

Analytical Methods

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Determination of trace elements in salt lake brines using inductively coupled plasma optical emission spectrometry after magnesium hydroxide precipitation

Liping Wang^{a, b}, Haijun Li^a, Yaping Dong^{a, *}, Jiaoyu Peng^{a, b}, Haitao Feng^a,
Wu Li^a

^aQinghai Institute of Salt Lakes, Chinese Academy of Sciences, 810008,

^bUniversity of Chinese Academy of Sciences, 100049, Beijing, China.

Abstract: A magnesium hydroxide coprecipitation method for the determination of trace elements for high-salt samples in salt lake brines by inductively coupled plasma optical emission spectrometry (ICP-OES) was developed. Some effects on the coprecipitation and analysis such as pH value and Na, Mg amount in primary brines have been thoroughly investigated and optimized. After adjusting the pH at 8.70 associated with sodium hydroxide, complicated matrix was removed from the high salt brines, and thus trace amounts of Al, Co, Cu, Fe, Mn, Ni, V, Zn were simultaneously coprecipitated and precisely determined. Recoveries of all the determined trace elements in the samples of both synthesized and real salt lake brines were more than 90%. The detection limit with the value of $0.62\mu\text{g}\cdot\text{L}^{-1}$ - $14.4\mu\text{g}\cdot\text{L}^{-1}$ was obtained and the precision was less than 3% relative standard deviation. The optimized method has been successfully applied for the determination of trace elements in the intercrystal brine mined from Dachaidan salt lake located in the Qaidam Basin, China.

Keywords: Magnesium hydroxide coprecipitation; Salt lake brines; ICP-OES; Trace elements;

*Corresponding author. E- mail: Dongyaping@hotmail.com

Phone: 86-971-6302023 Fax: 86-971-6310402

1. Introduction

Salt lake, a high salt system containing greater than 50 g/L saltness, was an excellent mineral source of lithium, potassium, magnesium, boron, bromine, iodine, rubidium, and cesium¹⁻⁵. Simultaneously, some trace metal cations such as Al, Co, Cu, Fe, Mn, Ni, V, Zn were coexisted in salt lake brines. These elements were difficult to be utilized, nevertheless, may affect the production engineering and the quality of products from salt lakes. Recently, the determination of these trace elements, in particular some metal ions with similar property to the mineral elements, for controlling the quality of primary products is of great importance. In addition, the accurate determination of these elements was essential for the geological scientists to reveal the formation and derivation mechanism of salt lakes.

Account for the high sensitivity, multi-elemental analysis⁶⁻⁸, inductively coupled plasma optical emission spectrometry has been widely used in the field of food, environment, medicine, and mineral for monitoring the trace elements⁹⁻¹³. However, the trace elements in salt lake brine samples are found difficultly determined without any

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3 pretreatments due to their high saline, complicated, and diverse matrix.
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5 High salt elemental ICP analysis by direct injection without dilution may
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7 damage the spectrometry and result in spectral interferences. To
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9 overcome these drawbacks, salt lake brine samples may be analyzed after
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11 hundreds of thousands of times dilution, moreover, dilution deviation was
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13 produced and the concentration of determined elements may be below the
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15 detection limits. Another drawback in the analysis of salt lake brines is
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17 the incapability of matrix matching method to eliminate the spectral
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19 interferences due to the changed main elements with the types, sampling
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21 points and exploited stages of salt lakes.
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29 In order to reduce the interference of high salt, many techniques have
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31 been investigated for the separation and preconcentration of sea water
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33 include solvent extraction¹⁴⁻¹⁸, ion exchange¹⁹⁻²⁵ and coprecipitation²⁶⁻²⁸.
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35 However, all the three approaches require detailed experiments of the
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37 preconcentration chemistries involved to avoid artifacts and foreign
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39 elements, which may produce some accuracy problems²⁸. These recent
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41 articles have suggested that magnesium hydroxide coprecipitation method
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43 was an effective technique to analyze multiple elements in sea water in
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45 capable of high sensitivity²⁸⁻³¹. Nevertheless it may require further
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47 investigation to apply the method to the salt lake brines, a higher salt and
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49 more complicated system. In this paper, magnesium hydroxide
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51 coprecipitation method has been selected to take full advantage of Mg
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4 source, which already presented in the determined samples as a major
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6 constitutes of salt lake brines. We present detail experiments that can
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8 remove the main salt matrix and coprecipitate the determined metal
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10 elements, focusing on the influence of pH, the levels of magnesium,
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12 sodium in the salt lake brines on the recovery and accuracy of measured
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14 elements. In addition, the accuracy, precision and detection limits of the
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16 method for the determination of eight metal elements have been
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18 investigated. Finally, the optimized method was used for the trace
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20 elemental analysis in actual salt lake brines, which confirms that the
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22 proposed method was accurate and reliable.
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28 **2. Experimental**

29 **2.1. Instrumentation**

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31 Trace elemental measurements were performed by the iCAP 6500 Duo
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33 ICP instrument (Thermo Fisher Scientific Inc. USA.) with the optimized
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35 operating conditions showed in Table 1. The analytical wavelengths were
36
37 preferred to avoid other element spectral interferences, which were also
38
39 given in Table 1. Proper pH adjustment was carried out by the PB-10
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41 pH-measurement (Sartorius. Germany.) Centrifugation of the samples
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43 after pH adjustment was performed by TG 16-WS Benchtop High-speed
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45 Centrifuge (Changsha Weierkang Xiangying Centrifuge Co., LTD. China)
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Table 1.

2.2. Standards and reagents

Deionized water (Resistivity: 18.25 M Ω ·cm) obtained from a water purification system (UPT - II - 20T, Chengdu Ultrapure Technology Co., Ltd. China.) was used in the preparation of all solutions. Multi elemental work standard solutions of the analytes (Al, Co, Cu, Fe, Mn, Ni, V and Zn) in 5% HNO₃ (v/v) were mixed and diluted progressively by the single element stock standard solution with the concentration of 100 mg·L⁻¹ (National Institute of Metrology, China).

Nitric acid of 1:1 volume ratio was diluted by concentrated nitric acid (65%, w/w) of guaranteed reagent quality (Aladdin Inc. China). Sodium hydroxide of 4% mass fraction was prepared by solid sodium hydroxide of guaranteed reagent (Aladdin Inc. China). Sodium chloride, potassium chloride, magnesium chloride and calcium carbonate used for the preparation of synthetic salt lake brine were spectral pure quality and supplied by Aladdin (Aladdin Inc. China).

2.3. Samples

Natural salt lake brine (intercrystal brine) was mined from the pore of saline-lake deposit in Dachaidan salt lake located in the Qaidam Basin, China. Synthetic salt lake brine containing 60 g·L⁻¹ Na, 30 g·L⁻¹ Mg, 5 g·L⁻¹ K and Ca was simulated the composition of natural brine by high pure reagents.

2.4 Sample pretreatment

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4 50 mL brines were measured accurately into a 100 mL beaker and were
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6 increased pH by 4% NaOH to a certain value with a consistent stirring.
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8 Stand the adjusted solution minutes without disturb until all the analytes
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10 were precipitated with $\text{Mg}(\text{OH})_2$. After that the sample was transferred
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12 into the centrifuge tube and centrifuged for 5 min at 8000 rpm. Then the
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14 clear solution was removed and the precipitation was decanted by the 4%
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16 NaOH solution and recentrifuged. This process was repeated 3 times to
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18 ensure that the main salt was removed. The resulting precipitation was
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20 dissolved in 5 mL 1:1 HNO_3 and transferred to a 50 mL volumetric flask.
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22 Then deionized water was used to fill the volumetric flask.
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28 29 2.5. Sample analysis

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31 Blank, standards and samples were prepared in 5% HNO_3 (v/v) to
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33 guarantee the same acidity. The elemental concentrations of standard
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35 solution were as follows: blank, 0.5, 1, 2, 5 $\text{mg}\cdot\text{L}^{-1}$ of Al, Co, Cu, Fe, Mn,
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37 Ni, V and Zn. The linear correlation coefficient of each standard curve
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39 was greater than 0.9999. In order to avoid contamination or memory
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41 effects blank, standards and samples were introduced to rinse the
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43 sampling system for at least 1 min before elemental detection. After that,
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45 each sample was determined 3 times and the final result was their average
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47 value.
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53 54 3. Results and discussion

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56 The Mg precipitation method has been proved to be one of the most
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4 effective methods to eliminate the interference of high salt for the
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6 determination of multi elements²⁸. An optimized and proper pH was the
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8 key factor to remove the main salt and ensure all the determined elements
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10 coprecipitated with Mg(OH)₂ in an excellent recovery. To adopt a proper
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12 pH for Mg(OH)₂ coprecipitation, experiments were carried out that
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14 manipulated (1) the remainder elements after different pH pretreatment,
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16 (2) the interference of determined trace elements with different Mg, (3)
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18 recoveries of determined elements with different pH values.
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24 3.1 Effect of pH on the removal of the main elements in salt lake brines.

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26 The spectral interference may still exists in the method of Mg(OH)₂
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28 coprecipitation due to the incomplete removal of high salts like Na, K, Ca,
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30 Mg resulting from the dissolution of precipitates. In order to investigate
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32 the effect of pH on the removal of the main elements, the brines have
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34 been adjusted to different pH (8.10, 8.30, 8.50, 8.70 and 8.90) with NaOH.
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36 The main elements (K, Na, Ca, Mg) were determined both in primary
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38 brines and samples after Mg(OH)₂ coprecipitation, which results were
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40 presented in Table 2 and Table 3 for synthetic and natural salt lake brines,
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42 respectively. From Table 2 and Table 3, we can draw a same conclusion.
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44 The concentration of Mg raises obviously with the improvement of pH
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46 due to the increase amount of Mg(OH)₂ precipitation. Thus other
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48 elements (K, Na, Ca) increase with the improvement of pH value because
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50 of the adsorption of Mg(OH)₂ precipitation. The maximum retention of K,
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4 Na, Ca was less than $40 \text{ mg}\cdot\text{L}^{-1}$, which spectral interference may be
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6 ignored compared with the high concentration of Mg.
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9 **Table 2.**

10 **Table 3.**

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13 3.2. Effect of Mg^{2+} amount in determined samples resulting from the
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15 dissolution of precipitates on the relative concentration of determined
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17 elements
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21 In this paper, potential interferences of Mg within the range of 0 to
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23 $5000 \text{ mg}\cdot\text{L}^{-1}$ on the relative concentration of determined elements (1.00
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25 $\text{mg}\cdot\text{L}^{-1}$) were investigated. It can be seen the data presented in Figure 1
26
27 that the massive Mg may reduce the spectral intensity of determined
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29 elements especially for Co, Cu, Fe, Ni. Additionally, to overcome the Mg
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31 spectra interferences for all eight determined elements, the concentration
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33 of Mg in determined samples should be less than $1000 \text{ mg}\cdot\text{L}^{-1}$. Therefore,
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35 corresponded to the results of Table 2 and 3, the pH value for $\text{Mg}(\text{OH})_2$
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37 coprecipitation method should be no more than 8.70.
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44 **Figure 1.**

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46 3.3. Effect of pH on the relative concentration of determined elements
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49 A satisfactory pH should be effectively selected to remove the majority
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51 medium and coprecipitate all the determined elements with the best
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53 recovery. In this paper, the analysis of natural brines added with 1.00
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55 $\text{mg}\cdot\text{L}^{-1}$ mixed standard solution was applied to reveal the effect of pH.
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4 Quantitative data of relative concentration of determined elements by
5 pretreatment of a different pH (8.10, 8.30, 8.50, 8.70 and 8.90) was
6 obtained and showed in Figure 2. As can be seen from Figure 2, the
7 increase of pH for $\text{Mg}(\text{OH})_2$ method improves recoveries of all the
8 elements until it increases to 8.70. When the value of pH was 8.70, a
9 complete coprecipitation of all the determined elements was achieved.
10 After that, recoveries of determined elements declined with the increase
11 of pH value for the spectra interference of Mg.
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24 According to the results of Table 2, 3, Figure 1, 2, a pH value of 8.70
25 was selected for the method to coprecipitate the elements with excellent
26 recoveries and avoid spectra interference of Mg, consequently.
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32 **Figure 2.**

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34 3.4. Effect of Na amount in primary brines on the relative concentration
35 of determined elements
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39 In many high salt systems such as seawater and salt lake brines, the
40 majority of matrix was sodium salt, which may not be involved in the
41 precipitation reaction. However, the main salt NaCl may affect the
42 process of determined elemental coprecipitation, furthermore, recoveries
43 of determined elements changes. In order to investigate the effect of Na
44 amount in primary brines on the relative concentration of determined
45 element, the primary brines contained 0 to $100\text{g}\cdot\text{L}^{-1}$ Na were prepared,
46 while other main elements were fixed ($\text{Mg } 30\text{ g}\cdot\text{L}^{-1}$, $\text{K } 5\text{ g}\cdot\text{L}^{-1}$, $\text{Ca } 5\text{ g}\cdot\text{L}^{-1}$).
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4 It was observed from Figure 3 that the sodium salt was beneficial for the
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6 complete coprecipitation of Co, Fe, Ni, V, Zn particularly, that may be
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8 due to the possible reduction of the solubility of these elements in a high
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10 ionic strength medium ²⁶. Be capable of coprecipitating all the eight
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12 elements with a satisfied high relative efficiency ($\geq 90\%$), the
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14 concentration of Na in primary brines should be more than $60\text{ g}\cdot\text{L}^{-1}$.
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19 **Figure 3.**

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21 3.5. Effect of Mg in primary brines amount on the relative concentration
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23 of determined elements
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26 The Mg in brines plays an important role on the formation of $\text{Mg}(\text{OH})_2$
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28 precipitation to coprecipitate the determined trace elements. In this paper,
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30 the influence of Mg amount in primary brines on the relative
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32 concentration of determined elements ($1.00\text{ mg}\cdot\text{L}^{-1}$) was studied between
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34 0 and $35\text{ g}\cdot\text{L}^{-1}$, where other elements were fixed (Na $60\text{ g}\cdot\text{L}^{-1}$, K $5\text{ g}\cdot\text{L}^{-1}$,
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36 Ca $5\text{ g}\cdot\text{L}^{-1}$). It was verified from Figure 4 that an obvious improvement of
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38 Co, Cu, Fe, Ni, V, Zn was obtained with a higher amount of Mg. The
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40 concentration of Al, Mn depends less on the Mg amount. With the
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42 objective of achieving ideal analytical results for all the 8 determined
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44 elements, more than $15\text{ g}\cdot\text{L}^{-1}$ Mg was required in primary brines.
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51 **Figure 4.**

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53 3.6. Detection limits of the method
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56 Detection limits (LODs) for each determined trace element, based on
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4 three times the standard deviation of the blank samples (synthetic brines)
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6 were obtained and given in Table 4 for this method. The blank samples
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8 with similar composition of actual brines were prepared by high pure or
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10 spectrum pure reagents and determined with 11 replicates. Detection
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12 limits of the determined elements were presented in Table 4 with a range
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14 of 0.62 to 14.45 $\mu\text{g}\cdot\text{L}^{-1}$. Compared with other elements, LOD values of Fe,
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16 Mn were poorer for the possible reasons of low spectral intensity or
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18 contamination originating from the reagents ⁶. Precision of the proposed
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20 method was also investigated in Table 4 based on the relative standard
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22 deviation of the actual samples (brines added with 10, 20 and 50 times
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24 higher than respective LODs), which were determined by 11 replicates. It
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26 is found that the RSD values for the determination of Al, Co, Cu, Fe, Mn,
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28 Ni, V, Zn by 10, 20 or 50 times higher than respective LODs in salt lake
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30 brines were generally less than 3% under the optimized conditions.
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32 Comparable satisfactory results of LODs and precision were obtained in
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34 this method for a much wide range of elements.
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44 **Table 4.**

45 3.7. Method application and accuracy

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48 In order to evaluate the validity of the proposed method, the optimized
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50 method was used to determinate the trace elements of Al, Co, Cu, Fe, Mn,
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52 Ni, V, Zn in actual samples (natural salt lake brines). In general the trace
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54 elemental concentrations in natural salt lake brines were showed in Table
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5 with a range from 0.0048 mg·L⁻¹ to 0.5364 mg·L⁻¹. As concentrations of all the determined elements were above the LOD level, it is evident that the proposed method met the demand for the determination of trace elements in salt brines. In order to estimate the accuracy of this method, elements in actual samples added with different concentrations of standard solutions were determined. The calculated recoveries of each element were showed in Table 5. Recoveries ranged from 91.5 % to 103.5 % for all elements were observed from Table 5, which suggested that the developed method for the determination of trace elements in salt lakes has an ideal accuracy. The determined concentrations as well as final sample concentrations of certified reference materials are showed in Table 6. Although there are relatively larger deviations on the concentrations of coexisting elements, excellent agreement was found for all investigated elements demonstrating the accuracy of the proposed method.

Table 5.

Table 6.

4. Conclusions

The main difficulty in the determination of trace elements in salt lakes is the high salt. To overcome this problem, Mg(OH)₂ coprecipitation method was applied to remove the high salt matrix and concentrate the determined elements. In this proposed method, Mg source in salt lakes

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4 was taken full advantage of without the need of other Mg agents, which
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6 reduce the foreign elemental interference and make the method
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8 economical. The procedure was carefully optimized and the effects of pH
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10 and Na, Mg in salt lake brines have been thoroughly investigated.
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12 Eventually, appropriate pH value of 8.70 was selected and the minimum
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14 amount of 60, 15 g·L⁻¹ for Na and Mg in primary brines was required for
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16 the determination of all the 8 elements.
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21 The detection limits, precision and accuracy of this method were also
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23 studied. The result suggested that, the developed method provided a
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25 sensitive, simple, accurate and economical technology to determine the
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27 trace elements of Al, Co, Cu, Fe, Mn, Ni, V, Zn in salt lake brines.
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29 Furthermore, it may be applied to the determination of other elements in
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31 high salt samples.
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Tables

Table 1 Operating conditions and analytical wavelengths of ICP-OES instrument

Instrument	iCAP 6500 Duo
RF generator power (W)	1150
Coolant gas flow rate (L·min ⁻¹)	15
Auxiliary gas flow rate (L·min ⁻¹)	0.5
Nebuliser gas flow rate (L·min ⁻¹)	0.55
Sample flow rate (L·min ⁻¹)	60
Observation mode	Auto
Analytical wavelengths (nm)	Al: 167.079, Co: 228.616, Cu: 204.379, Fe: 239.533, Mn: 257.610, Ni: 231.604, V: 292.402, Zn: 213.856.

Table 2 Changes of the main elements in synthetic brines with different pH pretreatment.

Element	Primary (g·L ⁻¹) ^a	After pretreatment (mg·L ⁻¹) ^a				
		pH=8.1	pH=8.3	pH=8.5	pH=8.7	pH=8.9
K	5±0.01	0.0234±0.0005	0.106±0.001	0.119±0.002	0.203±0.001	2.80±0.03
Na	60±0.12	3.21±0.004	7.77±0.03	18.8±0.05	20.0±0.04	39.0±0.06
Ca	5±0.01	0.240±0.0008	0.218±0.001	0.659±0.002	2.62±0.01	7.81±0.01
Mg	30±0.05	0.945±0.002	2.65±0.02	227±0.8	945±2	2090±4

^a Mean±2 S.D. (n=3).

Table 3 Changes of the main elements in natural brines with different pH pretreatment.

Element	Primary (g·L ⁻¹) ^a	After pretreatment (mg·L ⁻¹) ^a				
		pH=8.1	pH=8.3	pH=8.5	pH=8.7	pH=8.9
K	9.33±0.02	0.090±0.0004	0.127±0.001	0.148±0.001	0.236±0.002	0.553±0.004
Na	63.6±0.18	0.233±0.003	0.460±0.005	0.420±0.002	1.02±0.007	10.4±0.02
Ca	1.76±0.007	0.179±0.001	0.174±0.002	0.243±0.002	0.262±0.004	0.348±0.004
Mg	37.7±0.03	1.76±0.006	4.14±0.02	54.4±0.1	653±2	2419±5

^a Mean±2 S.D. (n=3).

Table 4 Limits of detection and precision of different elements

Element	LODs ($\mu\text{g}\cdot\text{L}^{-1}$)	RSD(%)		
		10 LODs	20 LODs	30 LODs
Al	3.24	2.64	2.50	1.02
Co	1.70	0.71	1.02	1.00
Cu	2.99	2.62	2.65	1.73
Fe	14.4	0.82	1.99	0.52
Mn	11.1	1.00	0.88	0.59
Ni	0.62	1.25	1.36	0.56
V	4.90	2.07	0.65	0.55
Zn	3.52	0.98	0.54	1.03

Table 5 Recoveries of different elements in natural salt lake brines

Element	Detected ($\text{mg}\cdot\text{L}^{-1}$) ^a	Added ($\text{mg}\cdot\text{L}^{-1}$) ^a	Found ($\text{mg}\cdot\text{L}^{-1}$) ^a	Recovery (%) ^b	Added ($\text{mg}\cdot\text{L}^{-1}$) ^a	Found ($\text{mg}\cdot\text{L}^{-1}$) ^a	Recovery (%) ^b
Al	0.313±0.01	0.5	0.802±0.03	97.8	1.0	1.286±0.02	97.3
Co	0.0048±0.0004	0.01	0.0141±0.001	93.0	0.02	0.0232±0.003	92.0
Cu	0.0138±0.001	0.02	0.0345±0.01	103.5	0.05	0.0624±0.006	97.2
Fe	0.356±0.02	0.50	0.843±0.02	97.4	1.0	1.315±0.05	95.9
Mn	0.536±0.05	0.50	1.03±0.08	98.8	1.0	1.525±0.02	98.9
Ni	0.0062±0.0004	0.01	0.0154±0.001	92.0	0.02	0.0245±0.0 3	91.5
V	0.058±0.007	0.10	0.150±0.02	92.0	0.20	0.243±0.02	92.5
Zn	0.0675±0.001	0.10	0.164±0.01	96.5	0.20	0.253±0.01	92.8

^a Mean±2 S.D. (n=3).^b $100 \times [(\text{Found} - \text{Detected})/\text{Added}]$.

Table 6 Results for the application of the proposed procedure on the certified reference

material

Element	Certified values (mg·L ⁻¹)	Measured concentrations (mg·L ⁻¹) ^a
Al	0.20	0.1926±0.004
Co	0.01	0.0094±0.001
Cu	0.02	0.0189±0.002
Fe	0.50	0.4927±0.03
Mn	0.50	0.5053±0.05
Ni	0.01	0.0093±0.0006
V	0.05	0.048±0.005
Zn	0.05	0.047±0.002

^a Mean±2 S.D. (n=3).

Figures

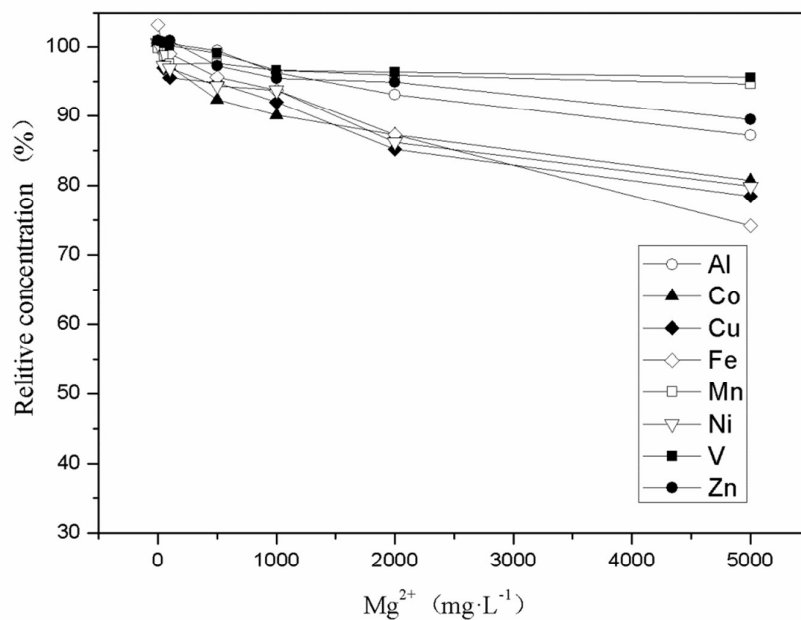


Figure 1. Effect of Mg^{2+} amount in determined samples on the relative concentration of determined elements

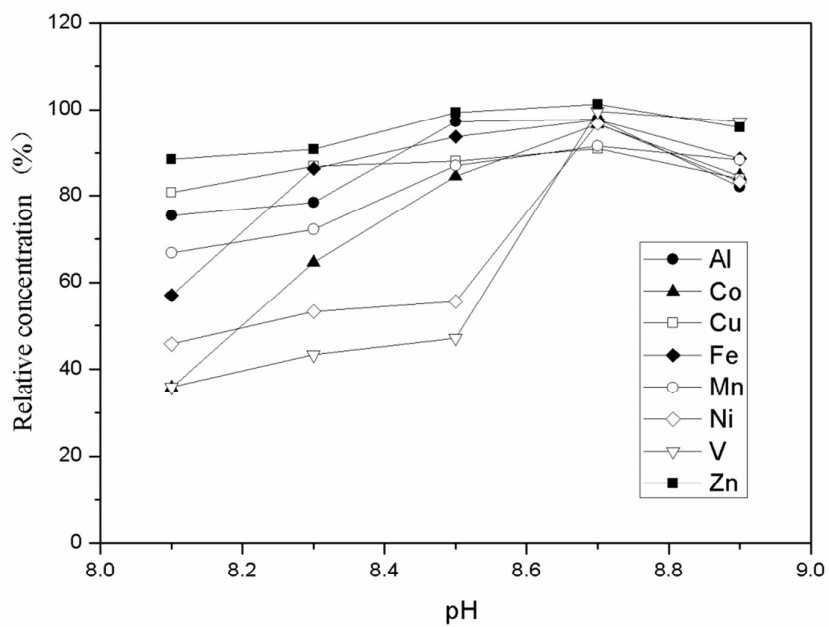


Figure 2. Effect of pH on the relative concentration of determined elements in natural brines.

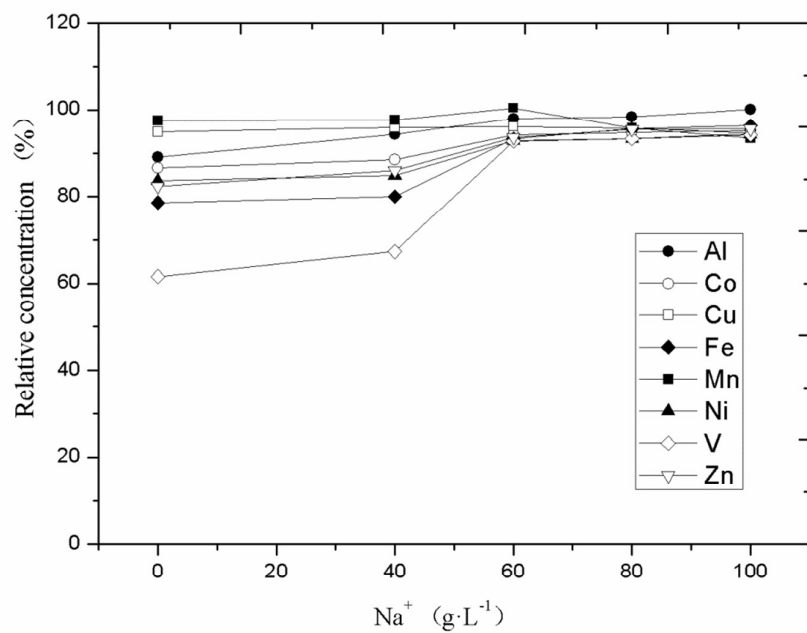


Figure 3. Effect of Na amount in primary brines on the relative concentration of determined elements.

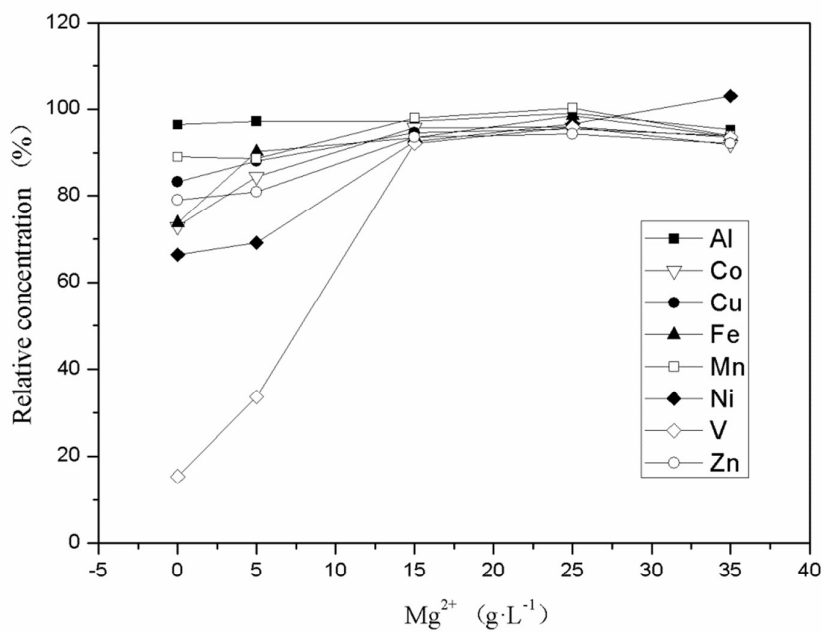


Figure 4. Effect of Mg in primary brines amount on the relative concentration of determined elements.