

## Simultaneous Determination of Ba and Sr in Oilfield Produced Water by ICP-AES

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**Abstract.** Oil is an important non-renewable resource for the world. The application of alkaline-surfactant-polymer flooding has successfully enhanced the oil recovery in Chinese oilfields. The oilfield produced water is the layer water that came from the oil well along with the oil in the alkaline-surfactant-polymer flooding. Thus, the treatment process of oilfield produced water to meet the reinjection standard is an important issue for oil production and environment. The component of the oilfield produced water complexly, and the salinity high is one of the characteristics of the oilfield produced water. The main reason is the existence of a large number of ions that easy to scaling (such as Ba<sup>2+</sup>, Sr<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>) and they are easy to form carbonate precipitation (such as BaCO<sub>3</sub>, SrCO<sub>3</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub>) in the production pipelines. Therefore, the determination of Ba and Sr in oilfield produced water is an essential step for water quality analysis of oilfield produced water. In this paper, a method for the simultaneous determination of Ba and Sr in oilfield produced water by ICP-AES was established. The working conditions of the apparatuses were optimized. The detection limit of Ba and Sr was 0.066 and 0.051. The relative standard deviation of Ba and Sr was 0.43% and 0.68%. The recovery within standard solution of Ba and Sr was 96.6% and 103.7%.

### Introduction

Oil is a value non-renewable resource for the world. Exploration rate has developed rapidly for the enhanced oil recovery. A large amount of water as the injected water is necessary to get the oil out for no matter water flooding oil recovery or alkaline-surfactant-polymer flooding oil recovery [1]. The oilfield produced water is the layer water that fetched out the oil well along with the oil in the oil production. The oilfield produced water as the reinjection water would be injected into layer again to supply the layer energy after treatment in wastewater treatment station [2,3]. The process of oil produced water reinjection into layer not only solves the injection water source issue, but also protects the environment. Thus, the treatment process of oilfield produced water to meet the reinjection standard is an important issue for oil production [4,5]. In addition, the oilfield produced water also is the dynamic force and supporting substance for hydrocarbon migration and oil and gas formation. Its chemical composition tends to reflect some characteristics of oil and gas [6,7]. Therefore, the research on the oilfield produced water and its geochemistry is significant for analyzing oil and gas formation, exploration and development the oil and gas, and hydrocarbon prospect evaluation and so on.

The composition of the oilfield produced water is very complicated, including different varieties as follows, the oil, water-insoluble inorganic pollutants (such as clay and heavy metal impurities), macromolecular organic pollutants (such as emulsified oil) and low molecular weight water-soluble organic pollutants. The fairly high salinity is one of the characteristics of the oilfield produced water.

The salinity of oilfield produced water is up to 10000 mg L<sup>-1</sup> in some regions of Daqing oilfield. The main reason is many positively charged ions that easy to scaling (such as Ba<sup>2+</sup> and Sr<sup>2+</sup>) with negatively charged ions (such as CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>). These scaling ions are easy to produce carbonate precipitation (such as BaCO<sub>3</sub>, SrCO<sub>3</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub>) at the injection wellhead, wellbore lifting equipment and so on. These would plug the pipeline, slow up the flow rate of production line, influence the water injection effect, and even destroy the layer water of oilfield. Therefore, the determination of Ba and Sr in oilfield produced water is an essential step for water quality analysis of oilfield produced water [8,9].

The atomic absorption spectrometry method and inductively coupled plasma atomic emission spectroscopy (ICP-AES) method are the main methods for the determination of Ba and Sr in water [10]. The former is inefficient, analysis speed is slow, linear is relatively narrow, and can only measure one element for one time [11]. The latter is efficient, analysis speed is fast, linear is relatively broad, relatively interference is small, detection limit is low, precision and accuracy is high, and many elements can be analysis at the same time [12,13]. In general, the ICP-AES is a very important determination apparatuses in modern chemical analysis, and it has been widely applied in many fields [14,15].

In this paper, the study was focused on the method for the simultaneous determination of Ba and Sr in oilfield produced water by ICP-AES. The working conditions of the apparatuses were optimized. The aim was set on improving the analysis method for the simultaneous determination of Ba and Sr in oilfield produced water.

## Experimental section

**Experimental apparatus and working conditions.** The below apparatuses were used in the experiments: inductively coupled plasma atomic emission spectroscopy (ICPS-7510, SHIMADZU), samples injected with concentric nebulizer, cyclonic spray chamber, standard quartz torch, axial observation, frequency output power was 1200 W, cooling air flow was 14 L•min<sup>-1</sup>, plasma gas flow was 1.2 L•min<sup>-1</sup>, carrier gas flow was 0.7 L•min<sup>-1</sup>, sample suction volume was 0.6 L•min<sup>-1</sup> and ultra-pure water machine (UPW-20NE, Beijing).

**Experimental chemicals and standard solutions.** HNO<sub>3</sub> (AR) was provided by Beijing Yili Fine Chemicals Co., Ltd. and experimental water was produced by ultra-pure water machine. Both of Ba standard ion stock solution and Sr standard stock solution was 1000 mg•L<sup>-1</sup>. The three different kinds of mixed standard solutions were prepared by adding proper quantities of Ba and Sr standard ion stock solutions into three different volumetric flasks, respectively. **Table 1** shows the concentration of Ba and Sr in the three different kinds of mixed standard solutions. Then HNO<sub>3</sub> (W<sub>HNO<sub>3</sub></sub>/W<sub>water</sub> = 1:1) was added into the three different kinds of mixed standard solutions to pH value ≤ 2, respectively. The oilfield produced water was sampled from Daqing oilfield. The water sample was filtered and the filtrate was acidified with HNO<sub>3</sub> (W<sub>HNO<sub>3</sub></sub>/W<sub>water</sub> = 1:1) to pH value ≤ 2.

Table 1 Concentration of Ba and Sr in mixed standard solution

Element	Mixed standard solution		
	No. 1	No. 2	No. 3
Ba (mg L <sup>-1</sup> )	2	6	10
Sr (mg L <sup>-1</sup> )	10	30	50

**Experiment method.** With ultra-pure water as a blank sample, the concentrations of Ba and Sr in the three different kinds of mixed standard solutions and blank sample were measured under the selected apparatus analysis conditions and the calibration curves were taken out. **Table 2** shows the correlation coefficient and linear range of the calibration curve of Ba and Sr. Then the concentrations of Ba and Sr in oilfield produced water sample were carried out according to the calibration curves under the same conditions with measurement of Ba and Sr concentrations in the mixed standard solutions and blank sample.

Table 2, Correlation coefficient and linear range of calibration curves

Element	correlation coefficient of calibration curve	linear range of calibration curve (mg L-1)
Ba	0.9998	0-30
Sr	0.9999	0-30

## Results and discussion

**Analytical spectral line selection.** Simultaneous determination of more than one characteristic spectral line of each element is one of the characteristics of ICP-AES. Synchronization background correction is one of the functions of ICP-AES. Thus, in this experiment, three spectral lines were selected for measurement of each element. Finally, the analytical spectral lines, which were high strength, good peak shape and small interference, were selected by comparing the strength, peak shape, interference, sensitivity, stability and background ratio of different spectral lines for each element. Table 3 shows the analytical spectral lines of Ba and Sr.

Table 3 Analytical spectral lines

Element	Ba	Sr
Wavelength of spectral line (nm)	455.404	407.771

**Detection limit.** Under the selected apparatus analysis conditions, the blank sample was measured for 10 times and standard deviation was calculated. The value of detection limit is triple of standard deviation. **Table 4** shows the detection limits of Ba and Sr. In **Table 4**, the detection limit is relatively low and sensitivity is relatively high.

Table 4 Standard deviation and detection limits

Element	standard deviation	detection limit (mg L-1)
Ba	0.022	0.066
Sr	0.017	0.051

**Method precision.** Under the selected apparatus analysis conditions, parallel determination for 10 times of the oilfield produced water to verify the precision of the method and relative standard deviation (RSD) was calculated. Table 5 shows the determination average values and relative standard deviation of Ba and Sr. From **Table 5**, the precision of the method was high because the relative standard deviation value of Ba or Sr was less than 1%.

Table 5 Method precision

Element	average value (mg•L-1)	RSD (%)
Ba	13.86	0.43
Sr	1.28	0.68

**Recovery within standard solution.** In order to test the accuracy of the method, the recovery experiments within standard solutions were taken. Mixed standard solutions were adding into the oilfield produced water samples and diluted to the ticks with ultra-pure water. Then parallel determination for 9 times of each element and recovery within standard solution was carried out. The results are shown in the **Table 6**. From **Table 6**, the accuracy of the method was good because the recovery of Ba or Sr was between 95% and 105%. The working apparatus was stable and precision was relatively high because the relative standard deviation value of Ba or Sr was less than 1%.

Table 6 Recovery within standard solution

Element	original amount (mg•L-1)	amount of added standard solution (mg•L-1)	measured value (mg•L-1)	recovery (%)
Ba	6.08	10	15.54	96.6
Sr	0.93	10	11.33	103.7

## Summary

In this research, we established a method for the simultaneous determination of Ba and Sr in oilfield produced water with ICP-AES by optimizing apparatus operating conditions, selecting analytical spectral lines, measuring detection limit, calculating precision and recovery within standard solution experiments. The detection limit of Ba and Sr was 0.066 and 0.051, respectively. The relative standard deviation of Ba and Sr was 0.43% and 0.68%, respectively. The recovery within standard solution of Ba and Sr was 96.6% and 96.8%, respectively. The precision and accuracy of the method was very good. The method, which has short residence time of the sample and operation quickly and easily, was credibility. In addition, the method could able to meet the analytical requirements of Ba and Sr in oilfield water and broaden the application of ICP-AES.

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