

## Study of Selenium by Electrothermal Atomic Absorption Spectrometry with Tantalum Platform

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### Abstract

A new approach for the direct determination of selenium by Electrothermal Atomic Absorption Spectrometry (ETAAS) is proposed, the method employs a 1.0cm x 0.3cm Tantalum metal platform placed in graphite tube. The experimental conditions for the determination of Se via this method have been optimized. Pyrolysis and atomization curves are constructed using uncoated graphite tube without and with platform. The calibration curves were linear over the rang 10-50 ng.ml<sup>-1</sup> of Se concentration, with relative standard deviation values, at 50 ng.ml<sup>-1</sup> level of 1.96%. The accuracy and precision of the method was evaluated by determining recoveries and percentage relative standard deviation using different concentrations of standard solutions of Se. this method was applied successfully for the determination of Se in human blood serum.

### الخلاصة

تضمنت الدراسة تطوير طريقة جديدة لتقدير عنصر السلينيوم مباشرة باستخدام مطيافية الامتصاص الذري الكهروحراري بوجود منصة معدنية من عنصر التنتالوم بابعاد اسم طول وعرض 0.3سم يتم وضعها داخل الفرن الكرافيتي بشكل منصة.

تم دراسة الظروف الالية لتقدير عنصر السلينيوم باستخدام الطريقة الجديدة .رسم منحنى الترميد والتذرية باستخدام الفرن الكرافيتي بوجود وبدون المنصة ووجد تطور كبير في المعطيات التحليلية بوجود المنصة .كانت خطية منحنى المعايرة ما بين 10-50 نانوغرام/ مل لعنصر السلينيوم مع انحراف قياسي نسبي مؤي قدره 1.96% عند مستوى 50 نانوغرام/ مل .درست دقة واتقان الطريقة بحساب استرجاعية و الانحراف القياسي النسبي المؤي لمحاليل قياسية معلومة طبقت الطريقة بنجاح لتقدير عنصر السلينيوم في نماذج من مصل الدم.

## **Introduction**

Selenium is one of the most significant essential microelement; it is present in all living systems and because of its high significance affect on the health of people and animals, and interest for selenium is recently rising<sup>1</sup>. Researches on selenium became one of the most interesting areas in many integrated scientific fields, notably, in medicinal, nutritional and environmental<sup>2-3</sup>. Spectrometric procedures have widely been employed for selenium determination, among which electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-mass spectrometry (ICPMS)<sup>4-7</sup>. Hydride generation (HG) together with inductively coupled plasma optical emission spectrometry (ICP-OES) is a widely used method for the determination of selenium<sup>8,9</sup>, the method could also be used in conjugation with flow injection technique (FI-HG-ICP-OES) to enables separation of selenium from the major components of the sample but it suffer from interferences from several transition metal ions and other volatile elements<sup>10</sup>. Chromatographic (IC-CD, GC-FID) and X-Ray Diffraction (XRD) techniques that allow the specific determination of several selenium species present or formed during bioremediation processes<sup>11</sup>. spectrophotometric determination of traces of inorganic selenium(IV) and/or selenium(VI) in tap and freshwater samples<sup>12</sup>. The analytical signal obtained for the direct sampling in ETAAS technique is inherently very sensitive to the variation of sample matrix components<sup>13-14</sup>, while the intrinsic low tolerance limit to the total dissolved salts (TDS) restricts the direct applications of ICPMS for saline sample matrices<sup>15</sup>. On

the other hand, atomic emission spectrometry (AES), flame AAS and fluorimetric cannot fulfill the requirements for ultra-trace determination of selenium<sup>16</sup>. Hydride vapor generation and flow injection hydride generation atomic absorption (FI-HG-AAS) has proven to be an elegant approach for eliminating matrix effects while improving the sensitivities for the determination of hydride/vapor forming elements<sup>17-23</sup>. Atomic fluorescence spectrometry (AFS) has a flow through detector compatible with on-line vapor generation system, which made it most suitable for measuring vapor forming species<sup>24-27</sup>. The high volatility of selenium, low wavelength (196 nm) of his resonance line, and its presence in an anionic form are some of basic problems in (ETAAS) determination of this element. For the elimination of matrix interference in pyrolysis stage, different modifiers such as Ni(NO<sub>3</sub>)<sub>2</sub>, Pd, Pd-ascorbic acid, Ni + Mg(NO<sub>3</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> were proposed<sup>28</sup>.

In this study a new atomization medium for selenium determination via ETAAS was developed. It is simple constructed, available, and gave accurate and precise results under mild heating cycle conditions in comparison with that used with commercial uncoated graphite tube and no need for chemical modifiers to be used.

## **Experimental**

### **Apparatus:**

A Perkin-Elmer 800S atomic absorption spectrophotometer equipped with a GFA graphite furnace atomizer, provide with auto sample changer, uncoated graphite tubes, A Perkin-Elmer hollow-cathode lamp for Se,

and D2 lamp for background correction were used.

#### **Reagents:**

A commercially available stock solution of Se 1000 ppm (as  $\text{H}_2\text{SeO}_3$  . FLXANAL) was used. Working solutions were freshly prepared by diluting aliquots of this solution with de-ionized water before use. Nitric acid ,sulfuric acid and hydrochloric acid (Analytical grade, FLUKA) was used.

#### **Procedure**

A series of Se standard solutions (10-50)  $\text{ng.ml}^{-1}$  prepared in 1%  $\text{HNO}_3$  were injected in a uncoated graphite furnace in which a piece of tantalum metal (1.0cm x 0.3cm) platform was inserted. The atomic absorption signal for each standard was measured after subjecting it to the heating cycle under optimum conditions.

#### **Preparation of samples**

0.25 ml of human blood serum was diluted with 1ml of 1% $\text{HNO}_3$  deionized water and 10 $\mu\text{l}$  of these solution injected in graphite tube.

#### **Results and discussion**

A method was developed for the determination of selenium concentrations. Selenium determination was performed by constructed pyrolysis and atomization curve with Ta platform, W platform, W spiral tungsten and uncoated graphite tub only using the initial experimental conditions given in Table (1) and (2).

The Pyrolysis and atomization curves of Selenium were plotted by using 20  $\text{ng.ml}^{-1}$  Se standard solutions in 1%  $\text{HNO}_3$ . Results showed that by using Ta platform have significant effects on pyrolysis and atomization temperatures (i.e. yield in a decrease of 300 °C and 700 °C respectively) which could be attributed to red hot tube wall phenomenon. Figure (1) shows the

Pyrolysis and atomization curves using different type of conditions, the study without any acid or platform and with different type of acids ( $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ ) and different type platform Ta, w and spiral tungsten. The results were summarized in Table (3).

#### **Calibration curves**

Under the optimum experimental conditions (pyrolysis and atomization temperature), calibration curves for the determination of Se in the presence of Ta, W, spiral tungsten and uncoated graphite tub were constructed Figure (2),and Table (4) show the calibration curves and analytical data obtain from calibration curves.

#### **Accuracy and precision**

The accuracy and the precision of the new methods were tested by the determining recoveries and percentage relative standard deviation of standard solutions prepared using different concentrations of Se, the results shows that Ta platform gives the best accuracy and precision. Table 5 shows the results obtained.

#### **Application of the developed method**

Three samples of human blood serum were analyzed using the optimum conditions with Ta platform to test the ability of this developed method. The results of determination of Se obtain from Calibration curve were show identical with the results obtained from standard addition methods as show in Table (6) .

#### **Conclusion**

It was shown that selenium could be determined by electrothermal atomic absorption spectrometry with Ta platform and its simple constructed and no need for chemical modifiers.

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Table 1: Instrumental conditions.

Parameters	Se
Wavelength	196.0 nm
Spectral width slit	1.0 nm
Calibration mode	Absorbance Peak height
Background correction	D <sub>2</sub> lamp
Lamp current	3 mA
Sample aliquot	10 µL
Gas	Argon

Table 2: Initial program heating.

Step	Atomizer operation	Temperature °C	Time (s)	Ramp (s)	Hold (s)
1	drying	100	25	-	
2	drying	130	15		-
3	pyrolysis	1100	3		-
4	atomizing	2600	3		-
5	cleaning	2700	2		-

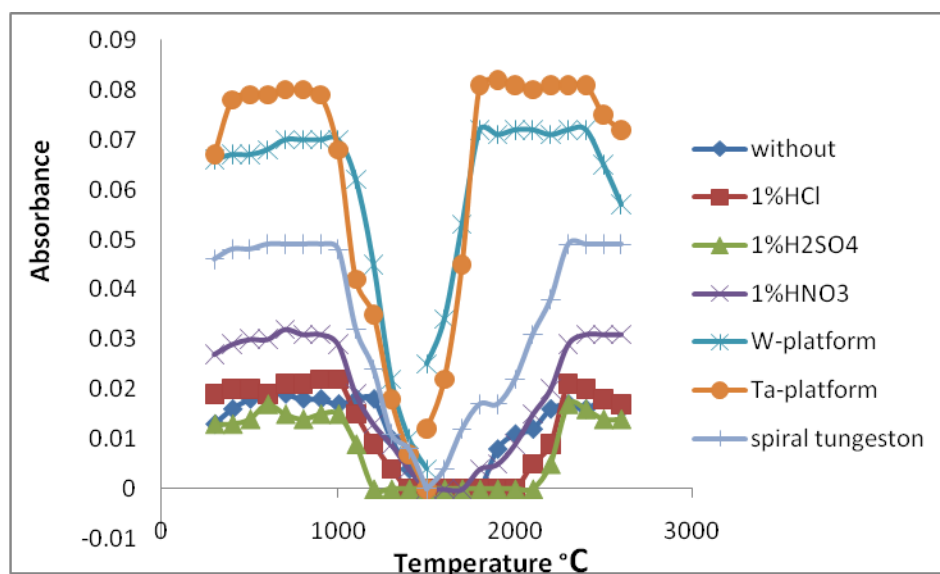


Fig 1: Pyrolysis and atomization curve using different type of modifiers.

Table 3: Recommended Pyrolysis and atomization curve.

Type of modifier	Pyrolysis Temperature °C	Atomizing Temperature °C
Uncoated graphite tub	1100	2600
Uncoated graphite tub+1%HCl	900	2400
Uncoated graphite tub+1%HNO <sub>3</sub>	900	2400
Uncoated graphite tub+1%H <sub>2</sub> SO <sub>4</sub>	900	2400
Ta platform+1%HNO <sub>3</sub>	800	1900
W platform+1%HNO <sub>3</sub>	900	2000
Spiral tungston+1%HNO <sub>3</sub>	900	2400

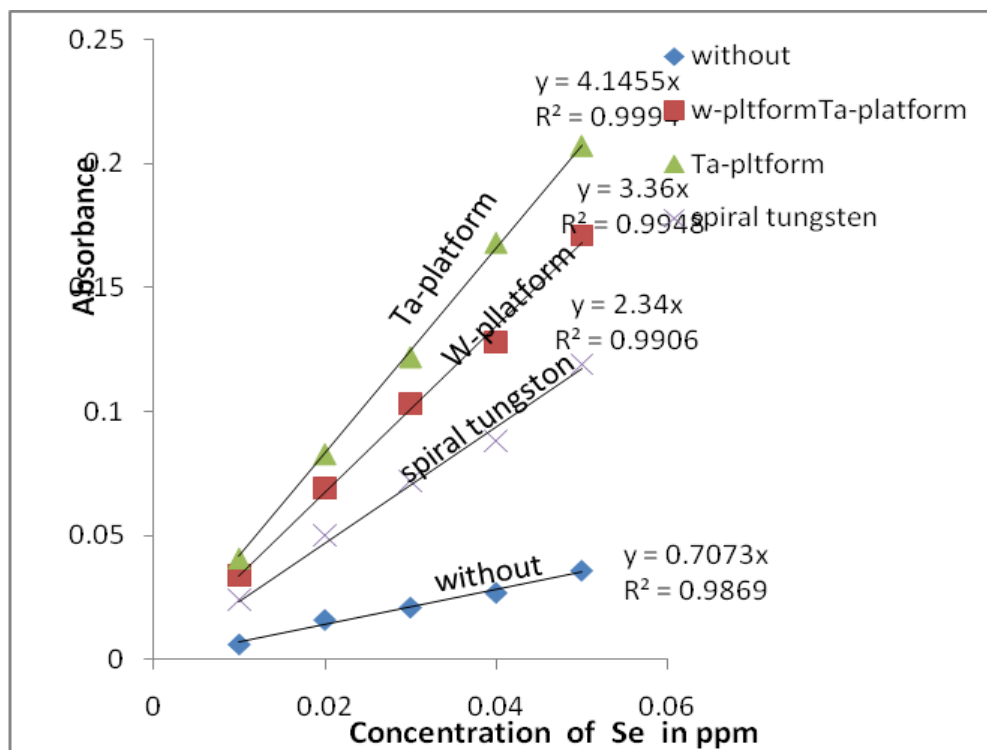


Fig 2: Calibration curve of Se in ppm.

Table 4: The analytical data of the determination of Se

Analytical data	Value			
	Without platform	With Ta platform	With W platform	With Spiral platform
Limit of detection	6.3 ppb	1.0 ppb	1.3 ppb	1.6 ppb
Absolute sensitivity	$6.5 \times 10^{-11}$ g	$1.07 \times 10^{-11}$	$1.3 \times 10^{-11}$	$1.85 \times 10^{-11}$ g
RSD%	5.6-8.5	3.8-.86	4.63-1.43	6.67-2.09

Table 5: Study the accuracy and the precision of the new methods

Conc. Of selenium in ppb	Type of modifier											
	Without platform			With Ta platform			With W platform			With Spiral platform		
present	10	30	50	10	30	50	10	30	50	10	30	50
found	11.3	27.9	52.6	9.9	30.3	50.4	9.8	29	50.5	9.1	28	48.4
RSD%	8.50	6.12	5.70	3.80	1.23	0.86	4.63	3.70	1.43	6.67	4.12	2.09
Error %	13.0	-7.0	5.5	-1.0	1.0	0.8	-2.0	-3.3	1.0	-9.0	-6.6	-3.2
Recovery%	113.0	93.0	94.5	99.0	101.0	101.0	98.0	96.7	101.0	91.0	93.4	96.8

Table 6: Comparison of calibration curve and standard addition methods.

sample	Standard addition method	Calibration curve method
1	98.6	98.8
2	94.3	95.0
3	98.8	100.0