



## Analytical Note

# Evaluation of quartz tubes as atomization cells for gold determination by thermospray flame furnace atomic absorption spectrometry

Ezequiel Morzan, Ornela Piano, Jorge Stripeikis, Mabel Tudino\*

Laboratorio de Análisis de Trazas, INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, (1428) Buenos Aires, Argentina

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## ABSTRACT

This work describes the development of a new analytical procedure able to determine gold by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) using nickel tubes (NiT) and quartz tubes (QT) as atomization cells. Experiments involving changes in the flow injection operational parameters, reagent concentrations and sizes of the QT were performed in order to optimize sensitivity. Under the same operational conditions, it was observed that the employment of QT increases the sensitivity of gold determination when compared to the nickel tube. Since solutions of highly concentrated hydrochloric acid showed the best performance as carriers, quartz tubes were also preferred due to its greater tolerance to corrosion by mineral acids in comparison to NiT. In addition, changes in the internal diameter of the QT revealed an important improvement in sensitivity for smaller tubes.

Under optimized conditions the main figures of merit showed values close to that of graphite furnace atomic absorption spectrometry with the addition of an excellent improvement of the sample throughput. They are: LOD (3 s):  $0.004 \mu\text{g mL}^{-1}$ , sensitivity:  $0.306 (\mu\text{g mL}^{-1})^{-1}$ , RSD% ( $n = 10, 1 \mu\text{g mL}^{-1}$ ): 2.5, linear range:  $0.01\text{--}4 \mu\text{g mL}^{-1}$  and sample throughput:  $72 \text{ h}^{-1}$ .

This new method was employed for the determination of gold in homeopathic medicines with no need of sample digestion. Validation of the analytical results will be shown.

A full discussion of the most relevant findings regarding the role of the atomization cell as a strategic key for improving sensitivity will be also provided.

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## 1. Introduction

The determination of gold is often difficult due to the extremely low concentrations usually found in the environment. Consequently, the poor limits of detection (LOD) and sensitivities provided by traditional techniques such as flame atomic absorption spectrometry (FAAS) are not useful for its quantification. This is in part due to the low nebulization efficiency and the short residence time of free atoms in the flame. Therefore, different alternatives of sample introduction into the atomizer have been tested along the years with the aim of improving sensitivity.

One of them was proposed by Berndt et al. [1]. In thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS), a liquid sample is transported through a ceramic capillary toward a metallic tube or flame furnace (FF) located over a combustion flame in the optical path of an atomic absorption spectrometer. The flame furnace has a hole where about 1 mm of the total tip length is inserted. This arrangement allows the introduction of the whole sample and an increased time of residence of the analyte in the furnace which improve limits of detection

and sensitivities up to the  $\mu\text{g L}^{-1}$  level for the volatile elements (Cd, Zn and Pb) [2–4].

It is well known that the traditional pneumatic nebulization of samples holding for example highly saline matrices, might clog the nebulizer capillary obliging the analyst to work on the analyte isolation. However, the direct introduction of this kind of sample is more feasible with a thermospray system. It has been demonstrated [5,6] that this approach reduces sample manipulation which in turn, minimizes losses of the analyte or external contamination, lowers reagent consumption and increases sample throughput.

Mostly, the TS-FF-AAS technique employs nickel tubes for atomization [7–13]. Up to date, just one work [14] reports the use of QT-TS-FF-AAS for the determination of Cd with preconcentration by cloud point extraction and introduction of the sample in a micellar phase.

Recently Peng Wu et al. [15] compared tungsten coil electrothermal vaporization and thermospray flame furnace for the determination of 25 elements showing that the most volatile yielded better sensitivity with the last approach, being the contrary with the refractory ones. In the case of gold, the authors found a limit of detection (LOD) of  $0.2 \mu\text{g mL}^{-1}$ . Bezerra et al. [16] also reviewed recent developments and applications on the production of thermosprays but no results involving gold were provided.

\* Corresponding author: Tel.: +54 1145763360; fax: +54 1145763341.  
E-mail address: [tudino@qi.fcen.uba.ar](mailto:tudino@qi.fcen.uba.ar) (M. Tudino).

In this work we present for the first time the employment of a quartz tube as the atomization cell for the determination of gold in homeopathic medicines by TS-FF-AAS.

On the knowledge that gold salts are frequently employed in the homeopathic treatment of rheumatoid arthritis, we decided to take advantage of direct sample introduction that might allow the thermospray methodology. As a matter of fact, the medicine *Aurea Oligoplex* seemed a good candidate since it is composed by a complex mixture of sugars and vegetable extracts in ethanolic solution that requires complete sample mineralization when flame atomic absorption spectrometry (FAAS) is used.

Basic studies on the analytical performance of NiT and QT as atomic furnaces were first performed. Obtained results will be shown and contrasted with those given by FAAS with pneumatic nebulization.

The application to the determination of gold in *Aurea Oligoplex* with no need of sample digestion will be presented. Validation of analytical results involving microwave digestion of the samples and gold determination by FAAS will be also shown.

## 2. Experimental

### 2.1. Reagents and materials

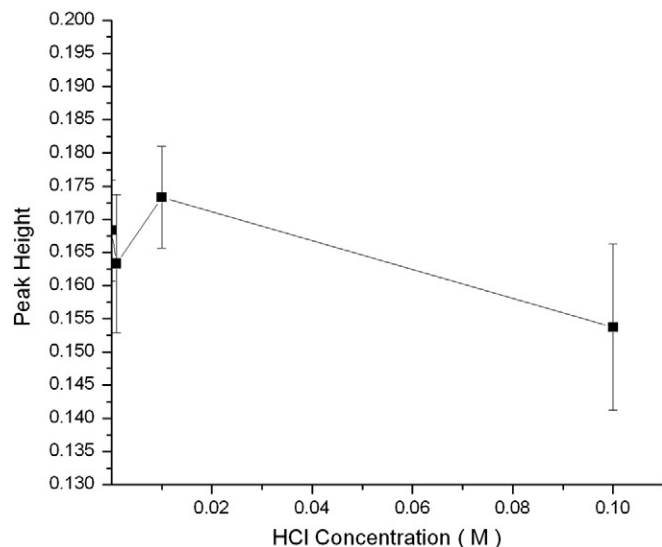
All solutions were prepared with analytical grade chemical reagents and double deionized water obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). All of the glassware was washed with EXTRAN (Merck) 1% v/v and kept in 10% (v/v) HCl with further cleaning with water. Gold standard solutions were prepared daily by appropriate dilutions of 1000 mg L<sup>-1</sup> stock solution.

HNO<sub>3</sub> Suprapur (Merck) was employed for sample mineralization when required.

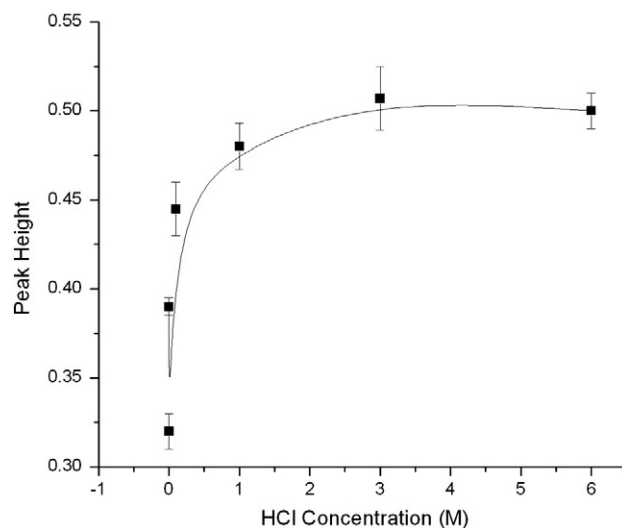
*Aurea Oligoplex* is composed of 0.001 g gold and sodium chloride; 8 mL *Crataegus Oxycantha* Dye 50% m/v; 1 mL *Strophantus Gratus* Dye 10% m/v, 0.1 g; Camphor, 12.75 g sugar; made up to 100 mL with ethanolic solution (96% m/v).

### 2.2. Apparatus

A flame atomic absorption spectrometer Shimadzu AAS 6800 (Kyoto, Japan) equipped with a hollow cathode lamp of gold as radiation source and a deuterium lamp for background correction was



**Fig. 1.** Peak height vs. HCl concentration (NiT), a standard solution of 2 mg Au L<sup>-1</sup> was employed for all measurements. Error bars were calculated as  $tS/\sqrt{N}$  where  $S$  is the standard deviation  $t$  is the 95% confidence student  $t$  factor and  $N$  is number of measures ( $N=5$ ).



**Fig. 2.** Peak height vs. HCl concentration (QT, i.d. = 6.7 mm), a standard solution of 2 mg Au L<sup>-1</sup> was employed for all measurements. Error bars were calculated as  $tS/\sqrt{N}$  where  $S$  is the standard deviation  $t$  is the 95% confidence student  $t$  factor and  $N$  is number of measures ( $N=5$ ).

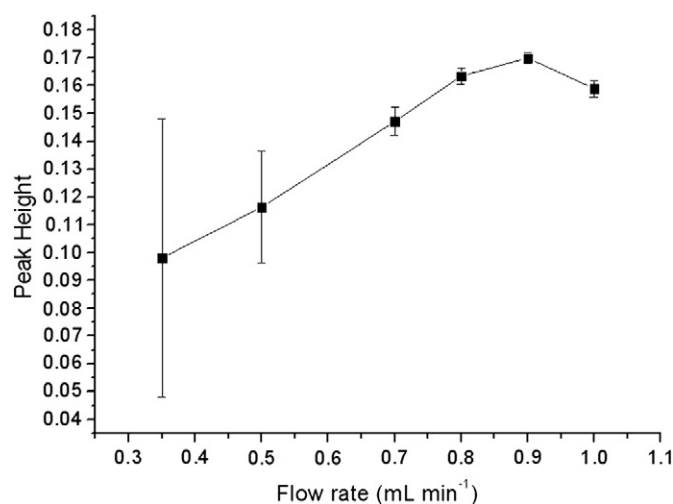
used. Instrumental conditions were those provided by the manufacturer. Transient signals were recorded in the peak height mode.

A closed-vessel microwave oven (MDS-2000, CEM Corporation, USA) equipped with temperature and pressure probe was used in samples digestion procedures.

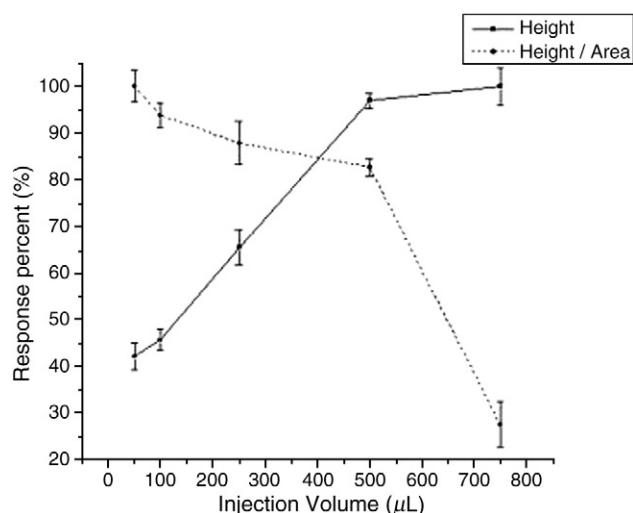
The TS-FF-AAS system was assembled with a peristaltic pump of eight channels and six rollers (IPC, Ismatec, Glatfbrugg-Zürich, Switzerland), a six-port rotatory valve VICI (Valco Instruments, Houston, TX, USA), 0.5 mm i.d. PTFE® tubings, a ceramic capillary (0.5 mm i.d., 6 cm length) and nickel or quartz flame furnace atomizers placed in turn on an oxidizing air/acetylene flame with the assistance of a homemade steel holder.

The nickel tube (Inconel 600® alloy, Camacam, São Paulo, Brazil) composition was >72% (m/m) Ni, 14–17% (m/m) Cr and 6–10% Fe as major constituents. The dimensions were 9.7 mm i.d. and 100 mm length.

Two quartz tubes were locally made with the following characteristics: 9.7 mm and 6.7 mm internal diameters respectively, 100 mm length, six holes (2 mm) located equidistant in the face toward the



**Fig. 3.** Peak height vs. carrier flow rate (NiT), a standard solution of 2 mg Au L<sup>-1</sup> was employed for all measurements. Error bars were calculated as  $tS/\sqrt{N}$  where  $S$  is the standard deviation  $t$  is the 95% confidence student  $t$  factor and  $N$  is number of measures ( $N=5$ ).



**Fig. 4.** Peak height percent vs. injection volume (full line), peak height/peak area percent (dash lines) vs. sample volume, a standard solution of  $2 \text{ mg Au L}^{-1}$  was employed for all measurements. Percentages are referenced to the highest obtained signal. Error bars were calculated as  $tS/\sqrt{N}$  where  $S$  is the standard deviation  $t$  is the 95% confidence student  $t$  factor and  $N$  is number of measures ( $N=5$ ).

burner allowing partial penetration of the flame inside the tube, a lateral hole (2 mm) where the ceramic tube described above was partially inserted.

### 2.3. Experimental procedure for the determination of gold in homeopathic formulat

#### 2.3.1. Flame atomic absorption spectrometry determination

In order to introduce the sample—an ethanolic extract of several vegetables, sugar and microamounts of gold salts—in the combustion flame by pneumatic nebulization, digestion is needed. Mineralization was performed by mixing 10 mL of the homeopathic preparation with 5 mL of nitric acid in a microwave digester. After complete mineralization, the obtained solution was made up to 50 mL volume and gold in the homeopathic formulat was determined by direct interpolation of the analytical signal in a working curve ranging between  $0.12$  and  $15 \mu\text{g mL}^{-1}$ .

#### 2.3.2. TS-FF-AAS determination

The flow system holding a quartz tube of 6.7 mm i.d. was employed for all measurements. Samples, spiked samples and standard solutions containing gold in 3 mol/L HCl were injected (injection volume = 500  $\mu\text{L}$ ) into a carrier stream of 3 mol/L HCl at a flow rate of  $0.9 \text{ mL min}^{-1}$ . Gold concentration in the homeopathic formulat was obtained by standard addition. Aliquots of 2 mL of the samples were diluted to 50 mL in HCl 3 mol/L. Spiking of standard gold solutions ranged between 0.5 and  $2 \mu\text{g mL}^{-1}$ .

## 3. Results and discussion

### 3.1. Optimization of TS-FF-AAS parameters

On the assumption that besides the pH of the media, the hydrochloric acid concentration might influence the volatility of the analyte by the production of chloroauric complexes, HCl concentration was raised up to 0.1 mol/L with the nickel furnace and up to 6 mol/L with both quartz tubes. Higher concentrations were not tested for the former due to its supposedly lower tolerance to corrosion by mineral acids.

Fig. 1 shows the influence of HCl concentration on the analytical signal when the nickel furnace is employed. Considering the experimental error, no significant changes were observed.

Fig. 2 shows the influence of HCl concentration when the quartz tube was employed instead. In this case, the signal increased up to 3 mol/L and reached a plateau from 3 mol/L onwards. Thus HCl mol/L was selected for the experiments. Note that this result reveals an advantage of the QT with respect to the NiT as the latter suffers deterioration when mineral acid concentration is raised. Considering the improvement in sensitivity for QT, further experiments were carried out with this material.

The carrier flow rate (Fig. 3) was varied between  $0.35$  and  $1.0 \text{ mL min}^{-1}$ . Upper values allowed the development of higher and narrower transient signals probably due to the increment in the rate of introduction of the analyte into the atomization cell. However, when the flow rate was increased above  $0.9 \text{ mL min}^{-1}$  a decrease in peak height was observed. This could be attributed to a decrease in the capillary temperature (in fact it is observed through the change of the capillary color as no temperature measurements were taken) yielding to a poor signal. Therefore, a flow rate of  $0.9 \text{ mL min}^{-1}$  was selected as optimum.

Regarding the influence of the sample volume on the analytical signal, a direct proportionality was observed since an increment of the injected volume of sample implies an increment of the atomic population into the flame furnace. However, this direct relation falls when the volume of sample fills the atomization cell. Then, a wider peak instead of a higher one is obtained.

In Fig. 4 peak height percent and the quotient peak height to peak area percent—which somehow represents the signal broadening, are plotted against the injected sample volume. It was observed that a sample volume of about 500  $\mu\text{L}$  gives the maximum peak height compatible with the minimal signal broadening (represented by the peak height/peak area ratio). So, 500  $\mu\text{L}$  was selected as it allows working with good sensitivity and high sample throughput.

### 3.2. Analytical performance

The figures of merit for the determination of gold by FAAS and by TS-FF-AAS using different furnace materials and diameters were obtained and they are displayed in Table 1. The first three columns devoted to TS show the results with DDW as carrier. The last column

**Table 1**  
Comparison of figures of merit for the different conventional analysis and atomization cells.

Figure of merit	FAAS	TS-FF-AAS Nickel furnace (i.d. = 9.7 mm)	TS-FF-AAS Quartz furnace (i.d. = 9.4 mm)	TS-FF-AAS Quartz furnace (i.d. = 6.7 mm)	TS-FF-AAS Quartz furnace (i.d. = 6.7 mm) Carrier HCl 3 M	GFAAS
Sensitivity ( $\text{mL } \mu\text{g}^{-1}$ )	$0.040 \pm 0.001$	$0.083 \pm 0.003$	$0.207 \pm 0.005$	$0.237 \pm 0.009$	$0.306 \pm 0.006$	$0.140 \pm 0.003$
DLR ( $\mu\text{g mL}^{-1}$ )	0.12–15	0.08–10	0.03–8	0.02–6	0.01–4	0.003–0.080
% RSD ( $N=10$ )	5.3	5.4	6.3	5.9	2.5	4.6
LOD ( $\mu\text{g mL}^{-1}$ )	0.04	0.026	0.010	0.006	0.004	0.0009
LOQ ( $\mu\text{g mL}^{-1}$ )	0.12	0.085	0.034	0.019	0.012	0.003
Sample frequency ( $\text{h}^{-1}$ )	70	72	72	72	72	10

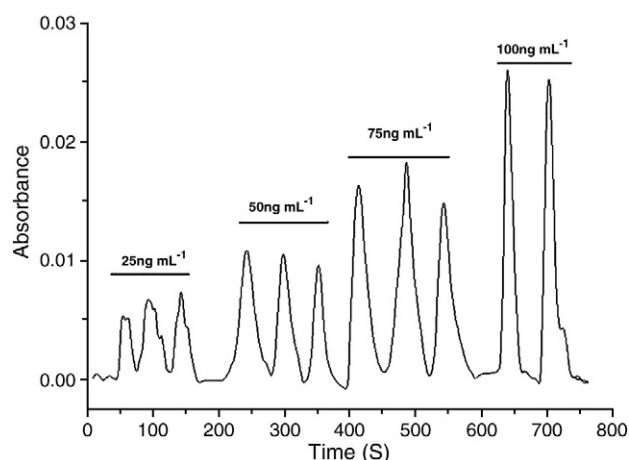


Fig. 5. Signals obtained for gold solutions (25, 50, 75, 100 ng mL<sup>-1</sup>) under optimized conditions with QT as the atomization cell.

shows the improved results when HCl 3 mol/L is employed as carrier. Limits of detection (LOD) and limits of quantification (LOQ) were calculated as 3 s and 10 s criteria, respectively.

From the analysis of Table 1, it can be observed that the NiT yields sensitivity two times higher than FAAS. When QT of the same size is employed instead, a 150% increase in sensitivity is observed.

When a QT of even more reduced internal diameter is employed, the sensitivity increases again. Consequently, the combined effect of changing the surface material and reducing the internal diameter of the tube renders a LOD 50 times improved with respect to the more recent publications on the subject [15].

Fig. 5 shows the analytical signals on a draft basis. Peak height instead of peak area was selected for quantification as reproducibility is better with the former.

### 3.3. Gold determination in homeopathic medicine

The homeopathic medicine analyzed here requires complete digestion for its determination by FAAS. This technique was replaced by the method developed in this work that employs direct sample introduction. Table 2 shows the analytical results obtained by both analytical procedures. Results are in good agreement for a 95% confidence level (*t* student, *n* = 5).

Since mineralization of samples is always time-consuming and prone to contamination, the TS-FF-AAS seems attractive as it allows direct introduction of the sample (no pre-treatment) together with simplicity, economy and high sample throughput (see Table 1). However, it is fair to say that the sample matrix influences the analytical signal and obliges to the standard addition methodology.

## 4. Conclusions

The use of TS-FF-AAS with quartz tubes of reduced inner diameter for the determination of gold is presented here for the first time. It

reveals itself as a promising methodology considering simplicity of operation and economy. The figures of merit are improved in comparison to others already reported. It should be noticed that the LODs are drastically improved with the proposed methodology. They are close to graphite furnace atomic absorption spectrometry (see Table 1) with the “bonus” of economy and a drastic increment in sample throughput: 72 h<sup>-1</sup> in this case vs. 15 h<sup>-1</sup> (typically) in GFAAS.

The method was applied to the determination of gold in homeopathic formulatates with no need of sample digestion and good agreement with results obtained by the standard FAAS technique.

Further investigation involving quartz tubes of different sizes as the atomization cells for TS-FF-AAS will be performed for other analytes on the belief that the dispersion of the atoms in the cell volume together with the interaction with the tube surface is strategic key for improving sensitivity.

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Table 2

Gold determination in *Aurea Oligoplex*: FAAS with sample digestion and direct sample introduction TS-FF-AAS.

Method of analysis	Sample 1 ( $\mu\text{g mL}^{-1}$ )	Sample 2 ( $\mu\text{g mL}^{-1}$ )	Sample 3 ( $\mu\text{g mL}^{-1}$ )	Sample 4 ( $\mu\text{g mL}^{-1}$ )	Sample 5 ( $\mu\text{g mL}^{-1}$ )
FAAS (digested sample)	$6.2 \pm 0.2^a$	$5.0 \pm 0.2$	$6.0 \pm 0.2$	$6.9 \pm 0.2$	$7.9 \pm 0.2$
TS-FF-AAS (direct introduction)	$6.0 \pm 0.3^a$	$5.0 \pm 0.3$	$6.1 \pm 0.3$	$7.0 \pm 0.3$	$7.8 \pm 0.3$

<sup>a</sup> Standard deviation (*n* = 5).

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