Determination of Anions and Cations Content in Romanian Drinking Waters by HPIC Method

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Abstract: This paper deals with a comparative study regarding quality of drinking water from diferent regions of Romania. Four types of drinking water were examined in four different regions of the country: West, Centre, North and East. Anions and cations determination was done with high-performance ion chromatography (HPIC). The device used was a Dionex – ICS 3000 type, particularized for anions and cations. The higher concentrations for anions and cations were determinate in the North part of the country.

Keywords: Sodium, Calcium, Potassium, Magnesium, Chloride, Sulphate, Nitrate, high-performance ion chromatography (HPIC), drinking water.

1. Introduction

The most significant 'water' refers to an omnipresent daily routine. In the dictionary, the term 'water' is defined as 'a transparent, odorless, tasteless liquid, a hydrogenated compound of oxygen that forms one of the layers of Planet Earth'. All this information represents the denotative meaning, the first-hand meaning of this word [1,2].

Drinking water usually comes from underground or surface water, rarely from other sources. The underground water is an important source, because, unlike surface water, the underground water is usually less or is not polluted at all and can be made potable with minimal resources, sometimes only by disinfection or without any previous treatment. Our health depends directly on the quality of the drinking water [3].

According to the European Union norms and regulations (Directives 98/83/CE from 1998, 80/778/EEC from 1980 regarding the water quality for consuming, Law nr. 311/2004 for mofification and filling, Law 458/2002, regarding drinking water quality), the water is considerate suitable for drinking if is free of chemical synthesis fertilizers, natural fertilizers and pesticides and the values for quality indicators are in the limits.

Inorganic substances/matters are present in the water in higher concentrations than the organic ones. Many of these substances are a result of natural conditions; the chemical composition for certain water is according to what type of rocks was in contact with. However, there are many inorganic components present, usually in lower concentrations that must be treated as pollutants and analysed from the point of view of their effect on the water and life quality [4].

The water research by correlation of physical and chemical properties of quality it is an applied method in faster monitoring.

For the water analyses specific, sensitive and accurate methods are needed. The High Performance Ion Chromatography separation method is based on ion-exchange processes occurring between the mobile phase and ion-exchange groups bonded to the support material.

The study wants to present the reliability of an innovating chromatographic system present on the market through taking some analyses of the drinking water from different regions of Romania. In this order the research looked at the measurement of the most important quality indicators of the water samples.

The paper deals with performance of experimental studys by measuring some important quality indicators.

2. Experimental

For determination purposes, various drinking water samples were used from the urban water supply network in four different areas of Romania. The water sampling was made in sterile recipients and kept in refrigerator at 4°C. Before analysis samples were allow to reach room temperature.

The following tests have been performed:
- pH and conductivity using pH Meter Seven Multi from Mettler Toledo;
- Concentration of anions and cations using Dionex ICS 3000.

Samples are injected into a stream of potassium hydroxide eluent, passed through an ion exchange column and measured by a conductivity detector. The first column, a guard column, protects the analytical column by removing particulate and organic matter. The analytical column separates anions/ cations by their relative affinities

for a low-capacity, strongly basic anion exchanger. The suppressor (between the analytical column and the conductivity detector) provides continuous suppression of background conductivity of the eluent and enhances response of the target analytes by acidification. The separated anions/cations in their acidified form are measured by conductivity. The anions/cations are identified based on retention times and quantified by conductivity relative to standard response [5-9].

3. Results and discussion

The calibration represents de major factor which depend on the accuracy of final results. The calibration standard solutions used are prepared from certified reference materials.

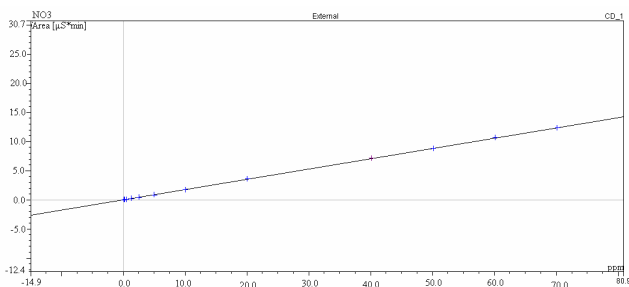The calibrations curves obtained for anion and cation determination are presented in figure1 to 8:

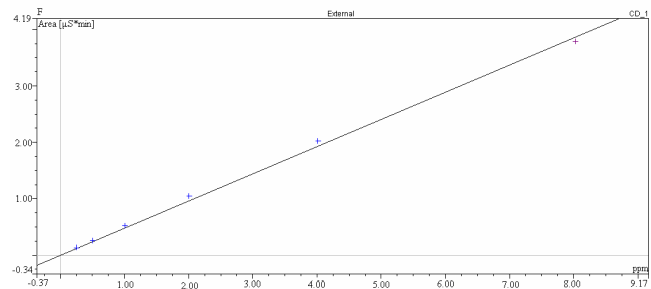Figure. 4. Calibration curves for F⁻ determination

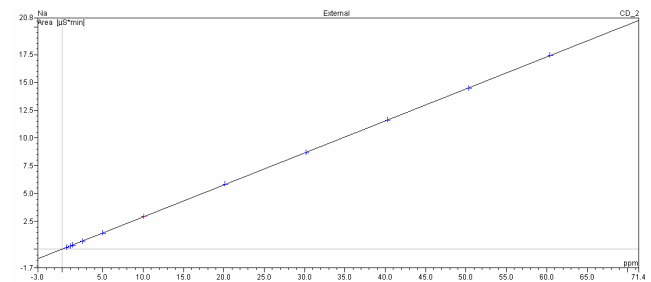Figure. 1. Calibration curves for Cl⁻ determination
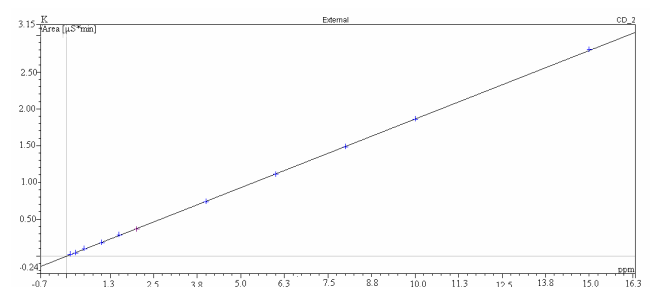
Figure. 5. Calibration curves for Na⁺ determination

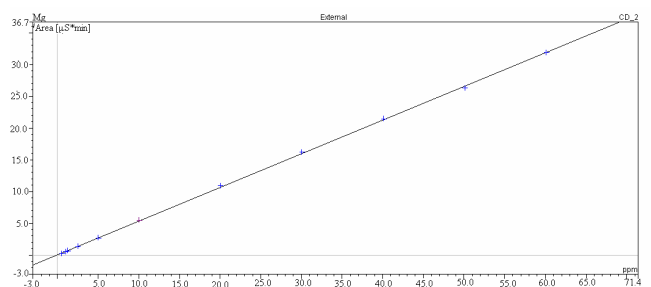Figure. 6. Calibration curves for K⁺ determination

Figure. 2. Calibration curves for SO₄²⁻ determination

Figure. 7. Calibration curves for Mg²⁺ determination

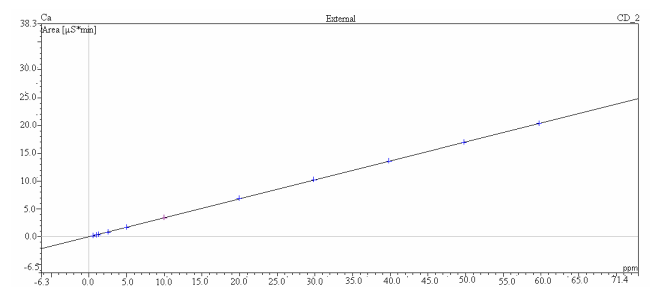Figure. 3. Calibration curves for NO₃⁻ determination

Figure. 8. Calibration curves for Ca²⁺determination

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The correlation coefficient for each anions and cations is presented in table 1:

TABLE 1. Correlation coeficients for anions and cations

Anion/ Cation	Slope	Offset	Correlation coeficient
Cl^-	0.321	0	0.999
SO_4^{2-}	0.240	$2 \cdot 10^{-5}$	0.999
F^-	0.481	0	0.997
NO_3^-	0.176	$4 \cdot 10^{-6}$	0.999
Na^+	0.288	4	0.999
K^+	0.185	10-5	0.999
Mg^{2+}	0.531	$5 \cdot 20^{-6}$	0.999
Ca^{2+}	0.341	$2 \cdot 10^{-5}$	0.999

The chromatograms for each sample, obtained after anion and cation analysis are presented in figures 9 to 12.
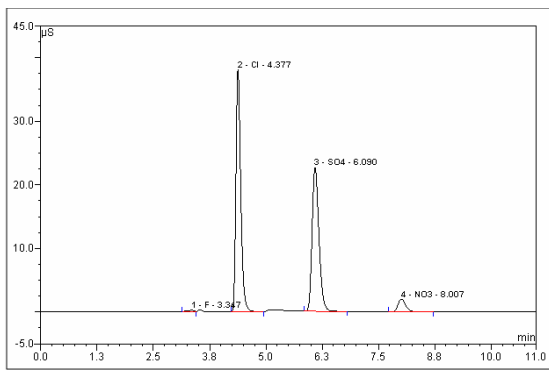

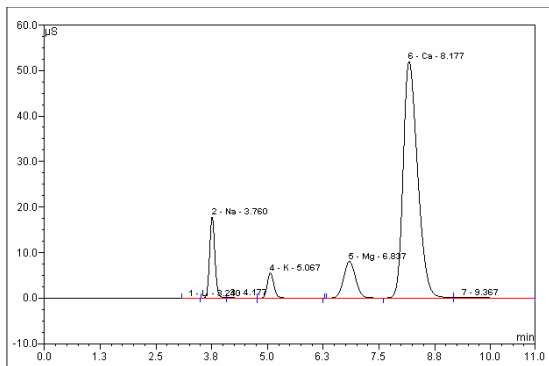Figure. 9. Anion chromatogram for sample A (Centre)

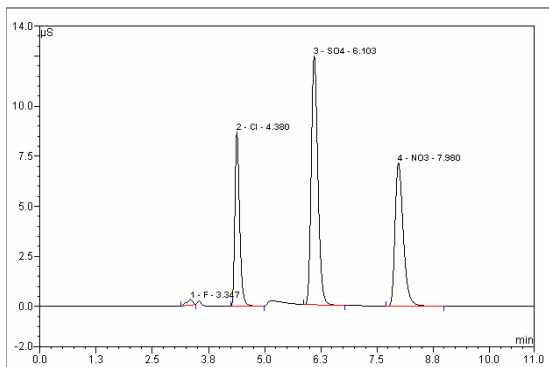Figure 10. Cation chromatogram for sample A (Centre)

Figure 11. Anion chromatogram for sample B (West)
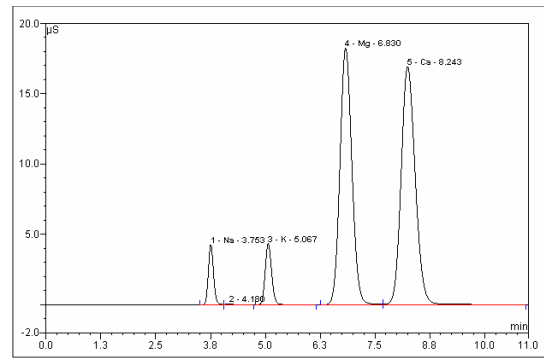

Figure 12. Cation chromatogram for sample B (West)
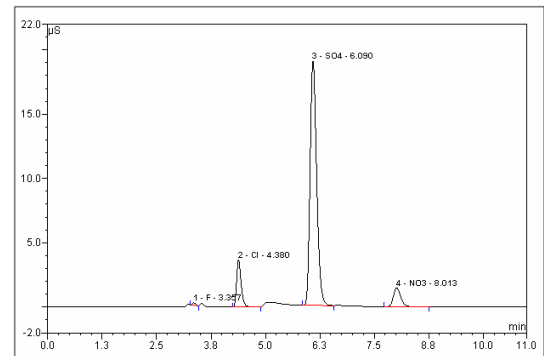

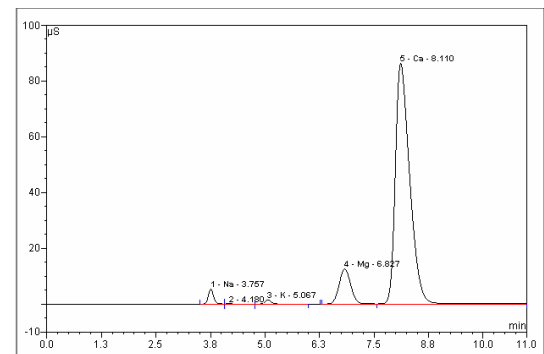Figure 13. Anion chromatogram for sample C (East)

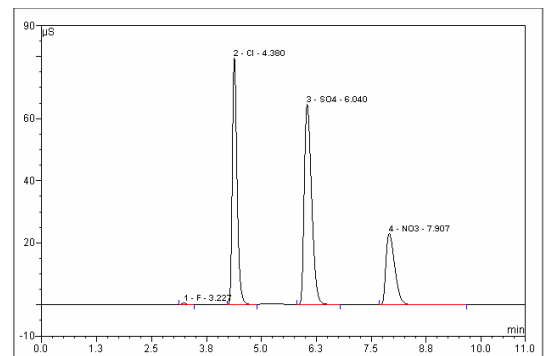Figure 14. Cation chromatogram for sample C (East)

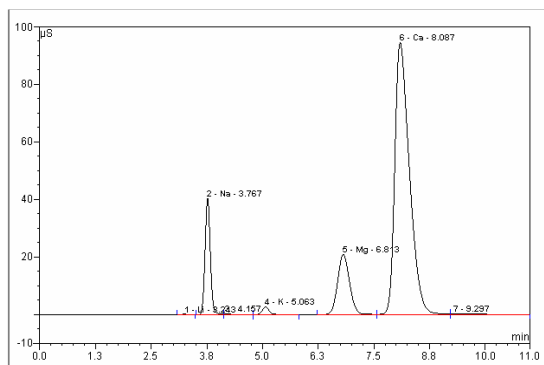Figure 15. Anion chromatogram for sample D (North)

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Figure 16. Cation chromatogram for sample D (North)

As concern the pH and conductivity, the results for each sample and the acceptance limit (E) are presented in the figure 13 and figure 14:
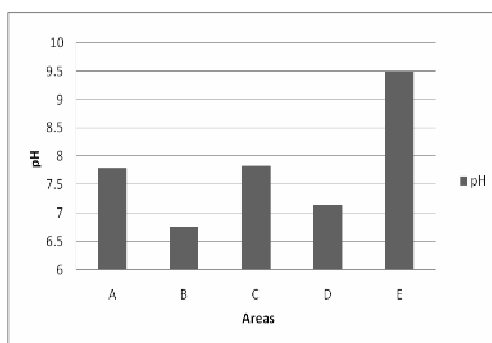

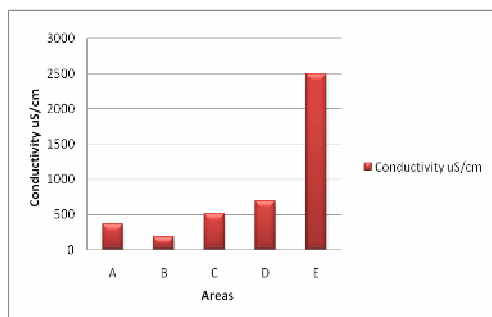Figure 17. Variation of pH for each area

Figure 18. Variation of conductivity for each area

In the graph it can be noticed that for pH, the maximum value is presented in C area (7.834), and the smallest one in B area (6.76). It can be concluded that pH values for considered samples are ranging between the allowable limits according to Romanian legislation.

The quantitative analysis of anion (Cl⁻, SO_4^{2-}, NO_3^-) and cation concentrations (Na⁺, K⁺, Mg^{2+}, Ca^{2+}) in water samples based on the calibrating plot method, led to the results given in Table 2 and Table 3.

Among the analyzed anions the shares of different anions were as follows: F⁻ from 0.036 % (C) to 0.146 % (D), Cl ⁻ from 1.392 % (C) to 31.230 % (D), SO_4^{2-} from 8.893% (A) to 52.258 % (D), NO_3^- from 1.618 % (C) to 30.178% (D) (Table 2).

TABLE 2. Anion analysis of drinking water samples

Samples	F[mg/L]	Cl⁻[mg/L]	SO_4^{2-}[mg/L]	NO_3^-[mg/L]
A	0.082	14.778	16.616	2.24
B	0.093	3.335	8.893	8.544
C	0.036	1.392	13.855	1.618
D	0.146	31.230	52.258	30.178
Acceptance limits	1.2	250	250	50

TABLE 3. Cation analysis of drinking water samples

Samples	Na⁺ [mg/L]	K⁺ [mg/L]	Mg^{2+} [mg/L]	Ca^{2+} [mg/L]
A	8.494	5.097	4.68	57.038
B	2.025	3.979	10.861	18.514
C	2.505	1.302	7.285	96.060
D	19.233	2.408	12.137	105.098
Acceptance limits	200	12	50	100

For cations the among were as follows: Na⁺ from 2.025 % (B) to 19.233 % (D), K⁺ from 1.302 % (C) to 5.097 % (A), Mg^{2+} from 4.680 % (A) to 12.137 % (D) and Ca^{2+} from 18.514 % (B) to 105.098 % (D) (Table 3).

HPIC analysis enabled the classification of drinking waters according to the anions and cations distribution in West, Centre, East and North regions of Romania.

For anions the highest concentration for fluoride (0.146 mg/L) was obtained in sample D from the North region, and the lower concentration was obtained in sample C (0.036 mg/L) from the East region. Chloride was highest in D (North) (31.230 mg/L) and lowest in C (East). Sulphate was highest in D (North) (52.258 mg/L), low in (West). Nitrate was highest in D (North) (30.178 mg/L) and lowest in C.

For cations the highest concentration for sodium (19.233 mg/L) was obtained in D from the North region. Na concentration was low in the other sample B (West). Potassium was highest in A (Centre) (5.097 mg/L) and lowest in C. Magnesium was highest in D (North) (12.137 mg/L) and low in A (Centre) (4.680 mg/L) and calcium was highest in D (North) (105.098 mg/L) and low in B (West) (18.514 mg/L).

4. Conclusions

This experiments illustrates the utility of high performance ion chromatography (HPIC) as an operational analytical tool.

In terms of mineral elements (anions and cations) content, the values obtained from analysis of water samples ranked within the legally allowed limits stipulated by the standards in force, except for the calcium values in the Northern area (105.098 mg/L).

The sample with the largest amount of anions and cations registered during the tests was taken from D area (113.812 mg/L total anions; 105.098 mg/L total cations) and the sample with the smallest content of anions was from C area (16.9 mg/L total anions), as for the cations content, the B area was representative (35.380 mg/L total cations).

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