Ionic balance in waters through inductively coupled plasma atomic emission spectrometry

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Abstract

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has been employed to carry out the determination of both major anions and cations in water samples. The anions quantification has been performed by means of a new automatic accessory. In this device chloride has been determined by continuously adding a silver nitrate solution. As a result solid silver chloride particles are formed and retained on a Nylon filter inserted in the line. The emission intensity is read at a silver characteristic wavelength. By plotting the drop in silver signal versus the chloride concentration, a straight line is obtained. As regards bicarbonate, this anion has been on-line transformed into carbon dioxide with the help of a 2.0 mol L⁻¹ nitric acid stream. Carbon signal is linearly related with bicarbonate concentration. Finally, information about sulfate concentration has been achieved by means of the measurement of sulfur emission intensity. All the steps have been simultaneously and automatically performed. With this setup detection limits have been 1.0, 0.4 and 0.09 mg L⁻¹ for chloride, bicarbonate and sulfate, respectively. Furthermore, it affords good precision with RSD below 6 %. Cations (Ca, Mg, Na and K) concentration, in turn, has been obtained by simultaneously reading the emission intensity at characteristic wavelengths. The obtained limits of detection have been 8×10^{-3} , 2×10^{-3} , 8×10^{-4} and 10^{-2} mg L⁻¹ for sodium, potassium, magnesium and calcium, respectively. As regards sample throughput about 30 samples h⁻¹ can be analyzed. Validation results have revealed that the obtained concentrations for these anions are not significantly different as compared to the data provided by conventional methods. Finally, by considering the data for anions and cations precise ion balances have been obtained for well and mineral water samples.

Keywords

Ion balance; bicarbonate; sulfate; chloride; drinking waters; fish farm waters; inductively coupled plasma atomic emission spectrometry.

1. Introduction

Major constituents of mineral and ground waters are positively and negatively charged ions. Among the formers one can find sodium, potassium, calcium and magnesium whereas common anions are chloride, sulfate and bicarbonate. The quality of a water chemical analysis is determined through the ion balance. This corresponds to the balance of positively and negatively charged ions. Water must accomplish the principle of electroneutrality and, thus the error of a given dataset corresponding to the content of ions is given by [1]:

$$Error = \frac{\Sigma[cations] - \Sigma[anions]}{\Sigma[cations] + \Sigma[anions]} * 100 \quad (1)$$

Where all the concentrations are given in equivalents L⁻¹. In order to obtain quantitative information of each one of the ions present in water, accurate, fast sensitive analytical methods are required.

There are several methods for the chloride quantification such as classical titrations (e.g., Volhard method), the use of ion selective electrodes [2,3] or colorimetric methods. In the later one, chloride forms a complex with mercury ions. The reduction in the absorbance of the complex formed between mercury and diphenylcarbazone is directly related with the chloride content [4]. Turbidimetric methods that avoid the use of toxic reagents have also been employed for chloride determination. In this case, silver ions are added to promote the formation of solid silver chloride [5]. Ion chromatography and capillary electrophoresis can also be employed for the determination of this ion with 0.2 mg L⁻¹ and 0.004 mg L⁻¹ typical detection limits, respectively [6,7]. Flame Atomic Absorption Spectroscopy (FAAS) has been applied to the indirect determination of chloride after precipitation with silver ions and the retention of the formed precipitate on a stainless-steel filter [8]. With a reversed flow approach this anion has been determined in the 0.3 – 10 mg L⁻¹ range with a 200 h⁻¹ sample

throughput. Chloride determination can also be performed by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). However, due to the fact that the most sensitive wavelengths at which chloride ions emit are below 150 nm (i.e. 134.7 and 135.166 nm) the optical system must be argon purged. This eliminates the species that absorb at wavelengths below 150 nm such as oxygen and water vapor, among others [9]. With this modification, detection limits for chloride are on the order of 0.5 mg L⁻¹. In another study, an argon purged ICP system has been applied to the analysis of botanical samples [10] showing three orders of magnitude dynamic ranges and 0.04 mg L⁻¹ detection limits. Additional work has been devoted to the determination of chloride in concrete samples by ICP-OES [11].

As regards sulfate, the addition of barium to the sample to promote the formation of barium sulfate particles has been proposed and the further detection has been based on either the decrease in the conductivity [12] or the increase in the solution turbidity [13]. The addition of lead and the use of a reversed precipitation flow-injection device has been applied to the sulfate determination by means of FAAS in the 2 – 20 mg L⁻¹ concentration range with a 60 h⁻¹ sample throughput [14]. Turbidimetric methods have also been automated [15,16]. In a sequential injection analysis approach the achieved detection limit was 2.0 mg L⁻¹ [17]. This anion was also determined together with chloride after the addition of either barium or silver to promote the production of barium sulfate or silver chloride particles [18]. The obtained detection limits were on the order of 0.7 and 1.3 mg L⁻¹ for chloride and sulfate, respectively. Meanwhile, sample throughput was about 10 samples per hour. In a recent report sulfate was determined together with sulfide in natural water samples through ICP-OES [19,20]. Sulfur emission intensity was measured at 180.669 nm. In order to suppress sulfide contribution to the analytical signal, samples were acidified and sparged with an argon stream that evacuated the H₂S generated from sulfide. Detection limits (close to 1.0 mg L⁻¹) were similar to those previously reported for turbidimetric [21] and chromatographic methods. In another study, a flow injection system was employed to

carry out the determination of several metals at low concentrations together with chloride and sulfate in riverine waters by inductively coupled plasma mass spectrometry (ICP-MS) [22]. In this case, solid phase extraction was used as a sample pretreatment in order to separate cations from anions. Once the signal for metals was recorded, the anions were eluted with a nitric acid solution. The obtained LODs were 0.2 and 0.06 mg L⁻¹ for chloride and sulfate, respectively [22].

Concerning bicarbonate, this anion has been classically determined by means of an acid-base titration. Due to the interest of determining it in water samples, ion-exclusion chromatography, potentiometric titration or direct potentiometry with a CO₂-responsive electrode have also been proposed [23]. In the case of chromatographic methods a retention time close to 15 min was recorded for this anion. Meanwhile, the potentiometric determination suffered from severe interferences caused by the presence of organic acids such as acetic. Recently, the electrochemical determination of this anion has been carried out with an array of electrodes constituting an electronic tongue [24]. In another study, a microflow analyzer containing a gas diffusion membrane was employed. Bicarbonate was transformed into carbon dioxide and determined through the measurement of the change in the conductivity of a distilled water acceptor solution. The obtained limit of detection was 2.3 mg L⁻¹ and the sample throughput was 15 samples per hour [25]. Carbon can also be determined by means of ICP-OES through the measurement of the intensity at 193.030 nm. This has been the employed procedure for the determination of carbon fractions (*i.e.*, total organic carbon, inorganic carbon...) in waste waters [26]. In this case, the sample was on-line pre-treated and introduced into the plasma. Thus, for example, in order to determine the organic carbon, the sample was acidified and purged with an argon stream. Inorganic carbon was transformed into carbon dioxide (that could be eventually measured) and abandoned the sample. Only non-volatile organic compounds remained in the sample. The achieved detection limits were 7·10⁻² and 7·10⁻⁴ mg carbon L⁻¹ for organic and inorganic carbon, respectively whereas up to 50 samples were analyzed per hour.

Inductively Coupled Plasma Optical Emission Spectrometry is a mature technique routinely applied to the determination of elements, especially metals [27,28]. Therefore, its use for the quantification of sodium, potassium, calcium and magnesium in mineral waters is well established. Furthermore, the above mentioned studies suggest that this technique is also appropriate for obtaining quantitative information of sulfate, chloride and bicarbonate in water samples. In this way, a single method could be applied to perform accurate and sensitive ionic balances. So far, there are no methods providing information about both anion and cation concentrations. Ionic chromatography, IC, is routinely used to determine chloride and sulfate concentration [29,30]. However, since a carbonate/bicarbonate buffer is normally employed, these anions cannot be detected [31]. Another pitfall of IC is the sometimes long analysis time (e.g., 12 min for mineral waters [32] and 22 min for saline waters [33]). Although cations are also determined by means of IC [30], it is necessary to employ different stationary and mobile phases, or sophisticated dual systems to carry out this kind of analyses [34] and, hence, the ionic balance is not simultaneously carried out. Furthermore, limits of detection obtained in IC for cations cannot compete with those normally achieved in ICP-OES. The goal of the present work was thus to develop for the first time a flow injection accessory easily adapted to a conventional ICP-OES apparatus to acquire information of cation and anion concentrations in water samples thus allowing to carry out rapidly the ionic balance.

2. Experimental

2.1. Reagents, solutions and samples

All reagents were of analytical grade. Sodium chloride, sodium sulfate and sodium bicarbonate (Merck, Germany) were taken to prepare standards diluted in ultrapure water ($R < 18 \text{ M}\Omega$) obtained with a Millipore water purification system (El Paso, TX,

USA). Nitric acid, silver nitrate and ammonia (Panreac, Spain) were also employed. Sodium, potassium, magnesium and calcium standards were prepared by a proper dilution of a 1,000 mg L⁻¹ multielement stock solution (Merck IV) with ultrapure water. Phenolphthalein, methyl orange and hydrochloric acid (Merck, Germany) were employed for bicarbonate titration.

The analyzed real samples were: ten commercially available mineral waters; nine well waters supplied by the company Labaqua, S.A. (Alicante, Spain); and eight synthetic sea water samples employed in a fishing farm. Conductivity at 20°C and pH of the mineral waters were between 205 and 560 µS cm⁻¹ and between 7.7 and 8.2, respectively. In the case of well waters, conductivities went from 30 to 170 µS cm⁻¹ whereas pH was included within the 6.4 to 8.1 range.

2.2. Ion chromatography

An ion chromatograph (IC) equipped with electrochemical suppression and conductometric detection (Thermo, DIONEX DX 500) was employed as reference system for the determination of chloride and sulfate. Before being injected into the apparatus, samples were filtered by means of 0.45 µm filter pore size (Filalbet, Barcelona, Spain). All the samples were kept at conductivity values below 2 mS cm⁻¹. Mobile phase consisted of carbonate 4.5 mmol L⁻¹ and bicarbonate 1.4 mmol L⁻¹ whereas the column employed was a AS22 DIONEX. IC most diluted standards were 1 mg L⁻¹ both for chloride and sulfate.

2.3. ICP-OES system

An Optima 4300 DV Perkin-Elmer ICP-OES spectrometer (Uberlingen, Germany) was used and the emission signals were axially taken. The system was equipped with a 40.68 MHz free-running generator and a polychromator with an echelle grating.

Segmented-array Charge-coupled Device (SCD) detectors allowed for the simultaneous measurement of several lines in the UV and visible electromagnetic spectrum zones. Table 1 summarizes the instrumental conditions.

Two different sample introduction systems were employed: (i) a conventional device consisting of a pneumatic concentric nebulizer (TR-30-A2, Meinhard Glass Products, USA) adapted to a cyclonic spray chamber (Glass Expansion, Australia), mostly employed in the present study; and, (ii) a ultrasonic nebulizer [35] (USN-5000AT⁺, CETAC Technologies, Omaha, Nebraska, USA). In this case, the aerosol was generated by means of a piezoelectric transducer. Before entering the plasma, this aerosol went through a desolvation system consisting of a 120°C heated tube followed by a -3°C cooled one. This latter system was employed to test the possibility of direct chloride determination.

2.4. On-line accessory for the ionic balance determination

Figure 1 shows a scheme of the system employed for the determination of chloride, sulfate, bicarbonate and cations through ICP-OES. The solutions were propelled by means of a peristaltic pump (Gilson Minipuls3 Model M312, Villiers-le-Bel, France). Sample water, distilled water or standard together with nitric acid and silver nitrate solutions were simultaneously aspirated at a 0.5 mL min⁻¹ flow rate and circulated by 0.76 mm id PTFE tubing. The sample was first merged with a silver nitrate solution and then with the nitric acid solution by means of two T-unions. A 0.9 m long 0.86 mm id PTFE capillary was employed as reactor to promote the complete transformation of bicarbonate into carbon dioxide and the quantitative precipitation of silver chloride. A 13 mm diameter and 0.45 µm pore size Nylon filter (Filalbet, Barcelona, Spain) was employed to trap the formed silver chloride particles.

Chloride concentration was determined by means of an indirect method. Initially, ICP-OES signal for silver (container B, Fig. 1) was continuously recorded when

distilled water was in container A, Fig. 1. This corresponded in fact to the blank signal. Then, standards of known chloride concentrations were sequentially aspirated. Because silver chloride particles were generated and trapped on the filter, the higher the chloride concentration, the lower the silver signal. The calibration line was obtained by plotting the drop in silver signal versus the chloride concentration. Finally, the sample was placed in container A, Fig.1 and the silver signal was recorded again.

Bicarbonate was determined by reaction with a nitric acid solution (container C, Fig. 1). The direct consequence of this process was the conversion of this anion in carbon dioxide. The resulting gas – liquid mixture was driven to the ICP-OES spectrometer and the carbon emission signal was recorded. This procedure was applied to the blanks, standards and water samples.

Finally, the determination of sulfate was performed by directly reading the signal for sulfur. The analysis procedure was, as for cations, external calibration with a series of standards.

With the present method, two sets of standards were prepared: one for anions and another one for cations. Because a simultaneous ICP-OES system was employed, the signals for both cations and anions in the samples were simultaneously and continuously taken.

3. Results and discussion

Once the system was adapted to the ICP spectrometer, both anions and cations were determined together in real water samples. In the case of anions determination all the experiments were repeated five times and the RSDs of the obtained concentrations were always lower than 6% what gave an indication of the method precision.

3.1. Chloride determination

As mentioned in the introduction section, ICP-OES has been previously employed for the determination of chloride by direct measurement of the emission signal for this ion [9]. In the present work, chloride standards were directly introduced into the spectrometer and chlorine emission intensity was recorded at a rather long emission wavelength (see Table 1). However, when a pneumatic nebulizer was employed, precise quantification of chloride below 100 mg L^{-1} was not possible. This fact evidenced the poor sensitivity obtained for this element. In contrast, when using the ultrasonic nebulizer, the mass of chloride that reached the plasma increased. Under these circumstances, the sensitivity improved by a factor close to 6 and the detection limit went down to 20 mg L^{-1} . However, this LOD was not low enough to perform direct determinations of chloride in some mineral water samples.

The indirect method was thus applied. The silver signal linearly decreased as the chloride concentration went up. The amount of silver in the solution of container B, Fig. 1 could be varied depending on the chloride level. In our case, 125 mg L^{-1} was the chosen concentration. As this solution was on-line merged with that for the sample or standards and that for the acid solution, the actual concentration in the stream was three times lower (*i.e.*, 42 mg L^{-1}). Taking into account the solubility constant for silver chloride and the maximum concentration considered in Figure 2 ($[\text{Cl}^-] = 41 \text{ mg L}^{-1}$ in container A, Fig 1) it was verified that the precipitation of AgCl was quantitative. Also noteworthy was the fact that there was a good linear relationship between the magnitude of the decrease in silver intensity and chloride concentration (see Figure 2). The drop in silver intensity was defined as the difference between the silver emission intensity measured when only deionized water was present in container A, Fig 1 (I_{blank}) and that registered when chloride was present in this vessel (I_{standard}). Therefore, this was considered to be an adequate method for the determination of the concentration of this anion in water samples. Limit of detection was calculated from the calibration line according to:

$$LOD = \frac{3 \cdot s_{x/y}}{m} \quad (2)$$

Where m was the slope of the calibration line and $s_{x/y}$ its covariance for n replicates given by:

$$s_{x/y} = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n - 2}} \quad (3)$$

Table 2 shows the LOD for chloride. This value was below the chloride concentration in most drinking waters.

By applying this method, a filter was used to trap silver chloride particles. The filter might saturate but no overpressure problems were observed after analyzing about 100 samples. Therefore it was recommended to replace the filter once a day.

In a further modification of the method, the AgCl particles were dissolved in a 1 mol L⁻¹ ammonia stream. This solution was introduced in the system by replacing container A in Fig 1 by a solution of this base. Silver dissolved as the complexes Ag(NH₃)⁺ and Ag(NH₃)₂⁺ formed. A transient signal (or peak) was obtained by plotting Ag emission intensity versus time and there was a good linear relationship between the peak height and chloride concentration. However, the detection limit increased up to 2 mg L⁻¹ what was likely due to the incomplete AgCl dissolution. Furthermore, the sample throughput decreased as more time was required for the re-dissolution of the precipitate. In any case, this could be a solution to clean the filter after using it for a while.

A potential drawback of the present method would be the co-precipitation of chloride with other interfering anions such as bromide or iodide thus giving rise to an overestimation of the chloride content. In the present work, an ion chromatograph was employed to evaluate the presence of halides others than chloride in the samples. For the analyzed samples very short peaks were found for bromide. The concentration in this anion was lower than 0.5% that for chloride. This observation was in agreement

with other previously published data in which the concentration of bromide was less than 1% that for chloride [32]. This situation is common for most of the cases, although in some instances bromide concentration may surpass this level [36]. Obviously, in these cases an interference would be produced that could degrade the accuracy of the results.

3.2. Bicarbonate determination

With a conventional ICP-OES equipped with a common liquid sample introduction device, bicarbonate could be directly determined by merely reading the emission intensity at the carbon characteristic wavelength. Unfortunately, as Figure 3 reveals, there was not a linear relationship between carbon signal and bicarbonate concentration. The reasons for this trend could be in direct connection with the fact that this anion was present as sodium bicarbonate. Therefore, the matrix effects induced by this easily ionized element were more pronounced at high than at low bicarbonate concentrations. This problem was overcome with the device developed in the present work. As it was experimentally verified, a 2 mol L⁻¹ nitric acid solution (container C, Fig. 1) was suitable to quantitatively transform bicarbonate into carbon dioxide. Once the solution was led to the nebulizer of the spectrometer, this gas was released in aerosol phase and efficiently driven towards the plasma. This fact had two major advantages: (i) the sensitivity increased; and, (ii) interferences caused by sodium were less severe because the analyte separated from the matrix inside the spray chamber (*i.e.*, prior to the plasma). With this new approach good calibration lines were obtained (Fig. 5).

By considering Figures 3 and 4 it was realized that the addition of nitric acid yielded an increase in the carbon signal by a factor close to 5 – 6 thus giving rise to low limits of detection (Table 2). This was observed in spite to the fact that high procedural blank signals were obtained. In fact the equation of the calibration line was Carbon signal = 3061,9 x bicarbonate concentration + 70236. This was due to the different

carbon sources: (i) carbon is present as a polluting element in the argon employed to sustain the plasma; (ii) dissolved carbon dioxide in the sample also contributes to the carbon signal, and; (iii) atmospheric carbon dioxide may diffuse towards the plasma central channel.

3.3. Sulfate determination

This anion was easily determined by direct introduction of the solution and the acquisition of the sulfur emission intensity. Under the operating conditions followed in the present work, acceptable calibration lines were obtained (Sulfur signal = 196 sulfur concentration + 254; $R^2 = 0.9998$). In this case, the signal for the procedural blank was registered and the obtained values were fairly low with good repeatability (1.5 % RSD). Limits of detection are summarized in Table 2. The device used in the present investigation (Fig. 1) provided similar LODs to those reported for ICP-MS. Note that in the latter case, it was necessary to follow the m/z of 48 corresponding to SO^+ ion [22] to avoid the strong spectral interference suffered by ^{32}S (due to the $^{32}O_2^+$ ion). Furthermore, unlike with ICP-OES, bicarbonate was not measured with ICP-MS due to the high background level.

3.4. Analysis of water samples

In order to validate the procedure developed in the present work several water samples were analyzed. The chloride concentrations found for real samples by means of ICP-OES are plotted versus the values measured through IC (figure 5.a). Two different groups of samples were considered: mineral waters and well waters. Good linear correlation existed between the data provided by both methods (*i.e.*, a straight line with a slope close to 1 was obtained). Figure 5.b, in turn, plots the correlation between the

bicarbonate concentration found in ICP-OES and that encountered by the classical titration methodology. Seven samples corresponded to mineral waters, whereas eight were synthetic sea water samples collected from a fish farm factory. As for chloride, the results obtained for both methods were similar. The designed method permits the determination of bicarbonate concentration in samples containing low organic carbon levels. For samples containing high concentrations of organic compounds, a liquid-gas phase separation system should be used [26]. Finally, sulfate concentration was obtained for eight mineral and seven well water samples. Also for this anion the ICP based methodology demonstrated to be an appropriate approach for its determination (Figure 5.c). In order to strictly compare the different methods the t-test was applied. Calculated t values were 0.26, 0.46 and 0.79 for bicarbonate, sulfate and chloride, respectively. Note that these values were below the tabulated Student t for a 95% confidence level and with 13 freedom degrees (*i.e.*, 1.77). This analysis confirmed that the data provided by the new method based on the use of ICP-OES and those encountered by applying conventional methods were not significantly different. The ICP-OES based method was finally applied to the determination of the ionic balance of mineral waters. Cations were directly quantified by using appropriate standards. The obtained results are gathered in Table 3 for different water samples. When available, the data provided in the label were taken as reference. As may be seen, the results afforded by the two methods were similar. With these data, those corresponding to the anion concentration and equation 1, it was possible to obtain the ionic balance error for the evaluated samples (Table 4). In all the cases an error below 10% was obtained. Combined uncertainty was determined to be lower than 2% in all the cases.

3.5. Classification of water samples

The concentration of major ions in groundwater depends on the geological and hydrochemical processes [37]. The data obtained by applying the present method

revealed that, with some exceptions, bicarbonate was the dominant ion, its concentration being generally lower than 150 mg L^{-1} for mineral waters and much higher ($250 - 350 \text{ mg L}^{-1}$) in the case of fishery waters. Sulfate covers a wide range of concentrations both for mineral and well waters (Figure 6). In the case of chloride, mineral waters exhibited rather low values, whereas well ones covered a range going from roughly 10 to 350 mg L^{-1} . The results for cations revealed that for mineral waters, calcium was the most abundant element whereas potassium was present at the lowest concentration. The situation for well waters was not that clear and they had a more variable nature.

In order to illustrate the potential of the method developed in the present work, the composition of several water samples was plotted according to the widely employed Piper diagram [38]. Figure 6 shows the corresponding diagram for ten mineral waters and nine well waters. In this case, the cationic trilinear plots take into account the concentrations of calcium, magnesium and sodium+potassium. Meanwhile, the anionic one considers the concentration of sulfate, chloride and bicarbonate(+carbonate). All the concentrations are given in meq L^{-1} In percentage. The points on the central diamond shaped graph are located by extending the points in the anion and cation trilinear graphs to the intersection points. The Piper diagram permits to plot in a single graph cation and anion compositions from which trends can be visually discerned. Additional diagrams have been extensively described that improve the quality of the interpretation of the results or incorporate additional information (*i.e.*, total content of dissolved solids) [39]. The main applications of the Piper diagram are: to evidence the geochemical evolution of a given water, to detect processes such as ionic exchange, to detect mixtures of different waters [40] and to evidence precipitation of ionic species. From Figure 6 it can be observed that most mineral waters grouped well according to the concentration of either anions or cations. Nine of them were Ca-Mg-HCO_3 type as it is evidenced by the fact that the points appear near to the left corner of the diamond diagram (2, Figure 6). One mineral water

was Na-K-HCO₃ type (4, Figure 6). As regards well waters, five of them were Ca-Mg-SO₄-Cl type (1, Figure 6), one was Na-K-SO₄-Cl type (3, Figure 6) and another one was Ca-Mg-HCO₃ type (2, Figure 6).

Conclusions

The use of a system based on the on-line addition of silver nitrate and nitric acid coupled to an Inductively Coupled Plasma Atomic Emission Spectrometry, ICP-OES, makes it possible to carry out the fast and precise determination of the ionic balance in mineral and natural water samples. In order to accomplish this, the elemental signals for cations, silver, carbon and sulfur are simultaneously registered. Acceptable limits of detection are obtained in the case of anions that permit their quantification in water samples of different nature.

So far the ionic balance has been considered as a slow assay involving the use of several analytical methods. With the present method, requiring a single instrument, a complete sample analysis takes only about two minutes. Moreover, the dynamic range is extended to around two orders of magnitude. All these facts make the ICP-OES to be considered as a promising methodology for anion quantification and fast water characterization and hydrogeochemical studies based on the use of diagrams. Additionally, other compounds, such as phosphate and related species, can be easily determined by selecting the appropriate wavelength as it has been recently demonstrated [41].

Table 1. ICP-OES instrumental conditions employed in the present work.

Emission lines measured / nm	C/ 193.030
	Ca/ 317.933
	Mg/ 285.213
	Na/ 589.592
	K/ 766.490
	S/ 181.975
	Ag/ 328.068; 338.289
	Cl/ 725.670
Number of replicates	5
Power / W	1300
Ar Flow / L min ⁻¹	15 (plasma)
	0.2 (auxiliary)
	0.6 (nebulizer)
Plasma View	Axial
Liquid flow / mL min ⁻¹	1.5 (0.5 mL min ⁻¹ /capillary)

Table 2. Limits of detection obtained in the present study for the different ions.

Analyte	LOD (mg L ⁻¹)
Chloride	1.0
Bicarbonate	0.4
Sulfate	0.09
Sodium	0.008
Potassium	0.002
Magnesium	0.0008
Calcium	0.01

*

Table 3. Cation concentrations in mineral and well waters and comparison with the data given in the label for the former ones.*

Sample	Calcium (mg L ⁻¹)		Magnesium (mg L ⁻¹)		Sodium (mg L ⁻¹)		Potassium (mg L ⁻¹)	
	ICP-OES	Label	ICP-OES	Label	ICP-OES	Label	ICP-OES	Label
1	25 ± 2	26.4	3.3 ± 0.2	3.2	6.6 ± 0.4	9.2	1.59 ± 0.07	n.d.
2	84 ± 5	88.7	23 ± 1	23.4	18.8 ± 0.9	18.6	1.50 ± 0.08	n.d.
3	25 ± 1	27.7	3.7 ± 0.1	4.5	10.8 ± 0.2	11.9	1.30 ± 0.01	n.d.
4	56 ± 3	56.9	25 ± 1	25.5	4.4 ± 0.2	5.3	1.28 ± 0.05	1.1
5	32.7 ± 0.6	35.5	7.7 ± 0.1	8.6	9.6 ± 0.1	11.9	1.31 ± 0.02	n.d.
6	n.d.	3	4.7 ± 0.6	3	3.8 ± 0.2	5	n.d.	n.d.
7	22.2 ± 0.4	22.8	n.d.	n.d.	88 ± 6	96.5	n.d.	n.d.
8	28.4 ± 0.2	27.2	21.6 ± 0.6	18.8	5 ± 0.4	4.8	n.d.	n.d.
9	88.8 ± 0.5	88.7	53 ± 1	51.6	18.4 ± 0.5	18.6	n.d.	n.d.
10	38.6 ± 0.6	38.5	19.1 ± 0.8	19.7	12.4 ± 0.7	13.2	n.d.	n.d.
11	5.9 ± 0.1		n.d.		n.d.		n.d.	
12	n.d.		n.d.		6.7 ± 0.6		n.d.	
13	3.9 ± 0.2		n.d.		25.6 ± 0.7		n.d.	
14	77 ± 3		51 ± 2		88 ± 4		n.d.	
15	4.9 ± 0.6		2.1 ± 0.3		10.2 ± 0.3		n.d.	
16	66.6 ± 2		8.1 ± 0.6		21.7 ± 0.8		n.d.	
17	77.4 ± 4		45 ± 3		72 ± 5		n.d.	
18	114 ± 7		34 ± 2		162 ± 7		n.d.	
19	107 ± 4		40 ± 2		190 ± 8		n.d.	

* Sample 1 to 10: Mineral waters

Sample 11 to 19: Well waters

Confidence intervals were obtained according to $\pm \frac{t s}{\sqrt{n}}$ were n = 5.

Table 4. Results of ionic balance for different mineral and well waters samples.*

Sample	Anions (meq L ⁻¹)	Cations (meq L ⁻¹)	Ionic balance error (%)
1	2.032	1.822	5.4
2	7.526	6.899	4.3
3	2.182	2.096	2.0
4	5.839	5.034	7.4
5	3.273	2.719	9.3
6	5.836	5.248	5.3
7	2.437	2.362	1.6
8	7.105	7.299	-0.7
9	3.074	3.312	-3.7
10	5.370	5.388	-0.2
11	0.5924	0.6566	-5.1
12	0.4143	0.4246	-1.2
13	1.587	1.391	6.6
14	12.25	11.926	1.2
15	0.8018	0.863	3.7
16	5.294	4.948	3.4
17	12.22	10.75	6.4
18	17.66	15.55	6.4
19	19.79	16.90	7.9

* Sample 1 to 10: Mineral waters

Sample 11 to 19: Well waters

Figure 1

Figure 1. Scheme of the setup employed to carry out the determination of the ionic balance through ICP-OES. A, Sample; B, silver nitrate; C, nitric acid; D, peristaltic pump; E, reactor; F, filter and holder. Sample and reagents (A, B and C) are aspirated at a 0.5 mL min^{-1} liquid flow rate.

Figure 2. Drop in silver emission intensity ($\text{Signal}_{\text{blank}} - \text{Signal}_{\text{standard}}$) versus chloride concentration. $[\text{Ag}^+]_{\text{blank solution stream}} = 42 \text{ mg L}^{-1}$.

Figure 3. Carbon emission intensity versus bicarbonate concentration with no nitric acid addition.

Figure 4. Carbon emission intensity versus bicarbonate concentration after the addition of 2 mol L⁻¹ nitric acid solution.

Figure 5. Comparison between the anions concentrations obtained in ICP-OES and those for conventional methods. (a) Chloride concentrations. Full symbols: mineral water samples, empty symbols: well waters; (b) bicarbonate concentrations. Full symbols: mineral water samples, empty symbols: fish farm waters; (c) sulfate concentration. Full symbols: mineral water samples, empty symbols: well waters.

Figure 6. Piper diagram for several water samples. Empty symbols: well waters; full symbols: mineral waters. (1) Ca-Mg-SO₄-Cl; (2) Ca-Mg-HCO₃; (3) Na-K-SO₄-Cl; (4) Na-K-HCO₃.

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