

# Determination of metals in Drinking water: Accreditation and Measurement Uncertainty



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## Introduction

The State General Laboratory as the official control Laboratory (Accredited by European /International Standard EN ISO/IEC 17025:2005 since 2002) implements a national monitoring program in order to ensure that the drinking water quality satisfies the requirements of the respective directive. The European Legislation Directive 98/83/EE demands strict control and monitoring for the presence of metals in drinking water. The national monitoring program covers mainly metals such as Pb, Cr, Mn, Cd, As, Se, Sb, Cu, Ni, Al and B includes not only tap water (distribution networks) but also bottled water, mobile water containers and vending machines which are widely used in Cyprus (Fig 1). The determination of these metals in bottled and drinking water requires the use of reliable and validated method and is performed by Inductively coupled plasma mass spectroscopy. ICP/MS is a very powerful screening tool for trace and ultra trace elemental analysis with high sensitivity, accuracy, and precision in analytical measurements. The estimation of uncertainty is an important tool for quality assurance of analytical measurements, providing traceability and reliability of the results presented by the laboratory.



## Analytical Procedure:

### Sample Preparation

For the direct analysis of total recoverable metals in drinking water where sample turbidity <1 NTU the sample is made ready for analysis by the appropriate addition of extra pure HNO<sub>3</sub> and then diluted to a predetermined volume and mixed before analysis.

### ICP-MS Analysis

The multi element determination of heavy metals (Pb, Cr, Ni, Cd, Se, As, Fe, Al, Sb, Cu, Mn, Al, Hg, and B defined in the Directive 98/83/EE in drinking water samples is performed by inductively coupled plasma mass spectroscopy ICP/MS Agilent 7500Ce. The determination is based on Standard method APHA 3125 B and has been accredited according to EN ISO/IEC 17025:2005 since 2009. Suitable analytical reagents, instrument optimization/tuning solution and standards of ultra pure quality are used.

### Quality Control

Quality control system during routine analysis includes certified reference materials, spikes, blanks, duplicates known addition samples and calibration verification standards. The limits of quantification of the various elements are ranging from 0,2 µg/L to 10 µg/L and recoveries of 96%-109% were achieved.the measurement range varies from 0,2 µg/L to 100 µg/L. Quality control system during routine analysis has demonstrated a very good method and instrument performance.

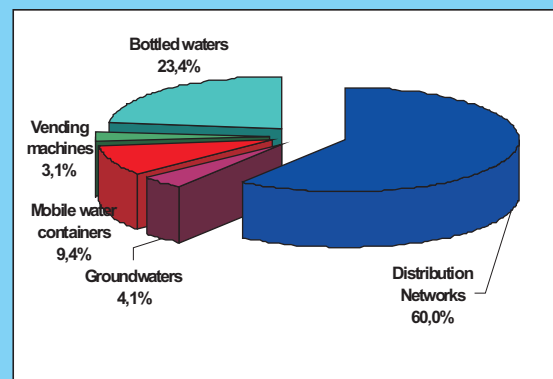


Fig 1: Various Types of Drinking water samples analysed in 2016

## Method Validation

The validation included the following steps:

trueness control, precision (repeatability and within laboratory reproducibility), check of the linearity of the standard calibration curves, determination of the detection /quantitation limits and method uncertainty evaluation. The results were satisfactory and within the accepted validation requirements. Representative calculated results of the above experiments are presented in Table 1.

Metal	Concentration (µg/L)	Precision (%RSDr)	Recovery (%)
Pb	10	0.8	96.8
Cd	5	1.9	95.9
Cr	50	2.7	108.7
Ni	20	1.3	102.1
Mn	50	3.3	99.0
As	10	3.0	104.8
Se	10	1.8	104.0
Cu	2000	1.4	96.7
B	1000	4.7	97.9
Al	200	1.3	96.9

Table 1: Method Validation data

Metal	% U (type A)	% Expanded Uncertainty	Legal Limit N. 87 (I)/2001 (µg/L)
Cr	5,9	6,7	50
Mn	10,8	11,3	50
Ni	5,9	12,6	20
Cu	5,8	8,3	2000
As	5,8	8,3	10
Se	3,5	6,7	10
Cd	7,6	8,2	5,0
Pb	2,9	11,0	10
Al	2,6	3,8	200
B	15	10,8	1,0

Table 2: % Type A and Expanded Uncertainty for the various metals.

### References:

- 1] Standard Methods for the Examination of water and wastewater 22th edition 2012.
- 2] Council Directive 98/83/EC on the quality of water intended for human consumption.
- 3] Directive EE 2015/1787.
- 4] Eurachem /CITAC Guide Guide CG4 Quantifying Uncertainty in Analytical Measurement Third Edition.
- 5] Agilent 7500 ICP-MS Chemstation (G1834B) Operators Manual (Agilent Technologies).

## Uncertainty evaluation:

The method combined standard uncertainty was evaluated using the Eurachem/CITAC Guide. The contribution of each of the following sources was studied in the determination of the above metals at the legal limit.

- The relative standard uncertainty of the method determined from interlaboratory reproducibility tests (R<sub>sD<sub>rel</sub></sub>).
- The uncertainty from the reference calibration curve (U<sub>c/C</sub>)
- The uncertainty due to the method and laboratory bias (U<sub>bias/Cbias</sub>). This was determined from sixfold recovery tests.
- The uncertainty from volumetrics flasks/pipettes used for the preparation of standard solutions (U<sub>v/V</sub>).

The % uncertainty source contribution to the final result has shown that the uncertainty determined from interlaboratory reproducibility tests was the dominant parameter. The Figure 2 shows the contribution of each uncertainty source to the method uncertainty for Manganese determination.

### Calculation of Uncertainty

Uncertainty was evaluated using the following equation:

$$U_c / C = \{ (RSD_{rel})^2 + (U_{v/V})^2 + (U_{cal} / C_{cal})^2 + (U_{rec} / Rec)^2 \}^{1/2}$$

where U<sub>c</sub> = Combined Standard Uncertainty  
C = Metal's concentration

The result is given as follows: C± U<sub>exp</sub>

where U<sub>exp</sub> = 2xU<sub>c</sub> at 95% confidence level.

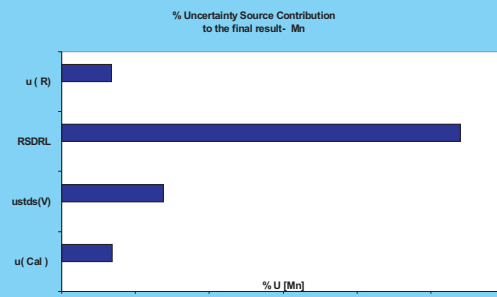


Fig 2: % Uncertainty Source Contribution to the final result for Mn

## Conclusions:

- The results of the annual surveillance have shown that the metal concentration for the majority of drinking and bottled water was far below the accepted legal limit.
- The validation data (e.g. linearity detection limit, reproducibility, accuracy, repeatability, uncertainty) were satisfactory and in compliance with the requirement of ISO/IEC 17025:2005 as well as with the Directive 98/83/EE, furthermore it confirms the suitability of the method for the intended use.
- Uncertainty was evaluated at the legal limit of all metals (Directive 98/83 EE).
- The % U of all the measured metals was lower than the accepted limits of the new Directive EE 2015/1787.
- The expanded Uncertainty is taken into consideration when the uncertainty affects compliance to a legal limit.