a 1000 mg L^{-1} of Y mono-elemental stock solutions (high-purity mono-element standard solutions) in 10 % of ammonia (NH4OH) solution to prevent the formation of AgCl. An aqueous calibration blank and rinse solution are also prepared containing HNO_3 and HCl in the same proportions, like the matrix samples, once digested with aqua regia mineralization after fire assay analytical procedure.

Instrumentation

All measurements were carried out using an inductively coupled plasma-optical emission spectrometer (ICP-OES) model Agilent Technologies 5110 equipped with a SPS4 autosampler (Agilent Technologies) with 0.5 mm ID sampling probe (Agilent Technologies, Part No.: G8410-80101). The instrument operating conditions are shown in table I.

The choice of an appropriate calibration method is critical for the compensation of these matrix effects for obtaining accurate results. Conventionally, the internal standard is mixed with the calibration standards and samples using a Y connection, when **OneNeb®** nebulizer is employed. However, the novel **MultiNeb®** (multinebulizer) allows a high mixing efficiency between two liquids, miscible or immiscible, since the mixing takes place under high pressure turbulent conditions in the tip of the nebulizer.

ICP-OES 5110 (Agilent Technologies)		
RF Power (kW)	1.5	
Plasma gas flow (L min^{-1})	15	
Auxiliary gas flow (L min^{-1})	1.0	
Spray chamber type	Glass cyclonic	
Nebulizers	OneNeb®	MultiNeb®
Nebulization gas flow (L min^{-1})	0.65	0.70
Pump speed (rpm)	10	7
Replicates	3	
Stabilization time (s)	15	
Rinse time (s)	40	
Fast pump	On	
Uptake time (s)	30	
Background correction	Off-peak	
Wavelengths monitored (nm)	Au 267.6 nm Y 371.0 nm (IS)	

Table I. Operational conditions using ICP-OES 5110 Agilent Technologies and SPS4 autosampler.

Sample preparation

Fire assay has been and still is the most common technique for the determination of precious metals in rock and ore samples. The accuracy of the fire assay technique is satisfactory for the analysis of the vast majority of precious metal-bearing ores. All CRM were prepared by triplicate using fire assay procedure following the instructions and recommendations detailed in the accredited methodology **ISO11426:2014** in an external laboratory certified in this procedure (Figure 1).

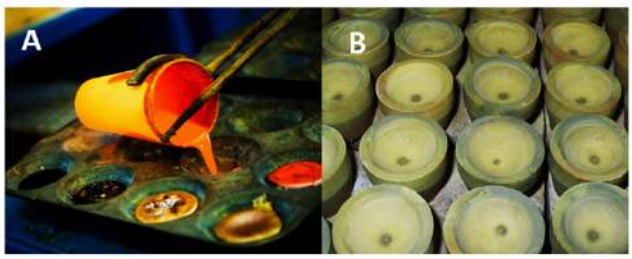

Figure 1. Fire assay procedure. A) First step: mineral fusion ; B) Second step: cupellation process.

Sample introduction configuration

The MultiNeb® nebulizer used in this study consists of two independent liquid inlets and a common gas inlet in a single nebulizer body of polytetrafluoroethylene (Figure.2).

Figure 2. MultiNeb® nebulizer.

The "MultiNeb®-based" configuration is composed by the MultiNeb® nebulizer associated with a cyclonic spray chamber without any additional modification required, as the MultiNeb® is built on the right dimensions to allow easy connection to any commercial spray chamber conventionally used in ICP spectrochemistry.

The "OneNeb®-based" configuration is composed by the OneNeb® nebulizer associated with the same spray chamber. For this configuration, the internal standard is mixed by means of a Y connection, while the MultiNeb®-based system the internal standard is mixed at the tip of the nebulizer (Figure 3).

3. Results

Signal stability and sensitivity

The MultiNeb® and OneNeb® nebulizers use Flow Blurring nebulization technology instead of the traditional Venturi effect. This allows the generation of a very fine droplet aerosol with a narrow size distribution (most droplets are smaller than 10 µm), which improves efficiency over a wide range of nebulization gas flow rates, especially 0.60-0.75 L min^{-1} (150-250 kPa nebulization pressure).

For the study of signal stability and plasma drift for gold determination, a monitoring standard solution containing 2 µg g^{-1} of this element was prepared. This solution was analyzed once every 5 CRM samples, in order to evaluate the stability of the signal. The recoveries must fall within the limits of 96-105 % and 98-103 % in this study using OneNeb® and MultiNeb®-based configurations, respectively.

The basis of fire assay method is that the geological sample for analysis is diluted with silver and, together with added lead, is melted in a cupellation crucible (magnesium oxide) so that the lead is progressively converted into lead oxide.

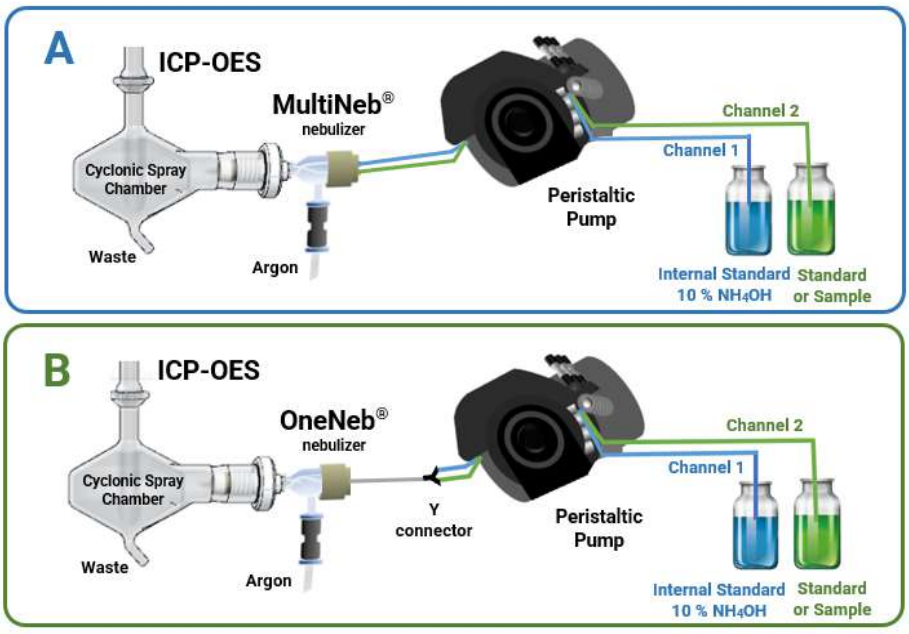

Figure 3. Schematic representation of both sample introduction systems. A: MultiNeb®-based configuration. B: OneNeb®-based configuration.

In this process, the lead oxide takes up the oxides of the base metal part in the form of a molten glass that drains away from the hot metal bead and diffuses into the porous crucible. The metal button remaining after this cupellation process essentially consists of gold and the excess of added silver. The silver is extracted from the flattened noble metal button in nitric acid leaving the gold. The gold content of the sample is then accurately determined by weighing or spectrometric determination.

More recently, the analytical technique mostly employed for gold detection is the inductively coupled plasma – optical emission spectrometer (ICP-OES) after aqua regia digestion process. The final solution containing higher contents of Ag^{+}, Cl^{-} generating silver chloride (AgCl) precipitates after hydrochloric acid addition. For this reason, at the end of the sample introduction sequence, ammonia (NH_4OH) is used for cleaning the nebulizer, dissolving any possible AgCl that may have precipitated out.

This fact causes perturbation in nebulization process, more pronounced when NH_4OH online solutions is not employed, consequently, the use of internal standard is mandatory. In this study, for evaluation of the effects in nebulization process, the pressure (kPa) was controlled in each analytical determination using both nebulizers as shown in Figure 4 using software ICPExpert (Agilent Technologies).

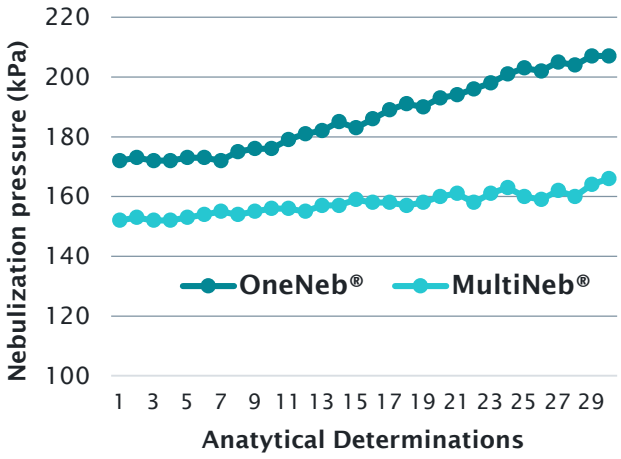

Figure 4. Graphic representation of pressure values (kPa) for each analytical determinations using both nebulizers.

The results represented in Figure 4 show an increase in nebulization pressure along the analytical sequence, more pronounced in the case of OneNeb®-based configuration in comparison with MultiNeb®-based configuration. This fact could be related with a high mixing efficiency between two solutions, miscible or immiscible, since the mixing takes place under turbulent conditions of high pressure at the tip of the MultiNeb®-based configuration preventing the pressure effects in nebulization process caused by AgCl precipitates. In addition, the matrix effects are reduced using MultiNeb®-based configuration as a consequence of the lower flow rate for sample introduction.

For the sensitivity study, a nebulization flow curve for using different pump speed for sample introduction was made using a solution of 5 µg kg^{-1} of gold element, obtaining the best results to 0.65 L min^{-1} and 10 rpm for OneNeb®-based configuration and 0.70 L min^{-1} and 7 rpm for MultiNeb®-based configuration (Figure 5). In addition, method detection limits (LODs) were established by analyzing eight replicate injections of the calibration blank and multiplying the obtained standard deviation by three. The results obtained are show in Table II.

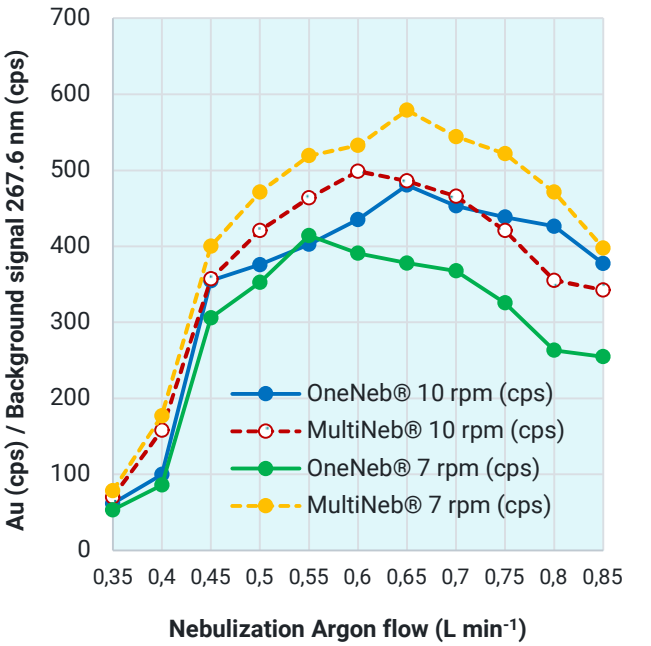

Figure 5. Nebulization flow curve for sensitivity evaluation using different nebulization gas pressure and pump speed for sample introduction represented as Intensity of 5 ppm Au (cps) / Background signal (cps).

Certified Reference Materials (CRM)	Certified values	Experimental values			
	Concentration (mg kg^{-1})	OneNeb®-based configuration		MultiNeb®-based configuration	
		LOD = 0.18 (mg kg^{-1})		LOD = 0.11 (mg kg^{-1})	
		Concentration (mg kg^{-1})	RSD (%)	Concentration (mg kg^{-1})	RSD (%)
OREAS 621	1.250	1.209	1.28	1.234	1.36
OREAS 622	1.850	1.836	1.52	1.861	1.30
OREAS 623	0.797	0.782	1.87	0.789	1.22
OREAS 624	1.160	1.129	1.33	1.174	0.98

Table II. Experimental and certified values for gold content, as well as the RSD obtained for 5 replicates of the different CRM using OneNeb® and MultiNeb®-based configurations employed in this study.

The results obtained in this study show higher sensitivity when the MultiNeb®-based configuration is employed, as is corroborated in the LODs (Table II).

Precision and reproducibility evaluation

Precision values were evaluated using geological matrix certified reference materials (CRM) after fire assay procedure and aqua regia digestion, as described previously.

Table II summarizes the experimental registered content of gold for wavelength monitored with both nebulizers' configurations evaluated, as well as the RSD obtained for five replicates of each of the CRMs following the experimental procedure described of this application note. Generally, MultiNeb®-based configuration shows better precision and reproducibility results that the OneNeb®-based configuration.

4. Conclusions

In this study, it has been demonstrated that the new MultiNeb® multiple nebulizer presents higher precision and reproducibility for gold determination in geological samples using ICP-OES after fire assay procedure.

Firstly, the results obtained in this study using MultiNeb®-based configuration provide better sensitivity to lower speed pump for sample introduction to the ICP-OES instruments compared to the OneNeb®-based configuration, therefore, matrix effects are proportionally reduced. This fact makes MultiNeb® nebulizer more appropriate for the analysis of samples with high content in corrosive acids, minimizing the deterioration of instrumental accessories and consumables of ICP-OES instruments.

On the other hand, the enhanced precision results obtained with the MultiNeb®-based configuration are related to the higher sensitivity and reproducibility obtained in comparison with the Y joint OneNeb®-based configuration, what demonstrates that the mixing of the internal standard and the calibration standard is much more efficient and complete in the MultiNeb than at a Y connection.

The novel MultiNeb® allows a high mixing efficiency between two liquids, miscible or immiscible, because the mixing takes place under high pressure turbulent conditions at the tip of the nebulizer, at the exact moment the aerosol is generated. This minimizes the effects on the nebulization process and therefore improves the analytical operation and results.

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