

## A COMPARISON OF CADMIUM CONTENT IN WATER SAMPLES WITH TWO METHODS

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### **Abstract**

Cadmium (Cd) is a natural element found in soils and rocks. It is used in the metal industry, plastics, ceramics, and in the manufacture of batteries. Due to leaching, it could be found in drinking water sources. Cadmium is toxic to humans. Thus, the aim of the research was to determine Cd in real water samples. A comparison was made between the methods of inductively coupled plasma mass spectrometry ICP-MS and graphite furnace atomic absorption spectroscopy (GF-AAS). The measurement uncertainty was determined. We have developed a useful method for trace analysis of Cd in waters in the microgram per litre range.

### **Introduction**

Cd is very toxic to humans. [1]. Occupational or environmental cadmium exposure can lead to a variety of adverse health effects. It attacks kidneys in such a manner that causes the formation of kidney stones or even renal failure. The stone formation could further lead to osteoporosis and skeleton damage.

About 5100 tons of sewage sludge are discharged into the sea every day [2], and this sludge contains toxic metals, such as Cd. Due to Cd pollution, several pathologies are observable in the area surrounding the source of pollution. Various analytical methods such as electrochemical methods and inductively coupled plasma mass spectrometers have been used for the determination of Cd. On the other hand, the application of graphite furnace (also known as electrothermal) atomic absorption spectrometry GFAAS is rather rare [3]. Some interferences are divided into physical, chemical, and spectral. Physical could be eliminated by careful use of standard solutions. Chemical interferences are caused by the volatility of the samples.

A method is proposed for the simultaneous determination of Cd and Pb in medicinal plants by direct mud sampling through GF-AAS [4]. The analytical performance in Thermo-Spray Flame Furnace Atomic Absorption Spectrometry (TS-FFAAS) by using different systems of sample injection was studied [5]. Comparison of the results obtained by the proposed technique with other validated methods showed good agreement.

The main objective of the work reported here was to determine the Cd concentrations in the selected water samples. A comparison was made between the two methods of inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectroscopy (GF-AAS).

### **Experimental**

#### *Samples*

Public pipe water (Maribor, Slovenia) was analyzed as a real water sample (denoted VT, VH, VG, VM). Next sample was rainwater (denoted DD) and bottled water (denoted Z). Samples were quantified in triplicates, and recovery data were calculated.

#### *Calibration curve preparation*

Certified reference material CRM12-3-10, SPS-WW1 was used.

Working standard solutions were prepared daily by diluting the stock solution with Milli-Q water in the range from 0.5 µg/L to 3 µg/L in 10 mL glass flasks. The GTAAS method was applied on Varian SpectrAA DUO AA 240Z GTA 120 Spectrometer in comparison with ICP-MS analyses (Figure 1). Graphite tube atomizer was used and programmable heated up to the atomization temperature. The photomultiplier tube served as a detector. The measurements were performed at 228 nm.



Figure 1. GTAAS (left) and ICP-MS

## Results and discussion

### Water sample analysis

Recoveries in the ranges from 90 % to 115 % for GF-AAS and from 95 to 105 % with ICP-MS were confirmed.

### Calibration curve

Calibration curve is presented in Figure 2. The correlation coefficient  $R^2$  values were greater than 0.999, and the quality coefficient was 2.14 %. The linearity was confirmed. Reproducibility was confirmed with  $RSD$  lower than 5 % as can be seen from Table 1. The limit of detection and the limit of quantification were determined at 0.47 µg/L. and 0.49 µg/L, respectively.

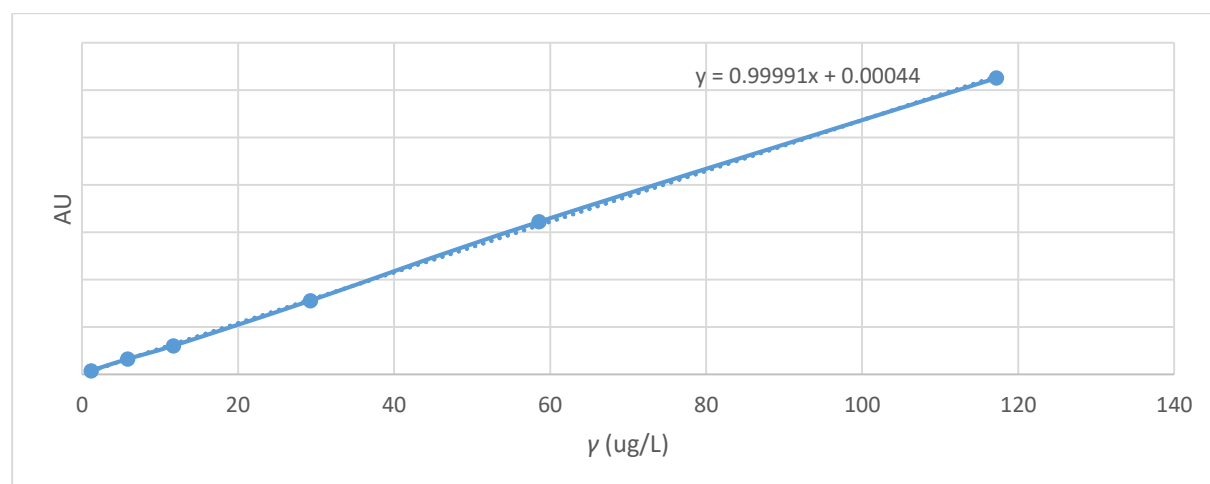


Figure 2. The calibration curve for Cd in the concentration range from 0.5 µg/L to 100 µg/L. The matrix effect was detected by t-tests. It is seen that in column 3 and 4  $t$  exceed  $t(\text{tab})$ , therefore there is a matrix effect with GF-AAS method.

Table 1. Matrix effect study

	<i>Blank</i>	<i>Blank+drinking water</i>	<i>Drinking water</i>
intercept	0.001	0.061	0.046
slope	1.001	0.847	0.843
<i>t</i>	0.076	9.096	11.328
<i>t</i> (tab)	2.776		

Rh was used as an internal standard in ICP-MS. There was no matrix effect detected.

Recoveries in the ranges from 90 % to 115 % for GF-AAS and from 96 to 104 % with ICP-MS were confirmed (Figure 3).

To evaluate reproducibility, 3 replicates were prepared for each concentration, and these were used to measure the recovery of Cd in the solution.

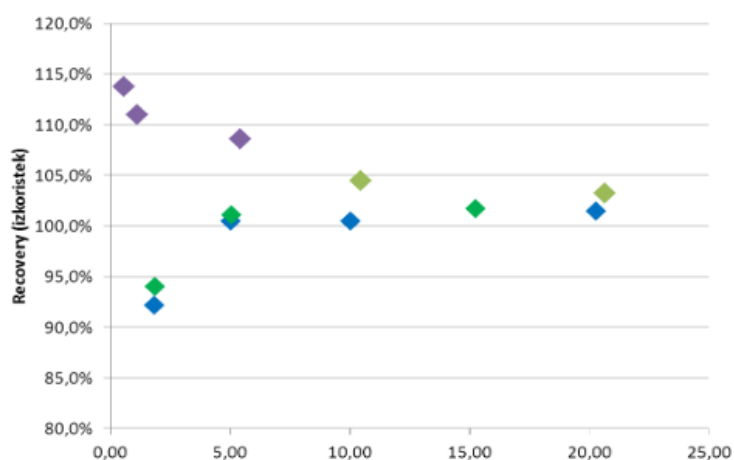


Figure 3. GF-AAS recoveries

*RSD* pooled was below the reported 5.3 % for Cd [3]. As seen from Table 2, *RSD* values for both methods were lower.

Table 2. *RSD* values for both methods

$\gamma$ [mg/L]	<i>RSD</i> (%) GF-AAS	<i>RSD</i> (%) ICP-MS
0.5	1.82	0.82
5	1.35	0.35
10	2.51	0.31
15	1.28	0.28
20	1.23	0.23
<i>RSD</i> pooled	1.95	0.45

### Reproducibility

Table 3 represents the reproducibility of the samples. The HORRAT and Grubbs tests were performed for GF-AAS. The outliers were not found.

Table 3. The HORRAT and Grubbs test's results

<i>Sample</i>	<i>HORRAT</i> <i>Max 2</i>	<i>Grubbs</i> <i>Max.1.887</i>	
		<i>Min</i>	<i>Max</i>
DD3	0.05	1.347	1.711
DD4	0.07	0.809	1.736
DD12	0.04	0.935	1.870
DD14	0.12	1.510	1.175
VCC	0.07	1.225	1.471

The obtained values for reproducibility were much lower using ICP-MS.

### Conclusions

The aim of this study was to determine the concentration of Cd in water samples using GF-AAS in comparison with ICP-MS. The method conditions were verified by determination of matrix effect, linearity, precision, accuracy, and LOD. The standard addition method was used and based on the slopes with the t-test it was determined that the matrix affects the measurements. The linearity of the method was confirmed with the correlation coefficients greater than 0.999 from 0.5 to 3.0 µg/L. The recoveries ranged from 90 to 115 %, which was satisfactory. The low RSD ( $\leq 1.9$  %) clearly indicates the reproducibility and the successful application of the developed GF-AAS method for the quantitative measurement of Cd in various real water samples.

### Acknowledgements

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