

## Multi-Element Determination of Cu, Mn, and Se using Electrothermal Atomic Absorption Spectrometry

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**Abstract:** Simultaneous multi-element graphite furnace atomic absorption spectrometer (SIMAA 6000) is used to get a new multi-element determinations methodology for Cu, Mn, and Se. Firstly, the optimum conditions for single-element mode are determined (which include: pyrolysis and atomization temperatures). Secondly, the optimum conditions for multi-element mode are also determined. The conditions in the two modes have been compared in terms of the characteristic masses, detection limits and pyrolysis and atomization temperatures. The effect of the matrix on the determination has been studied using urine standard sample from Seronorm (LOT 0511545). The accuracy of the developing methods has been confirmed by analysis different biological reference materials. Simultaneous multi-element GF-AAS offers a rapid, low cost and sensitive method for the analysis of trace elements.

**Keywords:** Simultaneous multi-element Determination, Copper, Manganese, Selenium

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### I. Introduction

One of the most instrumental techniques available for trace element determinations is Graphite Furnace Atomic Absorption Spectrometry (GFAAS) due to its high specificity, selectivity and sensitivity, low detection limits, ease of operation, low sample volume and low cost. GFAAS offers also several features, especially for routine analysis. However, GFAAS has a main disadvantage from the beginning that it is a single-element technique, which means a multiplied analysis time, when more than one element has to be determined [1].

The most important requirements in analytical atomic spectrometry are the ability for simultaneous determinations in small size samples in different matrices. This ability is very important in such fields as clinical and biochemical fields where a large sample size is difficult to obtain. Number of multi-element instruments have been used for the simultaneous multi-element determination of trace metals, such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-ray Fluorescence Spectrometry and Cathodic Stripping Voltammetry (CCV) [2]. The most important one is the ICP instruments. However, the use of ICP instruments were somewhat limited by difficulty in dealing with high salt concentrations and the need for relatively large sample volumes. Also the MS detector is rather complex and expensive, which limited the widespread used of ICP-MS for routine analytical work in labs and hospitals [3].

Number of multi-element Atomic Absorption spectrometers has been developed [4, 5]. Presently, the most widely used instrument is a line source simultaneous spectrometer, equipped with transversely heated graphite atomizer, THGA with integrated platform, Zeeman Effect background corrector and solid-state detector [6-20]. However, multi-element determinations carried out by SIMAAS need the adoption of compromised conditions, which can affect the sensitivity and the precision of analytical results [21, 22].

The aim of the present work is to develop simultaneous multi-element methodology for the analysis of copper, manganese and selenium in different biological samples.

### II. Material And Method

#### 1.1 Instrumentation

The instrument used was a SIMAA 6000 from Perkin-Elmer GmbH, Bodenseewerk. This atomic absorption spectrometer is with a longitudinal Zeeman-effect background correction system, Echelle optical arrangement, Solid-state detector, and Standard THGA tube with pyrolytic coated integrated platform. The rate of flow of the Ar was 250 ml.min<sup>-1</sup>. Stopped flow during the atomization was chosen. The lamps used were hollow cathode lamps (HCL) for the determination of Cu and Mn and electrodeless discharge lamp for Se from Perkin-Elmer. The sample injection volume was 20 µl. The integrated absorbance of the atomic absorption signal was used for the determination

## 1.2 Reagents and Samples

High purity water (18 MΩ cm) was prepared Milli Q, Millipore Corp. system. Analytical reagent-grade nitric acid (from KMF) was purified by sub-boiling distillation. AAS-Standard reference solutions of Cu, Mn, and Se (Brend Kraft GmbH) were used to prepare the standard analytical solutions. The chemical modifier solutions (ICP-Standard Palladium and AAS-Standard Magnesium) were from Bernd Kraft GmbH.

The accuracy of the method was confirmed by the determination of Cu, Mn, and Se in Trace Elements Urine Sample from Seronorm (LOT 0511545), Lyphocheck Urine Metals Control Level 1 from Bio-Rad (LOT 69061), and Pig Kidney from Institute for Reference Materials and Measurements (BCR-CRM 186).

### 1.2.1 Trace Elements Urine Sample (Seronorm 0511545)

Exactly 5 ml de-ionized water was added to the sample and let it stand for 30 min, and then transfer it to a plastic tube. The sample was then kept in a refrigerator at -20°C for later use. Before use, the sample was diluted 1:4 with 0.2% HNO<sub>3</sub>.

### Lyphocheck Urine Metals Control-Level 1 (69061)

The same procedure was applied as Seronorm sample except that, 25 ml de-ionized water was added and the sample was diluted 1:1 before use.

### 1.2.2 Pig Kidney (BCR-CRM 186)

The sample was digested as described by Ronald Treble [23]. Firstly, the sample was dried at 80°C for 4 h. and stored in desiccators before use. 0.5218 g (BCR-CRM 186) dried sample was allowed to digest in 5 ml concentrated distilled HNO<sub>3</sub> for a period of 72 h. at room temperature. The digested/acidified sample was transferred into 50 ml volumetric flask and diluted to the mark with de-ionized water. Before use, each sample was diluted as required

## 1.3 Contamination Control

All sample containers, auto-sampler cups, etc. were acid washed with 10% v/v nitric acid for 24h and then rinsed several times with de-ionized water before use. The analytical reference solutions were prepared daily by diluting with 0.2% nitric acid.

## III. Results And Discussion

### 1.4 Comparison between single-element and multi-element mode

When SIMAAS is used for single-element determination, all parameters are optimized for only one analyte. Therefore, the best optimized pyrolysis and atomization temperatures are obtained and used in the heating program, minimizing condensed and gas-phase interference. Mixture modifier (Pd + Mg) was used to stabilize the elements during the pyrolysis step. The same procedure was repeated for multi-element mode but for the three elements together. In this case, compromised conditions were obtained and used. The best pyrolysis and atomization temperatures were determined according to the pyrolysis and atomization curves and the absorbance peak for each element in the two modes. The temperature program was summarized in Table 1. Fig. 1 shows the pyrolysis and atomization curves for each element. The heating program for each element was used to determine the detection limits and the characteristic mass for each element and they were summarized in Table 2

**Table 1 Temperature program for Multi-element determination of Cu, Mn and Se with Pd+Mg modifier**

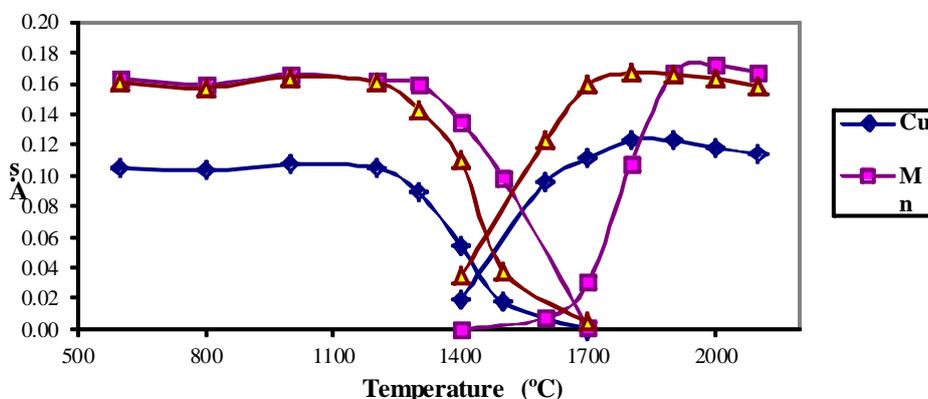
Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas Flow (ml min <sup>-1</sup> )
Drying 1	110	1	30	250
Drying 2	130	15	30	250
Pyrolysis	1200 <sup>a</sup>	10	20	250
Atomization	2000 <sup>b</sup>	0	5	0
Clean-out	2450	1	3	250

<sup>a</sup>1200, 1200, 1400°C for Se, Cu and Mn [in single-element mode]

<sup>b</sup>1900, 2000°C for Se and (Mn and Cu) [in single-element mode]

**Table 2 Comparison of detection limits and characteristic mass for two modes with Pd+Mg modifier**

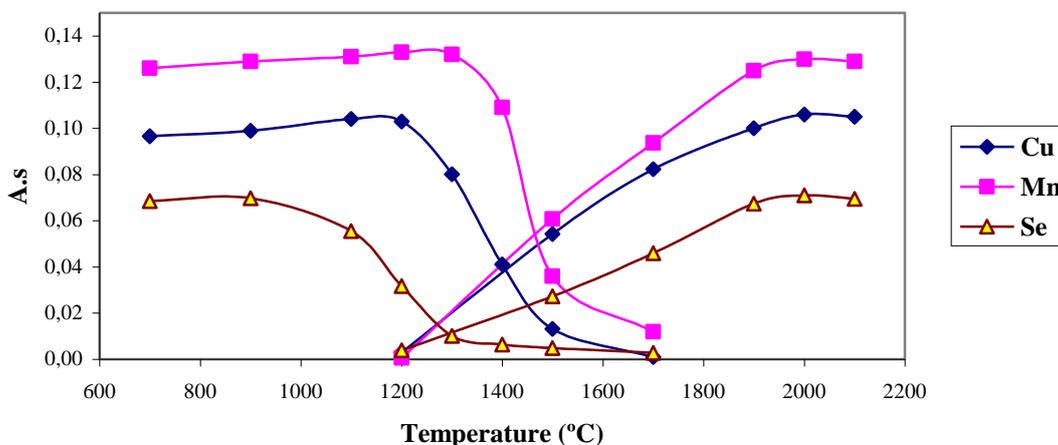
Element	Pyrolysis (Single) (°C)	Atomization (Single) (°C)	LOD (ppb)		Characteristic mass (pg)	
			Single	Multi	Single	Multi
Cu	1200	2000	0.13	0.20	19.6	20
Mn	1400	2000	0.051	0.070	5.0	5.2
Se	1200	1900	0.40	1.0	58.7	58.7



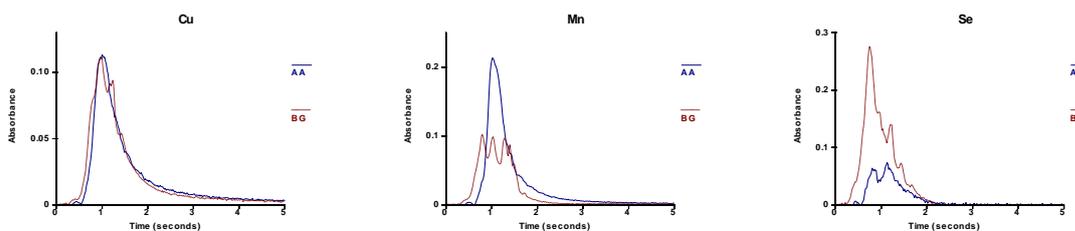
**Figure 1 Pyrolysis and atomization curves of Cu, Mn, and Se with Pd+Mg modifier**

**1.5 Study the effect of the matrix**

The diluted reference material (1:4) has been spiked with 10 ppb Cu, 6 ppb Mn, and 80 ppb Se. 20 µl diluted spiked reference material has been injected with 5µg Pd + 3µg Mg(NO<sub>3</sub>)<sub>2</sub> as a modifier into the atomizer each time during this study. Pyrolysis and atomization curves were carried out in order to define the compromise conditions for the simultaneous determination of these elements in the presence of the matrix. Fig. 2 shows the pyrolysis and atomization curves of each element in the diluted sample by using Pd+Mg as a modifier. The peak signal for each element at the optimum pyrolysis and atomization temperatures were shown in Fig. 3



**Figure 2 Pyrolysis and atomization curves of Cu, Mn and Se in diluted urine sample (1:4) with Pd+Mg modifier**



**Figure 3** Peak signals for multi-element determination in diluted urine sample with Pd+Mg modifier

### 1.6 Analysis of certified reference urine samples

The accuracy of the multi-element determination of this group was confirmed by the analysis of the following certified reference materials: Trace Element Urine Sample from Seronorm, Lyphocheck Urine Metals Control- Level 1 from BIO-RAD, and Pig Kidney from Institute for Reference Materials and Measurements. Each sample has been diluted according to the concentration of the elements in the sample.

### 1.7 Detection limits and precision

The detection limits (DL) and the relative standard deviations (RSD) were shown in Table 3. Detection limits were calculated as three times the standard deviation of ten replicate measurements of the blank. The detection limits values of sample results were similar to those of aqueous solution. The highest increasing in the values compared to aqueous solution were as follows: 1.2 times in Seronorm and Bio-Rad urine samples for Cu, 1.6 times in Bio-Rad urine sample for Mn, and 1.7 times in Seronorm and Bio-Rad urine sample for Se. Generally, the values were similar to those of aqueous solution. The RSD for the direct simultaneous determination of Cu, Mn and Se in the urine sample were in the range (0.5-8.4%).

**Table 3** Results of simultaneous determination of Cu, Mn, and Se in different biological samples

Sample		Cu	Mn	Se
Seronorm	Con. Found ( $\mu\text{g l}^{-1}$ )	72.8	13.5	59.3
	Con. Certified ( $\mu\text{g l}^{-1}$ )	78	12.3	58.6
	DL ( $\mu\text{g l}^{-1}$ )	0.24	0.09	1.70
	% RSD	2.7	2.6	8.4
Bio-Rad	Con. Found ( $\mu\text{g l}^{-1}$ )	7.3	1.7	75.1
	Con. Certified ( $\mu\text{g l}^{-1}$ )	7.0	<3.5	77
	DL ( $\mu\text{g l}^{-1}$ )	0.17	0.11	1.7
	% RSD	0.5	2.7	4.0
Pig Kidney	Con. Found ( $\mu\text{g l}^{-1}$ )	15.9	4.3	5.2
	Con. Certified ( $\mu\text{g l}^{-1}$ )	16.6	4.2	5.4
	DL ( $\mu\text{g l}^{-1}$ )	0.23	0.09	1.40
	% RSD	1.8	2.3	5.0

## IV. Conclusion

Simultaneous multi-element determination for number of elements can be carried out using Simultaneous Multi-element GFAA Spectrometer under compromised conditions which include pyrolysis and atomization temperatures and the use of a suitable modifier. The sensitivity and the accuracy of this technique are comparable between single- and multi-element modes. The detection limits were somewhat higher.

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