

THE EVALUATION OF THE QUALITY OF THE DRINKING SPRING-WATERS IN PITESTI REGARDING THEIR TOTAL HARDNESS

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(Received May 30, 2003)

Abstract: The record of physical and chemical properties of the drinking spring-waters is essential to protect people's health and environment. The purpose of this study is to determine the concentrations of calcium and magnesium ions in the drinking spring-waters located in the town of Pitesti. These evaluations were achieved using the following methods: atomic absorption flame spectral analysis for calcium and magnesium; complexometric analysis with EDTA in the presence of the indicator mixture green-murexide with naphthol B for calcium; visual absorption spectrophotometry analysis for magnesium. The evaluation of the concentrations of calcium and magnesium ions in the spring-waters located in Pitesti applies in the correct evaluation of their hardness and quality as drinking waters, from this point of view. The evaluation of the hardness of the surface waters is achieved using the complexometric analysis with EDTA at pH=10 in the presence of the indicator black-eriocrom T. We determined the experimental values of the hardness and of the concentrations of the calcium and magnesium ions for the waters of eight springs in the town of Pitesti. These experimental values were compared to the maximum permitted values for the surface drinking waters, establishing in this way their quality regarding their total hardness.

Key words: drinking spring waters, hardness, and concentrations of calcium and magnesium ions.

INTRODUCTION

The study describes the experimental techniques made according to the specific procedures issued by the National Company, "Apele Române" and the obtained results for pH and total hardness of the drinking spring-waters located in Pitesti town. To confirm the obtained values of the total hardness of these waters, the concentration of the calcium and magnesium ions were determined using standard procedures issued by the International Standardisation Organisation and Romanian Institute for Standardisation. The experimental determined values that are graphically shown and synthetic enclosed in a final table, are the basis for the conclusions concerning the quality of drinking spring-waters from the standpoint of their hardness.

EXPERIMENTAL TECHNIQUES

Drinking spring-water sampling and preparing

The water samples are taken in glass or plastics bowls, observing the actual prescriptions concerning the surface waters sampling issued by the National Company „Apele Române”. The cropped samples will be brought in the laboratory and stored, if is necessary in the refrigerator at 4°C temperature. The analysis of the waters samples is be made no later than 24 hours after crop.

In case of using of the atomic absorption spectrometric method, the water samples will be immediately acidulated with Hydrogen Nitrate having the density of $d=1,4\text{mg/l}$ up to $\text{pH}\sim 10$ and they can be kept up to 7 days.

The pH determination of drinking spring-waters

The principle of the method

The spring-water samples pH determination is made using electrometer method [6], [7], according to the specific working procedure issued by the National Company „Apele Române”.

The utilised apparatus

We used an electric pH-meter type OP-401-2, having the measuring electrode in glass and comparison electrode in calomel. (Fig. 1).

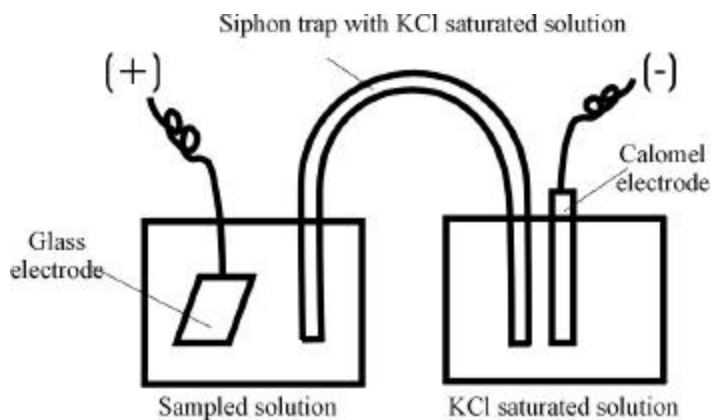


Fig. 1. – The scheme of electrometer pH determination

The working method

1. *Preparing electrodes.*
2. *Mounting electrodes.*
3. *Putting apparatus into operation.*
4. *Calibration of pH measuring scale.*
5. *Determination of pH in sample.*

The experimental results

The pH values of the drinking spring-waters from Pitesti, directly read on the apparatus scale are shown in the table at the end of the section. The comparison between the measured values and the allowed limits of pH for drinking spring-waters is shown in the diagram from figure 2.

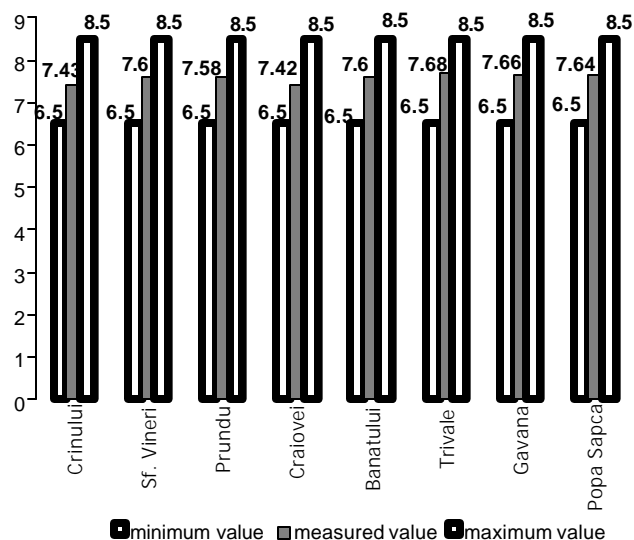


Fig. 2 – The pH values of the drinking spring waters in Pitesti town

The determination of the total hardness of the drinking spring waters

The water hardness is determined by its content in soluble calcium and magnesium salts. Depending on the nature of these salts the hardness can be temporary or permanent [6],[7].

Temporary Hardness (carbonated) represents the content in calcium and magnesium ions corresponding to the content in calcium and magnesium bicarbonates in water. Temporary hardness (D_t) is due to the calcium and magnesium hydro-carbonates.

By boiling, the temporary hardness disappears because the bicarbonates decompose; passing into the respective sparingly soluble carbonates which deposits. The reactions that take place are:



Permanent hardness (uncarbonated) represents the content in calcium and magnesium ions, corresponding to other calcium and magnesium salts in water excepting bicarbonates (sulphates, chlorides, and nitrates).

Total hardness represents the sum of the metallic cations existing in water, excepting cations of alkaline metals, in terms of equivalent concentrations in calcium. The total hardness (D_T) is given by the sum of temporary and permanent hardness:

$$D_T = D_t + D_p$$

The water hardness is measured in hardness degrees. In Romania, German degree for hardness is standardised, it represents a content of 10mg CaO in one litre of water and is symbolised with $^{\circ}\text{d}$. In order to show the hardness, the respective salts are converted in Ca O equivalent [6], [7].

The principle of the method

The total hardness of surface waters is experimental determined through the EDTA complexometry at pH=10 in the presence of indicator black-ericrom T, according to the

specific working procedure PSL-05, 2000 revision, issued by the National Company „Apele Române” [1].

The utilised apparatus

It was used a burette for titration and the reagents settled in standard working procedure.

The working method

The sample of drinking spring-water is mixed with black eriocrom T indicator and it is titrated with complexon III solution till the colour changes from red to net blue.

The experimental results

$$D_T = \frac{0,561 \times V_1 \times f}{V \times 10} \times 1000 = \frac{56,1 \times V_1 \times f}{V} \quad (1)$$

in which:

D_T = total hardness, in °d, where 1 hardness degree corresponds to 10 mg CaO/l water.

0,561 = the quantity of calcium oxide, in mg, that corresponds to 1 ml solution of complexon III 0,01 M;

V_1 = the volume of complexon III solution used in titration, in ml;

f = factor of complexon III solution;

V = the volume of water sample, in ml;

10 = quantity of CaO, in mg, corresponding to 1 hardness degree.

The hardness values of the drinking spring-waters in Pitesti are shown in the table at the end of the section.

The comparison between measured values and maximum allowed values for the hardness for drinking waters is shown in the diagram from figure 3.

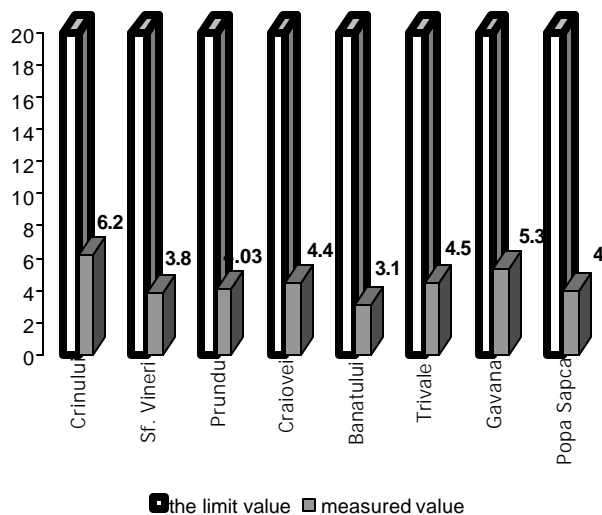


Fig. 3 – The values of the total hardness for drinking spring waters in Pitesti town

The determination of calcium and magnesium ions in drinking spring waters using spectral analysis of spectral absorption in flame method

The principle of the method

The calcium and magnesium are determined through atomic absorption spectral analysis in reducing flame air-acetylene by measuring the absorbency of the samples on

which, in order to reduce the interference, lanthanum chloride is added as is settled in the standard working procedure ISO 798-1986, issued by International Standardisation Organisation [2]. For calcium, the determinations are made at 422,7nm wavelength and for magnesium at 285,2nm wavelength, those being the wavelengths of spectral lines for absorption specific for the two elements with maximum intensity that determines a maximum detection responsiveness of the apparatus. [7],[8],[9],[10].

The utilised apparatus

For measurements through spectral analysis of atomic absorption was used atomic absorption/emission spectrometer with double beams Varian Tehtron, SpectrAA 110/220 model [5].

Interferences

When determine calcium and magnesium in drinking waters through spectral analysis of atomic absorption in flame, interferences with phosphate, sulphate, fluoride and aluminium ions are present. Those interferences are reduced by adding to the samples for analysis the lanthanum chloride in order to obtain lanthanum concentrations of 0,1÷1% [5],[7],[8],[9].

The working method

1. Apparatus operating parameters adjustment

2. Blank sample and standard samples preparation.

Blank sample consists of demineralised or double distilled water and it is used to zero calibration of absorbency both for calcium and for magnesium.

The standard samples for each of the two elements are prepared so that one gets the concentrations 1%, 2,5% and 5% in calcium and in magnesium respectively, according to ISO 7980-1986 [2] and to the calibration procedure for the apparatus, settled in instructions. [5]. The standard samples are used to calibrate the absorbance and to draw the calibration curves for each element.

3. Zero absorbency calibration, calibration curve drawing and ascertain of calcium and magnesium ions concentration in drinking spring water.

These operations are automatically done with computing aid that surveys the operation of atomic absorption spectrometer Varian Tehtron SpectrAA 110/220 [5].

Adjustment curves and calibration curve for calcium and magnesium respectively, experimental obtained are shown in the figures 4 and 5.

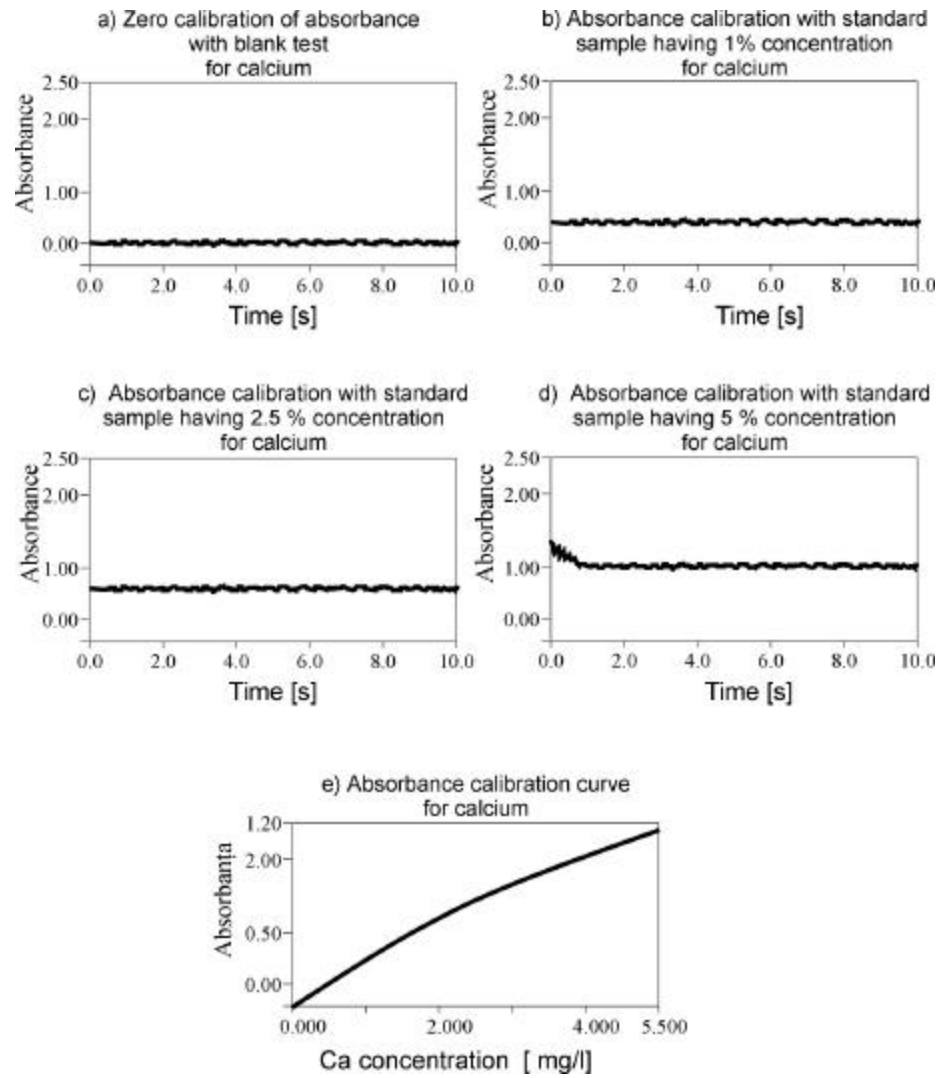


Fig. 4 – The adjustment curves and the calibration curve used to determine calcium ions in drinking spring waters from Pitesti town

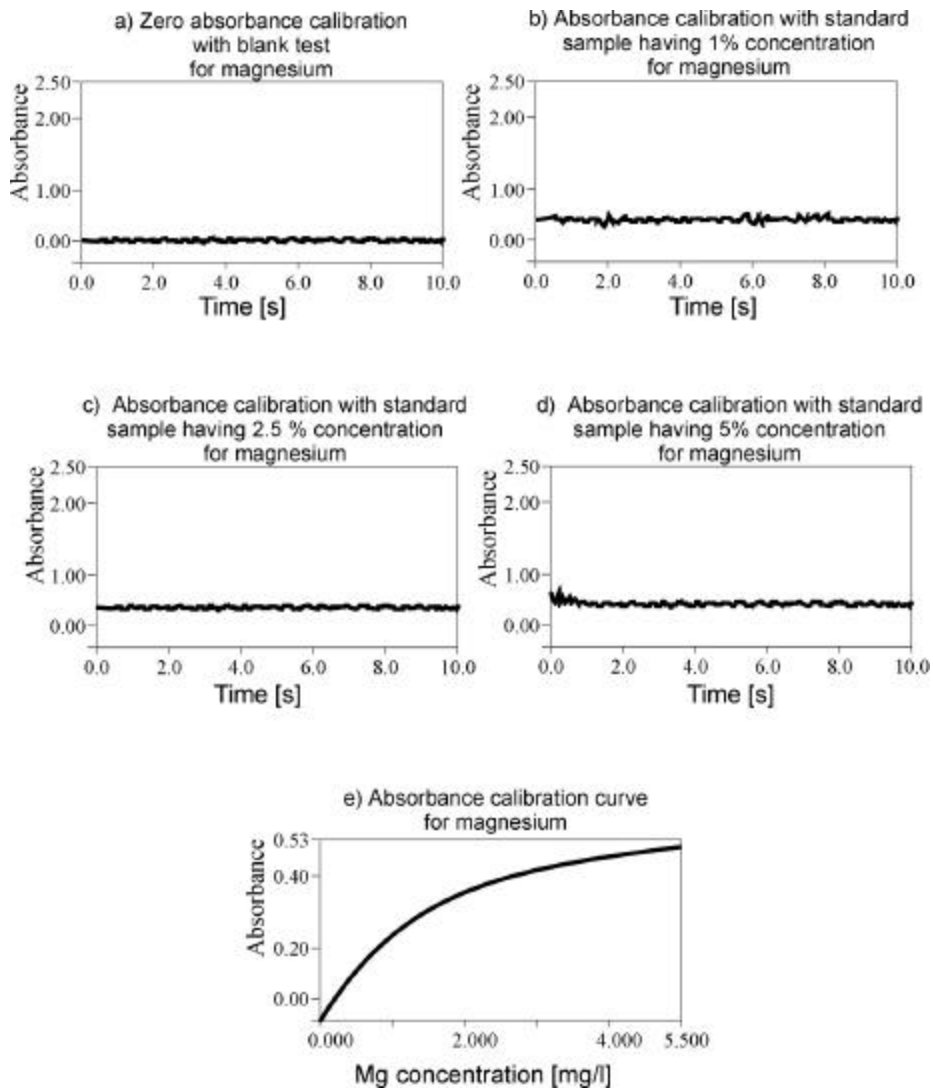


Fig. 5 – The adjustment curves and the calibration curve used to determine magnesium ions in drinking spring waters from Pitesti town

The accuracy of the determination

The accuracy of the concentration of calcium ions obtained in flame atomic absorption spectral analysis is 95,4÷96,5% and for magnesium ions is 93,1÷97,1% [5],[7],[8],[9].

The experimental results

It is automatically made using calibration curves with computing aid that survey the operation of Varian Tehtron SpectrAA 110/220 atomic absorption spectrometer [5]. The values of concentration of calcium and magnesium ions in drinking spring waters from Pitesti are shown in the table at the end of section.

The comparison between measured and maximum allowed values for the concentration of calcium and magnesium ions in drinking waters are shown in diagrams from figures 6 and 7.

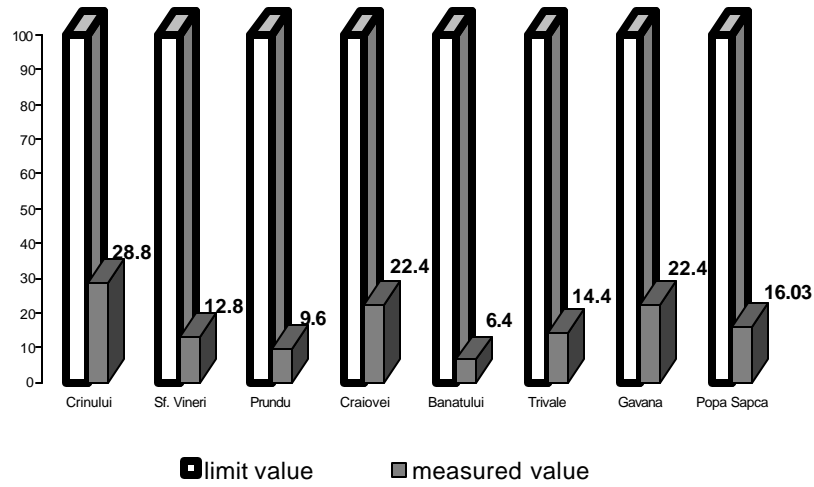


Fig. 6 - The values of concentration of calcium ions in drinking spring-waters from Pitesti town

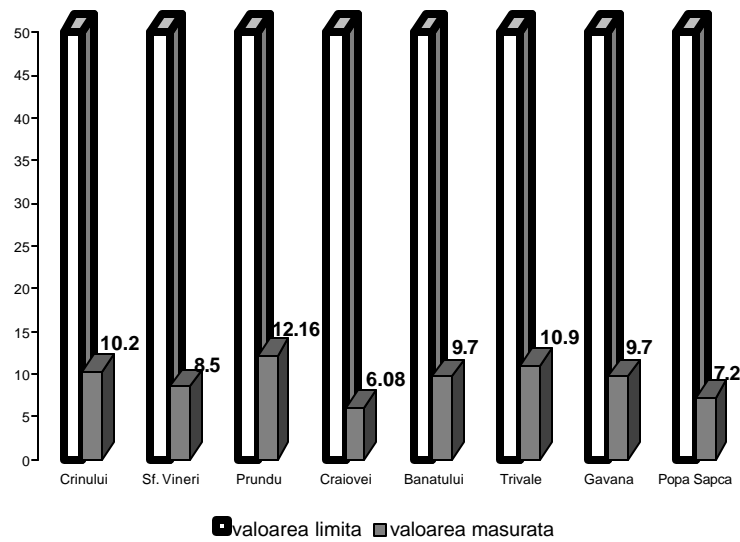


Fig.7 – The values of concentration of magnesium ions in drinking spring-waters from Pitesti town

The determination of calcium concentration in drinking spring-waters using complexometry method.

The principle of the method

The concentrations of calcium ions in drinking spring waters is determined using complexometry with EDTA at pH=12÷13 in the presence of the indicator mixture green-murexide of naphthol B. Magnesium ions deposits as magnesium hydroxide and doesn't interfere in determination.

The method used observes the National Standard STAS 3662-90, issued by Romanian Standardisation Institute [3].

The utilised apparatus

It was used a burette for titration and reagents settled in national standard.

Interference

In drinking water calcium determination by complexometry method, aluminium, barium, lead, iron, cobalt, copper and zinc interfere.

Orthophosphates in concentration greater than 1 mg /dm³ deposit the calcium at titration's pH. If the titration is made too slowly or at a content of calcium over 100mg/dm³, calcium carbonate deposits.

Adding in the samples, before dosage, 250mg sodium cyanide or 1÷3cm³ of triethanolamine eliminates the iron interference (in concentrations up to 30 mg/dm³).

Adding sodium cyanide the interference of copper, cobalt, and tin can be decreased.

The aluminium interference is reduced by adding triethanolamine [6],[7],[8].

The working method

The sample of spring water is mixed with the indicator green-murexide of naphthol B and it is tittered with EDTA at pH=12÷13 till the colour changes from red to violet.

The accuracy of the determination

The calcium ions concentration accuracy obtained by complexometry with EDTA method in the presence of indicator mixture green-molexide of naphthol B is of 80÷90% [3],[7],[8].

Experimental results

The content in calcium is in milligrams on litre and it is calculated using the formula:

$$C_{Ca} = \frac{1000 \times 0,4008 \times V_1 \times r}{V} \quad (2)$$

in which:

C_{Ca} – concentration of calcium ions, in [mg /l];

0,4008 = quantity of calcium, in milligrams, correspondent to 1 cm³ EDTA solution 0,01 M;

V_1 - the volume of EDTA solution used for titration, in ml;

r – the ration of solution dilution, if necessary;

V-the volume of spring water sample, in ml.

The obtained results using this method confirm the determinations obtained using in flame atomic absorption spectral analysis and they are harmonised with the values of drinking spring waters hardness.

Magnesium concentration ascertain in drinking spring waters using absorption's visual spectrophotometry method

The principle of the method

The concentration of magnesium ions in spring waters is determined using absorption's visual spectrophotometry, according to National Standard STAS 6674-90, issued by Romanian Standardisation Institute [4].

The utilised apparatus

A visual absorption spectrophotometer with monochromator and the reagents settled in National Standard was used.

The working method

Magnesium together with yellow titanium, in the presence of a protective colloid forms a varnish with orange-red colour. The colour intensity is in proportion to the quantity of magnesium from sample and it is determined by visual absorption spectrophotometry. The intensity of solution's colour is measured on the spectrophotometer, in a vat with coating thickness of 1 cm, at 545 nm wavelengths; face to a standard sample prepared in the same way but with distilled water instead of sampled ones. The ascertained value for extinction is read on the calibrating curve and the magnesium concentration, in mg, is founded.

The accuracy of the determination

The accuracy of magnesium ions concentration obtained by absorption visual spectrophotometry is 80÷85%.

The obtained results using this method confirm the determinations obtained using in flame atomic absorption spectral analysis and they are in accordance with the values for hardness of analysed drinking spring-waters [4],[7],[8].

The experimental results

$$C_{Mg} = \frac{C}{V} \times 100 \text{ [mg/l]} \quad (3)$$

In which:

C_{Mg} = concentration of magnesium ions in spring water sample

C – the content of magnesium in control sample colour measured, read on the calibration curve, in mg.

V - volume of sampled, in l.

The results obtained using this method confirm the determinations obtained using in flame atomic absorption spectral analysis and they are according to values for hardness of analysed drinking spring waters.

TABLE - The values of calcium and magnesium ions concentrations determined using in flame atomic absorption spectral analysis, pH and total hardness values in drinking spring waters from Pitesti town.

Denomination of the spring of drinking water	Concentration of Ca ²⁺ [mg/l]	Concentration of Mg ²⁺ [mg/l]	pH	Total hardness [°d]
Crinului	28.8152	10.2324	7.43	6.20
Sf. Vineri	12.8236	8.5167	7.60	3.80
Prundu	9.6153	12.1642	7.58	4.03

Craiovei	22.4261	6.0851	7.42	4.40
Banatului	6.43111	9.7134	7.60	3.10
Trivale	14.4173	10.9145	7.68	4.50
Gavana	22.4252	9.7211	7.66	5.30
Popa Sapca	16.0373	7.2432	7.64	4.00

CONCLUSIONS

The specific working procedure for the determination of total hardness in drinking spring-waters issued by National Company „Apele Române” is particular for our country and for its verification two standard procedures were used, one international, issued by International Standardisation Organisation and the other, national, issued by the Romanian Institute for Standardisation. The results confirm the alignment of specific working procedure to Romanian and International Standards and the values experimental determined using certain methods are comparable.

The determination of total hardness and concentrations of calcium and magnesium ions in drinking spring waters from Pitesti town direct to the conclusion that these waters correspond to the quality standards for drinking waters.

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