

QUANTITATIVE DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY FOR MICRO ELEMENTS OF MINERAL WATERS FROM ROMANIA

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ABSTRACT

The aim of this paper is to present the results of studies for some microelements from mineral water. Mineral water was collected from three different regions of Romania (West Region, Centre Region and North Region). The microelements: lead (Pb), nickel (Ni), manganese (Mn), iron (Fe), cooper (Cu), chromium (Cr), and cadmium (Cd) were analyzed by atomic adsorption spectrometry determination, using the graphite tubular electrothermic oven method VARIAN GTA 110. As a conclusion, the lead (Pb) maximum value recorded for the west region waters was in sample A1 (18.6 µg/L), the nickel (Ni) exhibits maximum value in center region, in sample C2 (54.15 µg/L), the manganese (Mn) reaches the maximum in the west region in sample A1 (360 µg/L), the iron (Fe) exhibits maximum value in sample B3 (6.25 µg/L) from north region, and for the cadmium (Cd), the maximum value was reached in sample A1 (8.18 µg/L) from the west region. When comparing the allowable limits for heavy metals, (**ORDER NO. 975 OF 16 DECEMBER 1998 ON THE APPROVAL RULES OF THE SANITARY HYGIENIC FOOD**) were not observed exceedances of microelements concentrations studied.

Keywords: mineral water, atomic adsorption spectrometry (AAS), micro elements, tubular oven, geographical regions

INTRODUCTION

For the determination of trace metals in natural and mineral waters different spectrochemical methods are used. However, flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for determining various elements with significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost.⁹ However, in some cases there are many difficulties in determining traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. (TAUTKUS, 2004)

The water contains some amount of mineral constituents which iron (Fe), magnesium (Mg), lithium (Li), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cobalt (Co), vanadium (V), arsenic (As), molybdenum (Mo), selenium (Se), lead (Pb) and so many others. The quality required of water varies with the use to which the water is to be put. Some people prefer bottled water to sachet water as they believe that it is hygienically prepared. Some people drink only bore hole water or well water as it is the only available source especially in rural areas where bottled and sachet are not produced or too expensive to buy. (OGBONNA, 2011; *** ISO 9174, 1990; *** ISO 8288, 1986)

Atomic spectroscopy is one of the most widely used methods for quantitative elemental analysis. There are a number of situations where elemental composition is important – e.g., how much iron in an ore sample, how much lead in your drinking water, calcium in intracellular fluids. In a sense, it's the simplest type of analysis, since there are only about 120 possible analytes. But to do the analysis, the sample has to be completely destroyed

(chemically and physically) and reduced to individual gas phase atoms (or related species, like ions) in well defined states that you can do spectroscopy on. Obviously this requires a very highly energetic environment and a lot of modification of the sample, both of which lead to a number of complications. These problems can be addressed if their presence is anticipated and the physical mechanism is understood. In addition to giving you a little experience with AAS (Atomic Absorption Spectrophotometry) and AES (Atomic Emission Spectrophotometry) for quantitative determination of a few elements.

(HTTP://WEB.PDX.EDU/~ATKINSDB/TEACH/427/EXPT-ATOMICSPEC.PDF)

The Flame Atomic Absorption Spectrometry (F-AAS) and Flame Atomic Emission Spectrometry (F-AES) are the most often used instrumental techniques for the determination of many elements in different types of natural waters, including rain waters, fresh waters, mineral waters, brines and wastewaters. (JOŃCA, 2004; *** DRINKING-WATER QUALITY, 2004)

MATERIAL AND METHOD

Spectrophotometer VARIAN Spectr AA 110; Electro thermal graphite tubular oven VARIAN GTA 110 type; Flame type: air/acetylene; Protection gas: argon; air flow: 3,50L/min; acetylene flow: 1,50L/min.

The water samples were taken from three different regions of Romania, as follows: West Region: Mineral water source 1 (A1); Mineral water source 2 (B1); Mineral water source 3 (C1); Centre Region: Mineral water source 1 (A2); Mineral water source 2 (B2); Mineral water source 3 (C2).

North Region: Mineral water source 1 (A3); Mineral water source 2 (B3); Mineral water source 3 (C3).

The lead (Pb), nickel (Ni), manganium (Mn), iron (Fe), cooper (Cu), chromium (Cr), and cadmium (Cd) elements determination was performed with the graphite tubular electrothermal oven because this method exhibits a greater sensitivity towards ppb concentration ($\mu\text{g/L}$)

The work parameters obtained on apparatus calibration in order to determinate lead (Pb), nickel (Ni), manganium (Mn), iron (Fe), cooper (Cu), chromium (Cr), and cadmium (Cd) elements, are shown in table 1 and the afferent calibration curves are shown in *figure 1*.

Table 1. Work parameters at Pb, Ni, Mn, Fe, Cu, Cr, Cd by atomic adsorption spectrometry determination, using the graphite tubular electrothermic owen method VARIAN GTA 110

Experimental conditions	Analyzed element						
	Pb	Ni	Mn	Fe	Cu	Cr	Cd
Sample taking	Automatic						
Calibration way	Concentration						
Measure units	$\mu\text{g/L}$						
Method used	Graphite tubular electrothermic owen						
Protection gas	Argon						
Measurement method	Pick height						
Standard precision [%]	1	5	1	1	5	1	1
Samples precision [%]	1	5	1	1	5	1	1
Expansion factor	1	1	1	1	1	1	1
Mediating degree, points	5	5	5	5	5	5	5
Wavelength, [nm]	283.3	232.0	403.1	372.0	327.4	429.0	228.8
Slot width, [nm]	0.5	0.2	0.2	0.2	0.5	0.5	0.5
Voltage on lamp, [V]	38	32	40	45	39	23	50
Electricity on lamp [mA]	10	4	5	5	4	7	4
Standard 1, [$\mu\text{g/L}$]	10	10	50	50	20	10	2
Standard 2, [$\mu\text{g/L}$]	20	20	75	75	40	20	4
Standard 3, [$\mu\text{g/L}$]	30	30	100	100	60	20	6
Standard 4, [$\mu\text{g/L}$]	40	40	-	-	75	40	8
Standard 5, [$\mu\text{g/L}$]	50	50	-	-	-	50	10
Measurement time, [s]	68	68	68	68	68	68	68
Working temperature °C	85-2100	85-2400	85-2400	85-2300	85-2300	85-2600	85-1800
The injected sample volume [μL]	20	20	20	20	20	20	20

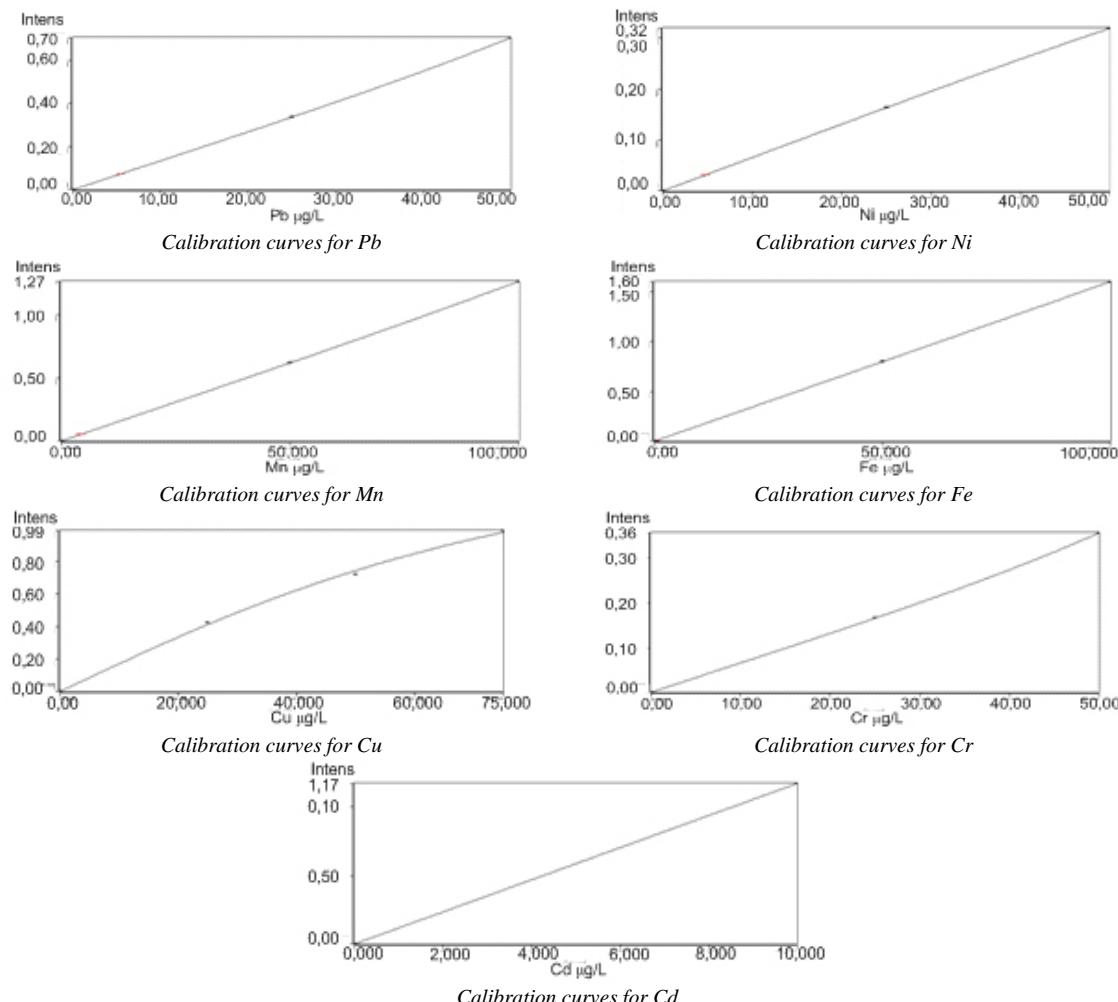


Figure 1. Calibration curves obtained for the analyzed elements

Pb, Ni, Mn, Fe, Cu, Cr, Cd elements determination by graphite tubular electrothermic own, has led to the following results, shown in *table 2*.

Table 2. Atomic adsorption determination of Pb, Ni, Mn, Fe, Cu, Cr, Cd elements

Chemical element µg/L	Mineral water samples								
	West Region			Centre region			North Region		
	A1	B1	C1	A2	B2	C2	A3	B3	C3
Pb	18.60	5.40	1.70	6.90	1.45	4.27	2.43	9.11	5.51
Ni	31.74	12.66	4.89	21.04	9.81	54.15	12.61	14.16	4.78
Mn	360	327	0.81	144	241	260	352	334	4.395
Fe	4.84	6.00	1.67	5.07	2.36	1.96	4.40	6.25	0.34
Cu	-	-	-	-	-	-	-	-	-
Cr	4.10	-	-	1.35	-	1.55	-	6.13	-
Cd	8.18	6.05	3.07	-	-	-	1.91	1.13	-

The atomic absorption analysis, using the graphite tubular electrothermic own, allowed the quantitative determination of (Pb, Ni, Mn, Fe, Cu, Cr, Cd) elements, from the three region of Romania, as follows:

West region (A1, B1, C1) samples - Pb, Ni, Mn, Fe, Cu, Cr, Cd

Regarding the west region, head exhibits the maximum in sample A1 (18.60 µg/L), for sample B1 the value recorded was 5.40 µg/L, and the minimum of 1.70 µg/L obtained was in sample C1. Nickel reaches the maximum in sample A1 (31.74 µg/L), the minimum for nickel

being recorded in sample C1 (4.89 µg/L), and for sample B1 there was obtained a value of 12.66 µg/L nickel. For manganum, the maximum reached was in sample A1 (360 µg/L), sample B1 reaches 327 µg/L value, and the minimum recorded for this element was 0.81 µg/L in sample C1.

The iron element, for the west region, exhibits the maximum value in sample B1 (6.00 mg/L), the minimum reached for iron being 1.67 µg/L in sample C1, while for sample a1 a value of 4.84 µg/L iron was obtained. The performed analysis for this region in the case of cooper, have led to negative results. The chromium element exhibits a single value in sample A1 (4.10 µg/L), for sample B1 and C1, respectively, the chromium is absent. Cadmium exhibits the maximum value in sample A1 (8.18 µg/L), sample b1 recorded a value of 6.05 mg/L, and the minimum obtained value for this element was recorded in sample C1 (3.07 µg/L).

Center region (A2, B2, C2) samples - Pb, Ni, Mn, Fe, Cu, Cr, Cd

The lead reaches the maximum of this region, in sample A2 (6.90 µg/L), sample C2 exhibits a 4.27 µg/L value, the minimum of lead being recorded in sample B2 (1.45 µg/L). For nickel, the maximum value was recorded in sample C2 (54.15 µg/L), sample A2 exhibits a value of 21.04 µg/L, the minimum recorded being of 9.81 µg/L in sample B2. The manganum exhibits the maximum value in sample C2 (260 µg/L), the minimum value being recorded in sample A2 (144 µg/L), and for sample B2 a value of 241 µg/L was obtained. The iron, in this region, reaches the maximum in sample A2 (5.07 µg/L), sample B2 exhibits a 2.36 µg/L value, and the minimum reached is recorded in sample C2 (1.96 µg/L).

The analysis performed for this region, in the case of cooper have led to negative results. The chromium records the maximum value vas of 1.35 µg/L, and for sample B2 the recorded results were negative. For cadmium, no positive results were recorded for this region.

North region (A3, B3, C3) samples - Pb, Ni, Mn, Fe, Cu, Cr, Cd

The lead reaches the maximum value for this region in sample B3 (9.11 µg/L), the minimum value for this element being recorded in sample A3 (2.43 µg/L), while sample C3 exhibits a value of 5.51 µg/L. The maximum value recorded for nickel was in sample B3 (14.16 µg/L), sample A3 exhibits a value of 12.61 µg/L, the minimum being recorded for nickel in sample C3 (4.78 µg/L). manganum reaches the maximum value for the North region, in sample A3 (352 µg/L), the minimum value being obtained in sample C3 (4.395 µg/L) and for sample B3 a value of 334 µg/L. In the case of iron, the maximum value was recorded in sample B3 (6.25 µg/L), sample A3 exhibits a 4.40 µg/L value, and the minimum recorded for this elements was in sample C3 (0.34 µg/L). The analysis performed in this region for cooper, have led to negative results. The chromium exhibits a single value in this region, in sample B3 (6.13 µg/L), the other analyses samples have exhibited negative results. For cadmium, the maximum value was recorded in sample A3 (1.91 µg/L), the minimum being 1.13 µg/L in sample B3, while sample C3 does not exhibit positive results in cadmium analysis. The lead reaches the maximum in waters from west region, in sample A1 (18.60 µg/L), sample A2 (6.90 µg/L) exhibits the maximum for centre region, and sample B3 exhibits the maximum value 9.11 µg/L for north region. (*Figure 2*)

For nickel, the maximum recorded value in waters from west region was 31.74 µg/L in sample A1, the centre region exhibits the maximum in sample C2 (54.15 µg/L), and sample B3 exhibits the maximum 14.16 µg/L in north region. (*Figure 3*)

Manganum reaches the maximum for waters from west region in sample A1 (360 µg/L), the centre region maximum for this element in sample C2 (260 µg/L), and the maximum value for north region is for sample A3 (352 µg/L). (*Figure 4*)

For iron the maximum for waters from west region in sample B1 (6 µg/L), the centre region maximum for this element in sample A2 (5.07 µg/L), and the maximum value for north region is for sample B3 (6.25 µg/L). (*Figure 5*).

Cooper was not identified in the analyzed mineral waters.

The chromium was identified in the west region waters and in north region in one sample A1 ($4.1 \mu\text{g/L}$) and B3 ($6.13 \mu\text{g/L}$) respectively, in centre region the chromium exhibits maximum in sample C2 ($1.55 \mu\text{g/L}$). (Figure 6)

Cadmium exhibited the maximum for waters in west region, in the case of sample A1 ($8.18 \mu\text{g/L}$), in the center region was not identified, and for the north region the maximum value was $1.91 \mu\text{g/L}$ in sample A3. (Figure 7)

As a conclusion, the leads' maximum value recorded for the west region waters was in sample A1 ($18.6 \mu\text{g/L}$), the nickel exhibits maximum value in centre region, in sample C2 ($54.15 \mu\text{g/L}$), the manganese reaches the maximum in the west region in sample A1 ($360 \mu\text{g/L}$), the iron exhibits maximum value in sample B3 ($6.25 \mu\text{g/L}$) from north region, and for the cadmium, the maximum value was reached in sample A1 ($8.18 \mu\text{g/L}$) from the west region. (Figure 8)

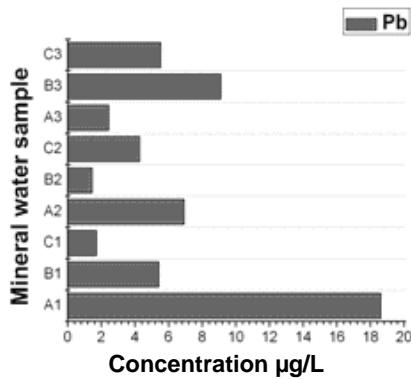


Figure 2. Pb concentration in the mineral water samples, taken into discussion

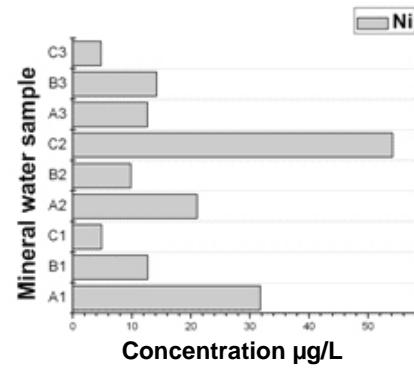


Figure 3. Ni concentration in the mineral water samples, taken into discussion

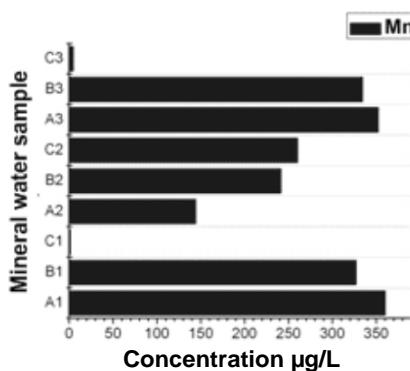


Figure 4. Mn concentration in the mineral water samples, taken into discussion

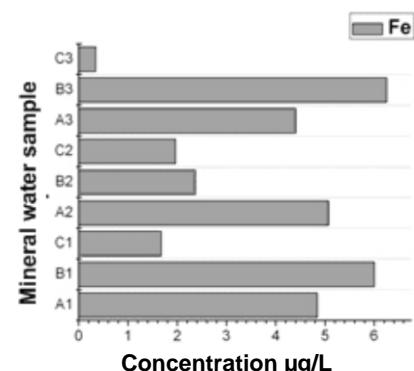


Figure 5. Fe concentration in the mineral water samples, taken into discussion

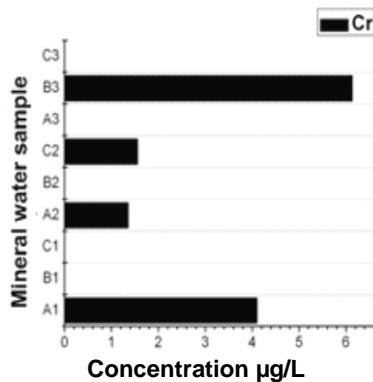


Figure 6. Cr concentration in the mineral water samples, taken into discussion

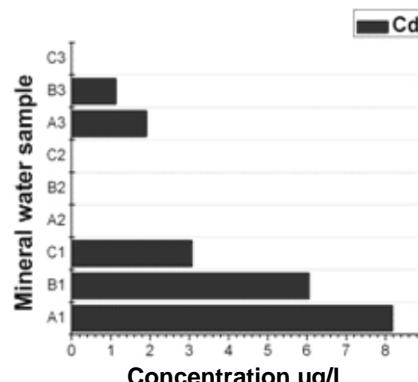


Figure 7. Cd concentration in the mineral water samples, taken into discussion

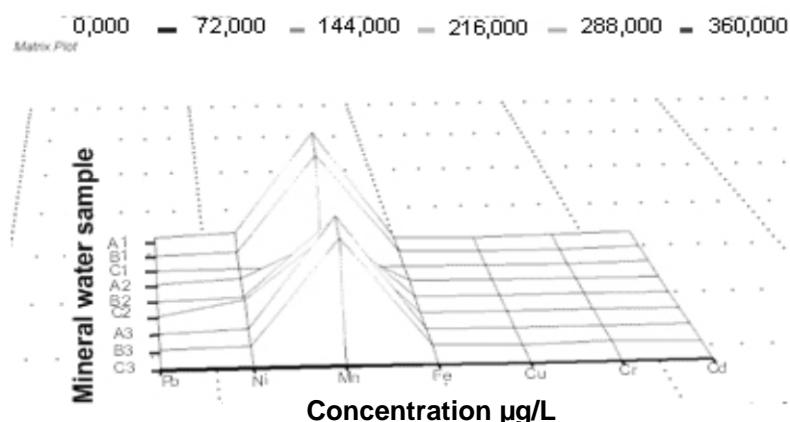


Figure 8. Pb, Ni, Mn, Fe, Cu, Cr, Cd concentration in the mineral water samples from three regions of Romania

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