# Determination of strontium traces in highly concentrated solutions and brines using flame atomic absorption spectrometry

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(Received: 05 May 2016, accepted: 10 June 2016)

**Abstract:** The natural brines are aqueous solutions strongly concentrated in oceanic salts. The total content of salts can attain 350 g/L. The studied matrix is very complex; it includes a multitude of elements; among them ($Mg^{2+}$, $Ca^{2+}$, $Na^+$, $K^+$), other miners and constituents in the state of traces such as lithium and strontium. This latter has not been studied previously. Considering what precedes; it is evident that the determination of the strontium in the state of trace by flame atomic absorption spectrometry is unsettled by phenomena of interferences due to the matrix effect. In order to understand such phenomena, this work was undertaken. Thus, the investigation of these interferences is necessary. This study allowed us to identify, for each filed of concentration of disturbing elements, the nature of interference phenomena. The obtained results showed that these interferences, are mainly chemical and spectral (interferences of ionization, dissociation, volatilization and superposition of bands). We succeeded to reduce the matrix effect, by using an analysis based on the optimization of the flame and the use of spectroscopic buffer. The persistence of the difficulties caused by presence of magnesium led to study of its quasi-total elimination of the medium.

**Keywords:** Determination of trace elements; strontium, interference phenomena, brine, flame atomic absorption spectrometry.

## INTRODUCTION

Natural brines, object of this work, are very rich solutions containing mainly alkali and alkaline-earth salts. These brines also contain traces of strontium [1]. This element can substitute lithium as tracer in geologic studies as well as to follow kinetics evaporation of natural brines [2]. It is important to note that the total salt content varies from 250 to 350 g/L. Consequently natural brines are highly ten times more concentrated then see water. The presence of four major cations ($Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) can be considered as source of interferences for traces elements analyses. In southern Tunisian natural brines, the ratio ($[Sr^{2+}]$ / [interfering ion]) is estimate to be in the range $10^{-2}$ to $2.10^{-4}$. Furthermore, these information show that the ratio ($[Sr^{2+}] / \Sigma X$) ($\Sigma X = \Sigma[cations]$ in brines is very low ($\sim 10^{-4}$) [3]. we noted in the literature several methods of analysis for the determination of strontium in solution such as Flame photometric method [4], Inductively Coupled Plasma (ICP) [5,6], Ion-Selective Electrode [7] and Atomic Absorption Spectroscopy [8,9]. Grace to advantages that it offers (the simplicity, speed, selectivity) flame atomic absorption spectrometry **(FAAS)** is the method used in this work. Interferences phenomena still constitute a serious problem in the field of **FAAS**. Some components accompanying an analyte in a sample assayed affect the analytical signal [10]. If this effect is not adequately taken into account during analysis, it has to be expected that the analytical results will be inaccurate. There are a number of different approaches used in FAAS helping to overcome the interference effects. The commonly used manners to reduce interferences in specific chemical ways are addition method, the use of spectroscopic buffers and sample pre-treatment [11, 12, 13].

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Analyses of strontium in natural brines by FAAS proved the existence of high perturbations.

The purpose of this work is to elucidate the impact of sodium, potassium, magnesium and calcium on strontium determination in synthetic brines using FAAS. The main target is to minimize interferences phenomena (nebulization, radiation, chemical and ionization interferences) by optimizing flame nature and/or spectroscopic buffers addition.

## EXPERIMENTAL

### 1. Reagents and standards

The chemical products used for the analyses are reagent grade. The diluting water is ultra-pure type (C=0,056 µS/cm) prepared using a Milli-Q. The Glassware used is of type borosilicate. The instrumentations of volumetric measurement are from the A class. The contamination of the sample is the first source of error in analysis of the traces. In order to avoid this phenomenon, first of all we rinse the glassware with diluted HCl and then successively do it two times with ultra-pure water. A stock solution of 100 mg/L was prepared by dissolving 0.3041g of $SrCl_2\,6(H_2O)$. The standard solutions were prepared daily by dilution of the stock solution.

### 2. Instrumentation

The determination of Strontium is achieved using an atomic absorption spectrometer with hollow cathode lamp; trademark ASA VARIO 6 (Analytik Jena, Germany). This device is controlled by the software Win AAs V3.15.L that allows to directly obtain the calibration curves and to measure the values of concentrations of the samples. This device is equipped with a nonspecific absorptions correction (corrector with deuterium) and a dual-beam monochromator. The analyses were performed on the primary analytical line of Strontium (460.7 nm) and using a lamp current of 6mA and the spectral bondpass of 0.5 nm. In this study, we used two types of flame air/ acetylene and nitrous oxide/ acetylene. In both cases, flame observation height of 6 mm and nebuliser free uptake rate of 5 ml $min^{-1}$ were used. A model of spectrometer JY2000 (JobinYvon, USA) was used to verify the reliability of the analysis of strontium in brine by Inductively Coupled Plasma-Optical Emission Spectrometry (**ICP-OES**). This spectrometer was executed in the conditions described by the manufacturer.

### 3. Preparation of synthetic brines

To judge the reliability of the analytical methods used, two sets of five synthetic brines ($S1_1$, $S1_2$, $S1_5$ and $S2_1$ ..........., $S2_2$, $S2_5$ ...........) were prepared. The first reproduces the characteristics of the natural brine of Zarzis while the second reproduces those of the natural brine of El Aldhibet.

Reagents used to reproduce natural brines composition are: KCl (+98% Fluka), NaCl (+99.5% Prolab), $MgCl_2.6(H_2O)$ (+99% Prolabo), $SrCl_2.6(H_2O)$ (+99% Himedia), $NaSO_4$ (99% Fluka), and $Ca\ Cl_2\ .2(H_2O)$ (+99% Fluka). The concentration of strontium in the prepared solutions varies from 10-100 mg/L.

### 4. Methods

In order to obtain the reliance in the results, matrix recovery (MR) was applied the samples analyzed. The matrix recovery is given by the following equation:

$$MR(\%) = ([Sr^{2+}]_{measured} / [Sr^{2+}]_{\mathrm{real}} * 100 \qquad (1)$$

For a sample that does not effect of matrix, MR must be included in the interval [95- 105%].

In this context, we define for each interferent the ratio %Xi as follows:

$$\%X_i = ([\mathrm{Interferent}] / [Sr^{2+}]_{real}) * 100 \qquad (2)$$

With $i = Na^+, K^+, Ca^{2+}, Mg^{2+}$ and $[Sr^{2+}] = 2ppm$

## RESULTS AND DISCUSSIONS

### 1. Determination of strontium concentration by conventional methods

The Strontium analysis was performed initially by the direct method, followed by the method of standard additions and by the **ICP-OES**.

To judge the reliability of method recommended for the determination of Strontium, it is necessary to manipulate with synthetic brines of similar composition to that of natural brines.

To have an idea on effect of the major elements on the determination of Strontium, two series of five synthetic brines ($S1_1$, $S1_2$, $S1_5$ ….. and $S2_1$, and $S2_2$ ..... $S2_5$) were prepared. The results obtained during this study are contained in Table I.

Results show that R% values are from outside of the mentioned interval [95- 105%]. We note that the direct method represents very important error risk during the strontium dosing. Recovery matrices for

**Table I:** Strontium determination by recommended methods

| | $S1_1$ | $S1_2$ | $S1_3$ | $S1_4$ | $S1_5$ | $S2_1$ | $S2_2$ | $S2_3$ | $S2_4$ | $S2_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $[Sr^{2+}]_{real}$ (mg/L) | 10 | 30 | 50 | 75 | 100 | 10 | 30 | 50 | 75 | 100 |
| $R(\%)_{direct\ standardisation}$ | 30.9 | 51.8 | 81.6 | 93.3 | 97.4 | 44.6 | 68.8 | 95.2 | 108.0 | 118.2 |
| $R(\%)_{addition\ method}$ | 116.5 | 106.2 | 94.1 | 107.2 | 97.5 | 121.0 | 126.0 | 109.1 | 114.4 | 129.9 |
| $R(\%)_{ICP\text{-}OES}$ | 87.2 | 90.2 | 89.0 | 88.9 | 89.7 | 88.3 | 87.0 | 84.6 | 91.0 | 90.3 |

the two series indicate the presence of a remarkable inhibitor effect of matrix. This effect decreases with increasing the concentration of strontium. The determination of Strontium in the synthetic brines presents many difficulties. These are related to interference phenomena caused by high concentrations of alkali and alkaline earth elements.

## 2. Interference phenomena

Thus, we propose in this part to identify the nature of interferences accompanying the determination of strontium by **FAAS**.

### 2.1. Spectral interferences

### 2.1.1. Spectral overlap of molecular bands

The formation of oxides and hydroxides and other probable molecular forms such as MgO, $Ca(OH)_2$, CaO, in a flame, can lead to errors during the determination of Strontium [14]. Indeed, these molecules may have molecular adsorption bands wide and absorb in domains near 460.7 nm. To verify the existence of this phenomenon, we measured the absorbance of solutions containing varying amounts of interfering elements only. This analysis has been performed at the wave length of the analytical ray of Strontium. The obtained results are summarized in Table II.

Except sodium, all interfering ions cause a matrix effect due to molecular bands superposition. This effect depends on interfering ion nature and concentration. As well as the interfering ion concentration rises the matrix effect increases. Calcium is considered to be the most perturbing element in the studied matrix.

### 2.1.2. Superposition rays

In order to demonstrate the existence of non-specific absorption of the various interfering, we recorded the emission spectra of hollow cathode lamps. These recordings were made in the vicinities of the analytical ray of Strontium. The obtained results are presented in Figure 1: (a), (b), (c), (d), (e).

The obtained results show that the intensity of relative emission is less than 0% at 460.7 nm for all interfering spectra. Consequently, it confirms the absence of this type of interference.

### 2.2. Vaporization interference

Vaporization interference existence is often verified by measuring the flow injection [15]. If any depression is noted, existence of the above mentioned interferences is confirmed. Thus solutions containing only one interfering component were prepared, flow injection measured and recapitulated in Figure 2. For all studied

**Table II:** Interference of bands superposing

| [Interfering] (g $L^{-1}$) | | 0.1 | 1 | 5 | 10 | 20 |
|---|---|---|---|---|---|---|
| Sodium | $[Sr^{2+}]_{measured}$ (mg/L) | 0.037 | 0.253 | 0.065 | 0.149 | 0.097 |
| Potassium | | 0.181 | 0.222 | 0.275 | 0.299 | 0.399 |
| Magnésium | | 0.137 | 0.112 | 0.129 | 0.378 | 0.503 |
| Calcium | | 0.165 | 0.282 | 0.477 | 0.626 | 0.851 |

concentrations flows injection is nearly constant, which affirms the absence of such interferences phenomena linked with considered interfering ions.

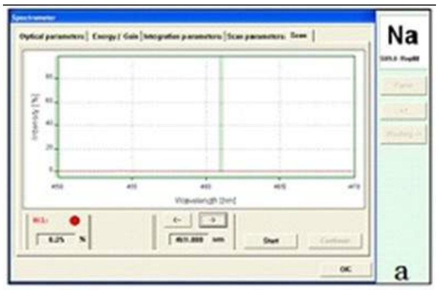
### 2.3. Chemical interferences

The main spectroscopic buffers allowing the elimination of chemical interference are salts of Lanthanum and Cesium [16]. The change in the nature of the flame well as the addition of these two buffers to the samples and standards, allow the identification of chemical interference. To identify this type of interference, we have prepared solutions containing only one interfering ion whose Strontium concentration is constant with varying concentrations of others elements.

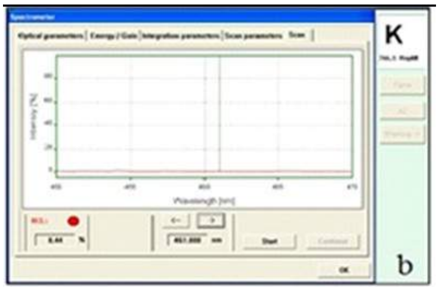
Subsequently, we measured the matrix recovery in eight different modes of analysis. Table III summarizes the analysis conditions for the eight modes mentioned.

These results have been valued by the appreciation criteria mentioned in the paragraph 2-4. A semi-logarithmic scale was used due to the important gap between the *ratio % Xi.*

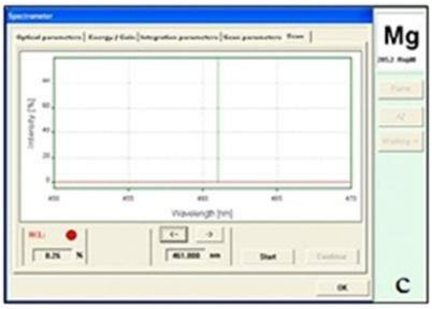
For each interfering ion, vertical lines traced to show approximately %Xi variation in case of natural brines **(**Figure 3**)**. Appreciation level in this issue (±5%) is represented by horizontal dash line.



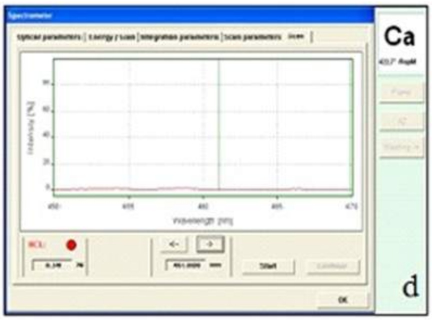
Emission spectrum of the sodium lamp



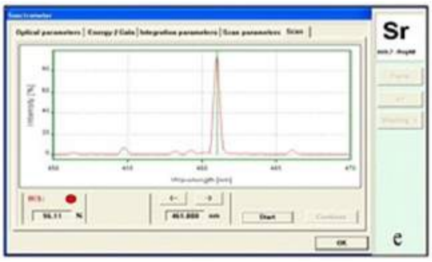
Emission spectrum of the potassium lamp



Emission spectrum of the magesium lamp



Emission spectrum of the calcium lamp



Emission spectrum of the strontium lamp

**Figure 1:** Lamp emission spectrum of the interfering

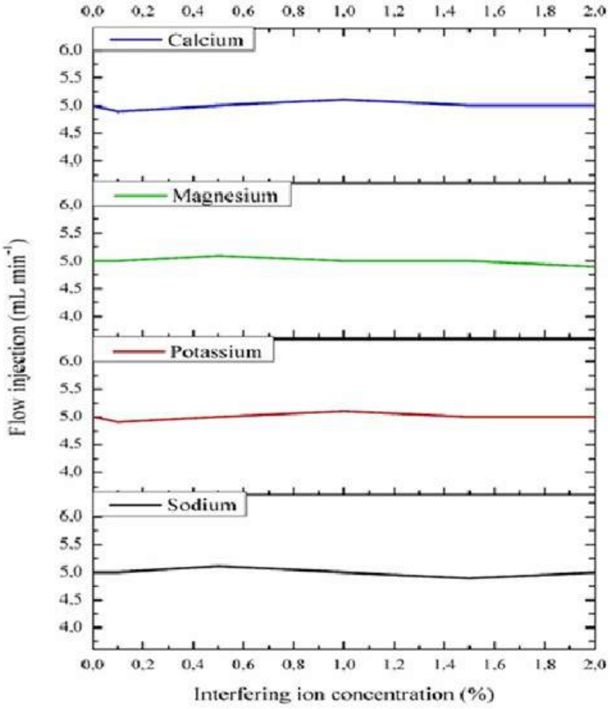


**Figure 2 :** Vaporization interference

**Table III:** Flame conditions

| Mode | Flame | Spectroscopic buffers |
|---|---|---|
| 1 | Air / $C_2H_2$ | - - |
| 2 | Air / $C_2H_2$ | Cesium (0.5%) |
| 3 | Air / $C_2H_2$ | Lanthanum (0.5%) |
| 4 | Air / $C_2H_2$ | Cesium (0.5%) and lanthanum (0.5%) |
| 5 | $N_2O$/ $C_2H_2$ | - - |
| 6 | $N_2O$/ $C_2H_2$ | Cesium (0.5%) |
| 7 | $N_2O$/ $C_2H_2$ | Lanthanum (0.5%) |
| 8 | $N_2O$/ $C_2H_2$ | Cesium (0.5%) and lanthanum (0.5%) |

The analysis results obtained have been reported in Figure 3.

In case of $N_2O/C_2H_2$ flame, ionization interferences are present for all interfering ions (Figure 3(b), (d), (f), (h)). Indeed, the switch air/ $C_2H_2$ flame to $N_2O/C_2H_2$ flame is accompanied by a significant enhancement in matrix recovery R%. This effect is attenuated with the addition of spectroscopic buffers. When talking about interference ionization, we expect a decrease of the measured concentration (inhibitor matrix effect), but in this case it is noted that it represents an exalting matrix effect. This is explained by the presence of interference de-ionization [17]. It is worth mentioning that the high concentration of calcium creates a very exalting matrix effect. In $N_2O/C_2H_2$, the matrix recovery reaches 410% **(**Figure 3(h)**)**. This observation is explained by the superposition of ionization interference and superposition of the bands. In addition, when using air/$C_2H_2$ flame, only the potassium element provides a matrix effect caused by ionization

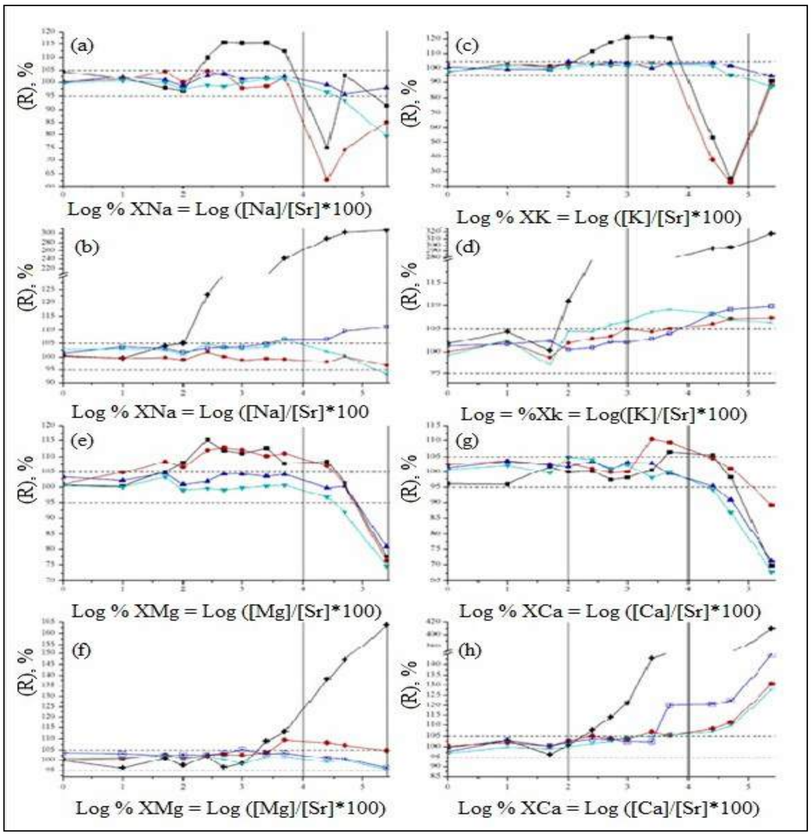


**Figure 3:** Chemical and ionization interferences

**Table IV:** Matrix effect correcting possibilities

| | Sodium | potassium | magnesium | Calcium |
|---|---|---|---|---|
| Mode 1 | - | - | - | - |
| Mode 2 | - | - | - | - |
| **Mode 3** | + | + | - | + |
| Mode 4 | - | - | - | + |
| Mode 5 | - | - | - | - |
| Mode 6 | + | - | - | - |
| Mode 7 | - | - | + | - |
| Mode 8 | - | - | + | - |

*+: possible correction*
*- : impossible correction*

interference. In absence of nebulization interferences, we observed depressions using air/$C_2H_2$ flame (Figure 3(a), (c), (e), (g)) and at high concentration of interfering ions, can be attributed to volatilization and dissociation interferences. This is confirmed by complete disappearance of these phenomena with $N_2O/C_2H_2$ flame or by using lanthanum with air/$C_2H_2$ flame, which eliminates interferences in sodium and potassium case.

## 3. Elimination of interference phenomena

### 3.1. Optimization of conditions for the determination of Strontium

Table IV summarizes the possibilities of correction of matrix effects according to the method of analysis used.

Considering the presented results we notice that the effect of Mg can be eliminated only in mode 7 and 8. However, these conditions do not eliminate the effects of other elements. Moreover, results attest that the best correction is achieved for mode 3. These operating conditions allow the simul-taneous elimination of the effects of Na, K and Ca. Indeed, by using the flame air/acetylene the ionization interference are minimized. Moreover, the interferences of dissociation, volatilization and band superposition, are eliminated by the addition of lanthanum. These finding show that the identification of the concentration of Strontium in synthetic brines, can be successfully achieved without Magnesium, using mode 3.

### 3.2. Application of the optimal conditions to synthetic brines without Magnesium

In order to verify previous findings, complementary experiments were conducted. Solutions containing the three interfering and variable Strontium content have been prepared. The determination is performed by mode 3. Table V summarizes the results of this study.

The results obtained show that the matrix recovery is ameliorated by adding 1% lanthanum. When adding 1.5%, matrix recovery responds to chosen appreciation criterion. This proves the elimination of interferences.

## CONCLUSIONS

Natural brines or similar synthetic solutions are very complex systems were traces elements such as strontium are hard to determine due to interferences phenomena. This work allowed the understanding of perturbation sources. So for each interfering ion ($Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) concentration field, interferences phenomena nature were indentified. It was established that the main perturbation are chemical, ionization and radiation types.

In the second part of this study, the effect of $Na^+$, $K^+$ and $Ca^{2+}$ is eliminated under established

**Table V:** Lanthanum quantities optimization

| | | $S1'_1$ | $S1'_2$ | $S1'_3$ | $S1'_4$ | $S1'_5$ | $S2'_1$ | $S2'_2$ | $S2'_3$ | $S2'_4$ | $S2'_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[Sr^{2+}]_{real}$ (mg/L) | | 10 | 30 | 50 | 75 | 100 | 10 | 30 | 50 | 75 | 100 |
| Mode 3 | R (%)<br>0.5 % $La^{3+}$ | 73.5 | 80.1 | 88.6 | 97.1 | 97.4 | 65.1 | 77.9 | 80.7 | 90.2 | 90.7 |
| | R (%)<br>1 % $La^{3+}$ | 85.8 | 89.9 | 92.8 | 100.9 | 96.2 | 80.6 | 82.2 | 85.8 | 91.5 | 94.5 |
| | R (%)<br>1.5 % $La^{3+}$ | 96.9 | 99.4 | 103.1 | 102.3 | 98.5 | 97.7 | 99.2 | 97.9 | 101.9 | 98.4 |

operating conditions (mode 3) which allow the analysis of brines containing these three components. Nevertheless, magnesium perturbation persists. Thus, the elimination of magnesium from the brines is essential but remains to be resolved.

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