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Experimental design in the analysis of interferential effects for the determination of Sr in high Ca/Sr ratio brine by inductively coupled plasma atomic emission spectroscopy technique

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The ICP-AES technique and experimental design were employed to precisely determine the content of strontium in high Ca/Sr ratio oil field brine of Qaidam basin (Qinghai province, western China). From the statistical analysis using six factor factorial, it was found that Ca²⁺ is the significant interfering element for the recovery of strontium. Accurate strontium content was derived by eliminating the interference contribution according to the influencing model. The experimental results indicate that, under optimal conditions, the ICP-AES method for strontium determination has low LOD and LOQ, and the precision and accuracy are good with the relatively standard deviation below 1% and recovery between 98.0% ~ 105.0%.

Keywords: experimental design; strontium; high Ca/Sr ratio brine; inductively coupled plasma optical emission spectrometry

1. Introduction

Due to great reserves of solid strontium ore in China (the total strontium mineral reserve of China is the largest of the world, and China is the world's leading producer of strontium with more than two thirds of the global market share) and wide applications of strontium in electronics, ceramics, magnetics and metallurgy [1–3], the solid ore of strontium resources are of great interest and have been continuously exploited in China. However, a recent geology survey indicated that the strontium reserves in solid ore are greatly reduced, owing to many years of exploitation, which makes further exploitation costful and laborious; therefore it is imperative to find a new strontium resource to meet the requirements of the international market. Recently, it has been found that the concentration of strontium in the underground brine resources in the Qaidam basin (an arid basin located in central Qinghai province, western China; salt marshes occupy most of the area), especially in oil-field waters, is much higher than in most other brines. An example is the Nanyishan oil-field brine of Qaidam basin. Nanyishan is located in the

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western part of Qaidam basin between $90^{\circ}07'$ to $92^{\circ}10'$ north latitude and between $37^{\circ}50'$ to $38^{\circ}35'$ east longitude. Here the average strontium concentration reaches 5364 mg L^{-1} , which greatly exceeds the minimum concentration for industrial exploitation [4]. These brines therefore have a great potential for large-scale industrial exploitation. In order to extract strontium from the brines, precise determination of the strontium content is the vital first step. As part of our ongoing efforts to extract Cs, Rb and Sr from the salt lake brines, we thus concentrated our efforts on developing an efficient method to precisely determine the content of strontium.

The conventional methods of determination of the strontium content are chemical titration [5,6], Sr²⁺-selective electrode [7,8], spectrophotometry [9,10], atomic absorption spectrometry (AAS) [11,12], ion chromatography [13,14], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [15,16] and X-ray fluorescence spectrometry (XRF) [17–19]. Our several experiments indicated that chemical titration, Sr²⁺-selective electrode, spectrophotometry, atomic absorption spectrometry (AAS) and ion chromatography are all inefficient for determination of strontium in our system. It has to be understood that the strontium rich brine mentioned in this paper is the high-salinity calcium chloride type in the Sulin classification [20], and the Ca/Sr ratio is high (between 2.5 and 126) [4]. Belonging to the same family, calcium is similar to strontium in chemical and physical behaviour and is the biggest interference element for strontium determination in each analytical method [17,20]. Taking this into account, ICP-AES may be a possible method to solve the problem, for it is reported that ICP-AES could be employed to analyse strontium (in low Ca/Sr ratio) with a low level of interference, and that the precision and recovery of standard addition are satisfactory [21]. Thus, we explored its application in determining the concentration of strontium in high Ca/Sr ratio samples by running the experimental design to eliminate the interferences. In this study, we carried out the research using the following procedure: (1) using the experimental design to determine the significant interferential element(s); (2) investigating the quantitative contribution of the interfering element(s); (3) modelling the interfering effect by setting up an empirical equation; (4) calculating the accurate strontium content by eliminating the quantitative contribution of the interfering element. Experiments indicated that the method is simple and accurate, and the results are satisfactory.

2. Experimental

2.1 Apparatus and operating conditions

The measurements were carried out on an IRIS Intrepid II XSP inductively coupled plasma optical emission spectrometer (Thermo, Waltham, MA, USA). The analytical line and operation parameters were optimised and are listed in Table 1. The design, analysis of the experiments, and the fitting, have been carried out with MINITAB Version 15 for Windows [22].

2.2 Standard solution and reagents

All chemicals used in the experiment were of analytical grade and double distilled water (abbreviated as ddH_2O) was used throughout this work. Strontium stock solution (1.0 g L^{-1}) was prepared by dissolving SrCO₃ in an appropriate amount of high purity hydrochloric acid and then diluted with ddH_2O . Calcium and Li stock solutions (5.0 and

| BE | 1150 |
|------------------------------------|--------------------|
| KF generator power (w) | 1150 |
| Frequency of RF generator (MHz) | 27.12 |
| Auxiliary gas flow $(L \min^{-1})$ | 0.5 |
| Analysis pump rate (rpm) | 130 |
| Solution(s) uptake $(mL min^{-1})$ | 2.4 |
| Nebuliser gas pressure (PSI) | 20 |
| Integration time (sec) | 5 |
| Analytical wavelength (nm) | Sr(II) 346.446(97) |
| | Y(II) 371.030(90) |
| | |

Table 1. Operation parameters of Intrepid II XSP ICP-AES.

 1.0 g L^{-1}) were prepared from their carbonates. Yttrium and Mg stock solutions (both are 1.0 g L^{-1}) were prepared from Y₂O₃ and MgO respectively, by dissolving them in high purity hydrochloric acid and then diluting with ddH₂O. Boron stock solution (1.0 g L^{-1} as B) was prepared by dissolving H₃BO₃ in ddH₂O. Potassium and Na stock solutions (both are 1.0 g L^{-1}) were prepared by dissolving KCl and NaCl in ddH₂O. Working standard solutions were prepared by stepwise dilution of their stock solutions with ddH₂O.

Yttrium standard solution $(20 \,\mu g \,m L^{-1})$ was used as internal standard reference.

2.3 General procedure

A series of working standard solutions containing strontium $(0-100 \,\mu g \,m L^{-1})$ were prepared by diluting the strontium stock solution with ddH₂O, to which no hydrochloric acid was added. Under optimised conditions, each solution was measured three times. The standard curve was generated automatically by the spectrometer.

Natural brine samples were collected and filtered by qualitative filter paper (pore size is $30 \,\mu\text{m}$). The filtrates were diluted to avoid the damages to the apparatus caused by high salinity, and then subjected to the analytical procedure described above.

2.4 Experimental design

Experimental design, or design of experiments (DOE), is a systematic approach in which the investigator manipulates a variable(s) under strict controlled conditions and examines whether changes occur in a second variable(s). The method has very broad application for determining factors that are most important in achieving useful goals in a process [23–27]. It considers all the variables simultaneously and predicts response over a wide range of values [28]. Under the designer's control, these factors are systematic varied over two or more levels. Experiments are then conducted, according to an orthogonal array to show the effects of each potential primary factor. The results are statistically analysed to reveal which of the factors are most effective in reaching our objective and how these factors should be eliminated. In the present work we apply the method of experimental design to evaluate which of the coexisting interferential ions has a significant influence on the determination of strontium.

According to a previous study [29], the main ions in the oil-field water of Nanyishan are Ca^{2+} , K^+ , Na^+ , B, NH_4^+ , Sr^{2+} , Mg^{2+} , Li^+ , Cl^- and SO_4^{2-} . Among them, Ca^{2+} , K^+ ,

| | K^+ | Na ⁺ | Ca ²⁺ | Mg^{2+} | Li ⁺ | В |
|---|-------|-----------------|------------------|-----------|-----------------|------|
| $Max(C_i)/Min(C_{Sr})$ | 6.84 | 18.18 | 126.01 | 3.36 | 1.41 | 8.32 |
| C _{i(High level)} /C _{Sr(addition)} | 10 | 20 | 150 | 4 | 2 | 10 |
| High level ($\mu g m L^{-1}$) | 100 | 200 | 1500 | 40 | 20 | 100 |
| Low level $(\mu g m L^{-1})$ | 0 | 0 | 0 | 0 | 0 | 0 |

Table 2. Interferential factors and level settings for the experimental design.

Notes: C_i : Concentration of the interferential ion; C_{Sr} : concentration of strontium ion. Max(C_i): Maximum concentration of the interferential ion in previous survey [4]. Min(C_{Sr}): Minimum concentration of strontium ion in previous survey.

 $C_{i(High level)}/C_{Sr(addition)}$ ratio is the upper rounding of $Max(C_i)/Min(C_{Sr})$ value.

Sr²⁺ found Standard Run Ca^{2+} K^+ Mg^{2+} Li⁺ Na⁺ $(\mu g m L^{-1})$ order order В 10.33 9.871 9.866 9.885 10.46 9.912 9.952 10.39 9.892 10.46 10.17 10.58 10.67 10.06 10.65 10.74

Table 3. Factors and levels of the experimental design and Sr^{2+} recovery.

Na⁺, B, Mg²⁺ and Li⁺ are more likely to effect the precise determination of Sr. Therefore we chose these six coexisting ions as the interferential factors. Considering the extreme conditions, the C_i/C_{Sr} ratio was used to set the experimental levels, of which the $Min(C_i)/Max(C_{Sr})$ ratio is the low level setting basis and the $Max(C_i)/Min(C_{Sr})$ is that of the high level. To be simple and convenient, the strontium additions were all 10 µg mL⁻¹ in this experiment, and the low levels of all the interferential ion concentrations were set as 0. Each high level of them was the strontium concentration (10 µg mL⁻¹) multiplies its corresponding $C_{i(High level)}/C_{Sr(addition)}$ value. The detailed interferential factors and level settings are listed in Table 2.

Owing to the high number of experiments for a full two-level factorial design (2^6) , we run a 2^{6-2} factorial design in order to perform a lower number of experiments. Table 3 shows the experimental design matrix and the recovery of strontium derived from each run. The sequence for the experimental work was randomly established to minimise the effect of possible uncontrolled variable(s).

| HCl addition (mL) | Rep1 (Cts/S) | Rep2 (Cts/S) | Rep3 (Cts/S) | Average intensity (Cts/S) | SD | RSD (%) |
|----------------------|-----------------|-----------------|-----------------|---------------------------|--------|------------|
| 0 | 0.1180 | 0.1171 | 0.1175 | 0.1175 | 0.0005 | 0.43 |
| 1 | 0.1178 | 0.1188 | 0.1192 | 0.1186 | 0.0007 | 0.59 |
| 2 | 0.1191 | 0.1190 | 0.1191 | 0.1191 | 0.0001 | 0.08 |
| 3 | 0.1186 | 0.1190 | 0.1180 | 0.1185 | 0.0005 | 0.42 |
| 5 | 0.1202 | 0.1203 | 0.1202 | 0.1202 | 0.0001 | 0.08 |
| 10 | 0.1192 | 0.1196 | 0.1194 | 0.1194 | 0.0002 | 0.17 |
| 20 | 0.1194 | 0.1193 | 0.1187 | 0.1191 | 0.0004 | 0.34 |

Table 4. Effects of HCl addition on the measurement of Sr^{2+} .

Notes: Cts/S = Counts/Second, is a measure of the signal intensity, indicates the amount of photons reached the detector per second.

3. Results and discussion

3.1 Effect of acidity

The concentration of strontium in each solution of the series was $5 \mu g m L^{-1}$. To each solution, high purity concentrated hydrochloric acid ranging from 0 to 20 mL was added, respectively (concentrations of hydrochloric acid solutions are from 0 to $5 m ol L^{-1}$). After being diluted to the mark with ddH₂O, they were examined on the spectrometer. Measured results are given as signal intensity values and are presented in Table 4.

From the results, the average intensity values of each measurement are basically identical with the standard deviation (SD) of 0.0008, which is in accordance with the SD of a single measurement. The total relative standard deviation (RSD) is 0.30%, together with the RSD of a single measurement, is less than the allowable deviation (1%) of the instrument. So it can be concluded that the concentration of hydrochloric acid $(0-5 \text{ mol } L^{-1})$ has no significant impact to the determination of strontium.

Studies on the effects of acidity were carried out prior to the optimisation of operating conditions. Thus, hydrochloric acid was not added in the tests of strontium determination.

3.2 Coexisting ions interference

3.2.1 Investigation of interferential ions by experimental design

Significance of the effects was checked by analysis of the variance (ANOVA) using *P*-value significance levels. This value expresses how much the probability of a factor is due to random errors. A factor is considered significant if *P* is less than 5%. Results of Table 5 demonstrated that except Ca²⁺, the other five factors (K⁺, Na⁺, Mg²⁺, Li⁺ and B) and their interactions were statistically insignificant (*P*>0.05), while blocks were not effective (*P*>0.05). The calculated results are shown in Table 5.

Interaction is present when the response at a factor level depends upon the level(s) of other factors, which means the factors may affect the response interactively and not in an independent way. Calculated results in Table 5 indicate that the interactions between those pair of ions are not statistically significant (P > 0.05), so it can be concluded that the main coexisting ions have no significant synergistic effect on the determination of strontium. This is a reasonable result, because in the plasma flame, all chemicals were atomised and ionised; therefore chemical interference was mostly eliminated. In this system, the full frame spectral scanning indicates that the spectral overlap interferences are also negligible.

| Term | Effect | Coeff. | SE Coeff. | Т | Р |
|---------------------------------|---------|---------|-----------|--------|-------|
| Constant | | 10.243 | 0.03839 | 266.82 | 0 |
| Block | | -0.0739 | 0.05804 | -1.27 | 0.293 |
| K^+ | 0.0186 | 0.0093 | 0.04104 | 0.23 | 0.836 |
| Na ⁺ | 0.0273 | 0.0136 | 0.03839 | 0.35 | 0.746 |
| Ca^{2+} | 0.5471 | 0.2735 | 0.04104 | 6.67 | 0.007 |
| Mg^{2+} | -0.0185 | -0.0092 | 0.03839 | -0.24 | 0.825 |
| Li [∓] | 0.0439 | 0.0219 | 0.04812 | 0.46 | 0.679 |
| В | 0.0407 | 0.0203 | 0.04104 | 0.5 | 0.654 |
| $K^+ \times Na^+$ | 0.1047 | 0.0523 | 0.04176 | 1.25 | 0.429 |
| $K^+ \times Ca^{2+}$ | -0.0055 | -0.0027 | 0.03812 | -0.07 | 0.954 |
| $K^+ \times Mg^{2+}$ | -0.0435 | -0.0217 | 0.04176 | -0.52 | 0.695 |
| $K^+ \times Li^+$ | -0.0497 | -0.0249 | 0.04176 | -0.60 | 0.658 |
| $\mathrm{K}^+ 	imes \mathrm{B}$ | 0.0357 | 0.0179 | 0.03812 | 0.47 | 0.721 |
| $Na^+ \times Ca^{2+}$ | -0.0497 | -0.0249 | 0.04176 | -0.60 | 0.658 |
| $Na^+ \times Mg^{2+}$ | -0.0237 | -0.0119 | 0.03812 | -0.31 | 0.808 |
| $Na^+ \times Li^+$ | -0.0055 | -0.0027 | 0.03812 | -0.07 | 0.954 |
| $Na^+ \times B$ | -0.0390 | -0.0195 | 0.04176 | -0.47 | 0.722 |
| $Ca^{2+} \times Mg^{2+}$ | -0.0390 | -0.0195 | 0.02961 | -0.66 | 0.577 |
| $Ca^{2+} \times Li^{+}$ | 0.1047 | 0.0523 | 0.02961 | 1.77 | 0.219 |
| $Ca^{2+} \times B$ | -0.0237 | -0.0119 | 0.02703 | -0.44 | 0.703 |
| $Mg^{2+} \times Li^+$ | 0.0357 | 0.0179 | 0.02703 | 0.66 | 0.576 |
| $Mg^{2+} \times B$ | -0.0497 | -0.0249 | 0.02961 | -0.84 | 0.490 |
| $Li^{+} \times B$ | -0.0435 | -0.0217 | 0.02961 | -0.73 | 0.539 |

Table 5. Estimated effects and coefficients for found strontium (coded units).

Notes: Coeff. = Regression coefficients; SE Coeff. = Standard errors for regression coefficients; T = T value; P = Probability level.

Calcium has significant interference for the measurement. It can be argued that the background continuum emission contributed by calcium cannot be completely eliminated by the background correction.

The evaluation of the effect of each interference ion on the recovery of strontium may also be verified in Figure 1. The Pareto chart (top of the figure) gives the relative importance of the individual and interaction effects. Student's t-test was performed to determine whether the calculated effects were significantly different from zero and these values for each effect are shown in the Pareto chart by horizontal columns. All the standardised effects were in absolute values (to verify which were positives and negatives, see the bottom graph of Figure 1). For 95% confidence level and 3 degrees of freedom, the Student's t-value for two-sided test is equal to 0.1409. The vertical dashed line indicates minimum statistically significant effect magnitudes for a 95% confidence level. Horizontal column lengths are proportional to Student's t-test values for each effect. Any effect or interaction that exceeds vertical line is considered significant. The normal probability plot displayed in Figure 1 confirmed the significance of the factors. The normal probability method is especially useful for analysing the effects in an experiment without replicates. It illustrates the statistical significance and magnitude of standardised effects. The points in this plot should generally form a straight line if the residuals are normally distributed. If the points on the plot depart from a straight line, the normality assumption may be invalid, which denotes that the residuals probably are significant and are obviously not related to experimental random errors. In this plot, all the points deviated from the oblique line on the probability plot, have the same trends as those introduced as significant factors



Figure 1. Pareto chart (top) and normal probability plot (bottom, the vertical dashed line indicates the 95% confidence interval) for the standardised effects and related interactions at 95% confidence interval.

by Pareto chart. Analysing the graphs of Figure 1 and the values of Table 5, it can be inferred that the Ca^{2+} is the significant variable of the process.

3.2.2 Setting interferential model by regression analysis

As the calcium ion was discovered as the effective factor for the recovery of strontium, a regression analysis was performed to investigate the interferential model, which can be expressed as:

$$[\mathrm{Sr}^{2+}]^* = 9.951 + 0.000389 \times [\mathrm{Ca}^{2+}] \tag{1}$$

| Source | DF | SS | MS | F | Р |
|----------------|----|--------|--------|---------|-------|
| Regression | 1 | 1.1615 | 1.1615 | 3209.25 | 0.000 |
| Residual error | 25 | 0.0090 | 0.0004 | | |
| Lack of fit | 7 | 0.0053 | 0.0008 | 3.67 | 0.012 |
| Pure error | 18 | 0.0037 | 0.0002 | | |
| Total | 26 | 1.1706 | | | |

Table 6. Analysis of variance for the regression model.

Notes: DF = Degrees of freedom; SS = Sum of squares; MS = Mean squares; F = F ratio; P = Probability level.

where P equals 0.000, and $[Sr^{2+}]^*$ represents the apparent strontium concentration while the actual concentration was $10 \,\mu g \,m L^{-1}$. Although ANOVA test results indicated that the regression is meaningful as the P value is less than 0.05, the fitting is not very good $(R^2 = 0.854)$ in this factorial experiment, so another experiment specified on the effects of calcium was carried out to investigate its quantitative interference.

A series of the solutions were prepared (strontium concentrations are all $10 \,\mu g \,m L^{-1}$, and calcium concentrations are 0, 100, 200, 400, 600, 800, 1000, 1200 and $1500 \,\mu g \,m L^{-1}$, respectively), and each solution was examined on the spectrometer three times. Measured results are presented as found strontium ($\mu g \,m L^{-1}$), and the regression analysis suggests that an appropriate model can be expressed as:

$$[\mathrm{Sr}^{2+}]^* = 9.995 + 0.000423 \times [\mathrm{Ca}^{2+}]$$
(2)

where *P* equals 0.000. As listed in Table 6, the ANOVA test results suggest that the regression is also meaningful (P < 0.05) although the lack of fit is significant (P < 0.05), and goodness-of-fit for this model was evaluated by the coefficient determination. In this calcium interferential experiment, the fitting is very well ($R^2 = 0.992$) and only 0.8% of total variance was not explained by the model. The adjusted regression coefficient equals the regression coefficient, and is also an indication for high significance of the proposed model.

The residuals should also be examined for normal distribution. Anderson-Darling test is one of the most powerful statistics to assess whether a sample comes from a normal distribution, and used to determine if data follow a normal distribution. Figure 2 shows the normal probability plot of residual values obtained by the Anderson-Darling test. A quantitative measure for reporting the result of the Anderson-Darling normality test is the *p*-value. A small *p*-value is an indication that the null hypothesis is false. It could be seen that the experimental points were reasonably aligned suggesting normal distribution. The *P*-value for test (0.919 > 0.05) denotes that the null hypothesis could not be rejected and it concludes that residuals follow normal distribution. All these verify the fact that the model does not violate regression assumptions. Since the strontium addition for each solution was $10 \,\mu g \, m L^{-1}$, the correlation between actual strontium concentration and interfering calcium concentration can be expressed as $[Sr^{2+}]^* = 0.000423 \times [Ca^{2+}]$.

Generally in the Sulin classification, calcium chloride is the major salt in calcium chloride type brine. The content of calcium can be determined easily by conventional EDTA titration method. As the reported calcium contents are the summation of calcium and strontium, the correlation between actual strontium concentration and titrated calcium concentration can be expressed as $[Sr^{2+}]^* = (0.000423/1.000423) \times [Ca^{2+}]$.



Figure 2. Normal probability plot for the regression residuals.

3.3 Detection and quantification limit

Under optimised conditions, the blank was measured 10 times to obtain a standard deviation $(0.0051 \,\mu\text{g mL}^{-1})$. The limit of detection (LOD), calculated as three times of the standard deviation, was $0.015 \,\mu\text{g mL}^{-1}$. The limit of quantitation (LOQ), calculated as 10 times of the standard deviation, was $0.051 \,\mu\text{g mL}^{-1}$ accordingly [30,31].

3.4 Precision and accuracy

The precision was estimated as the relative standard deviation (RSD) in repetitive measurements for a standard solution containing $30 \,\mu g \,m L^{-1}$ of strontium for 10 times. The standard deviation (SD) is $0.0719 \,\mu g \,m L^{-1}$, and the RSD is 0.24%.

3.5 Validation and applications

In the absence of a reference sample which can match the brine matrix and has certified strontium content, the accuracy of the method was checked for strontium recovery by analysing the natural samples and synthetic mixtures, and the results are shown in Table 7. The found strontium concentrations were slightly higher than the certified values, but they were in good agreement after using the correlation to eliminate the interference of calcium. So it can be concluded that this method is suitable for the determination of strontium in such high Ca/Sr ration system.

4. Conclusions

In summary, we use ICP-AES technique and the experimental design to precisely determine the content of Strontium in high Ca/Sr ratio oil field brine of the Qaidam basin. From the statistical analysis using six factor factorial, it was found that Ca^{2+} is the

| Case | Sr^{2+} detected by ICP-AES (µg mL ⁻¹) | Ca^{2+} found by EDTA titration (g L ⁻¹) | Actual Sr^{2+} conc. ($\mu g m L^{-1}$) | Recovery (%) |
|----------|--|--|--|-----------------|
| Sample 1 | 180.75 | _ | 180.75 | 98.0 |
| Sample 2 | 116.46 | _ | 116.46 | 103.5 |
| Sample 7 | 55.29 | _ | 55.29 | 102.5 |
| Sample 3 | 67.24 | 5.44 | 64.94 | 104.3 |
| Sample 4 | 11.94 | 2.09 | 11.05 | 102.2 |
| Sample 5 | 171.31 | 16.41 | 164.37 | 101.8 |
| Sample 6 | 210.19 | 27.38 | 198.61 | 104.2 |
| Sample 7 | 55.29 | 0.55 | 55.06 | 102.5 |
| Sample 8 | 33.47 | 3.11 | 32.16 | 102.4 |
| Sample 9 | 12.51 | 1.55 | 11.86 | 101.3 |

Table 7. Analytical results of sample and recovery test.

Note: Actual Sr^{2+} concentration was calculated by employing the regression model to eliminate the contribution of calcium.

significant interfering element for the recovery of strontium, and its quantitative contribution can be eliminated by the empirical formula. It is clear that the method is an economic and effective method for the interference investigation of strontium determination in high Ca/Sr concentration ratio system.

The experimental results indicate that, under optimal conditions, the ICP-AES method for strontium determination has low LOD and LOQ, and the precision and accuracy are good with the RSD below 1% and recovery between $98.0\% \sim 105.0\%$. The method is fairly rapid and involves no separation or other operation of the analyte. It is an easy and convienient method beside ICP-MS and the method has been successfully applied for quantitative analysis of strontium in the oil field brine of the Qaidam basin.

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