Simultaneous Determination of Ca and Mg in Oilfield Produced Water by ICP-AES

Haiming Wu[a], Xin Sui[a], Baohui Wang, Jing Dong, Hongjun Wu, Li Li and Dandan Yuan

Northeast Petroleum University, College of Chemistry & Chemical Engineering, Provincial Key Laboratory of Oil & Gas Chemical Technology, Daqing 163318, China

[a]zhisx_81@163.com

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 got out of 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 composition of the oilfield produced water is very complex, and the salinity is relatively 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 Ca^{2+}, Mg^{2+}, and CO_3^{2-}) and they are easy to form carbonate precipitation (such as $CaCO_3$, $MgCO_3$) in the production pipelines. Therefore, the determination of Ca and Mg in oilfield produced water is an essential step for water quality analysis of oilfield produced water. In this paper, a method of the simultaneous determination of Ca and Mg in oilfield produced water by ICP-AES was established. The working conditions of the apparatuses were optimized. The detection limit of Ca and Mg was 0.014 and 0.0021. The relative standard deviation of Ca and Mg was 0.61% and 0.71%. The recovery within standard solution of Ca and Mg was 104.3% and 96.8%.

Introduction

Oil is a significant non-renewable resource for the world. Exploration rate has developed rapidly for the enhanced oil recovery. Amount of water as the injected water is necessary to take 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 got out of 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 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 many 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 salinity is relatively high is one of the characteristics of the oilfield produced water. The salinity of oilfield produced water is up to 10000 mg•L-1 in some regions of Daqing oilfield. The main reason is there are a large number of negatively charged ions that easy to scaling (such as Ca^{2+} and Mg^{2+}) and positively charged ions (such as CO_3^{2-} and SO_4^{2-}). These scaling ions are easy to form carbonate precipitation (such as $CaCO_3$, $MgCO_3$, $CaSO_4$) 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 harm the layer water of oilfield. Therefore, the determination of Ca and Mg 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 Ca and Mg 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 Ca and Mg 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 Ca and Mg in oilfield produced water.

Experimental Secation

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^{-1}, plasma gas flow was 1.2 L•min^{-1}, carrier gas flow was 0.7 L•min^{-1}, sample suction volume was 0.6 L•min^{-1} and ultra-pure water machine (UPW-20NE, Beijing).

Experimental Chemicals and Standard Solutions. HNO_3 (AR) was provided by Beijing Yili Fine Chemicals Co., Ltd. and experimental water was produced by ultra-pure water machine. Both of Ca standard ion stock solution and Mg standard stock solution was 1000mg•L^{-1}. The three different kinds of mixed standard solutions were prepared by adding proper quantities of Ca and Mg standard ion stock solutions into three different volumetric flasks, respectively. Table 1 shows the concentration of Ca and Mg in the three different kinds of mixed standard solutions. Then HNO_3 (W_{HNO3}/W_{water} = 1:1) was added into the three different kinds of mixed standard solutions to pH value $\leq$ 2, respectively. The oilfield produced water was sampled from Daqing oilfield. The water sample was filtered and the filtrate was acidified with HNO_3 (W_{HNO3}/W_{water} = 1:1) to pH value $\leq$ 2.

Experimental Method. With ultra-pure water as a blank sample, the concentrations of Ca and Mg 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 Ca and Mg. Then the

concentrations of Ca and Mg in oilfield produced water sample were carried out according to the calibration curves under the same conditions with measurement of Ca and Mg concentrations in the mixed standard solutions and blank sample.

Table 1 Concentration of Ca and Mg in mixed standard solution

Element	Mixed standard solution		
	No. 1	No. 2	No. 3
Ca [mg L^{-1}]	8	16	32
Mg [mg L^{-1}]	100	200	300

Table 2 Correlation coefficient and linear range of calibration curves

Element	correlation coefficient of calibration curve	linear range of calibration curve [mg L^{-1}]
Ca	0.9993	0-30
Mg	0.9981	0-80

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 measuring 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 Ca and Mg.

Table 3 Analytical spectral lines

Element	Ca	Mg
Wavelength of spectral line [nm]	393.366	279.553

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 Ca and Mg. From 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}]
Ca	0.0047	0.014
Mg	0.0007	0.0021

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 Ca and Mg. From Table 5, the precision of the method was high because the relative standard deviation value of Ca or Mg was less than 1%.

Table 5 Method precision

Element	average value [mg L^{-1}]	RSD [%]
Ca	9.33	0.61
Mg	1.56	0.71

Recovery Within Standard Solution. In order to choose the accuracy of the method, the recovery experiments within standard solutions were taken. Mixed standard solutions were added

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 Ca or Mg was between 95% and 105%. The working apparatus was stable and precision was relatively high because the relative standard deviation value of Ca or Mg 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 [%]	RSD [%]
Ca	16.08	20	38.63	104.3	0.03
Mg	1.92	10	11.54	96.8	0.08

Summary

In this research, we established a method for the simultaneous determination of Ca and Mg 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 Ca and Mg was 0.014 and 0.0021, respectively. The relative standard deviation of Ca and Mg was 0.61% and 0.71%, respectively. The recovery within standard solution of Ca and Mg was 104.3% 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 Ca and Mg in oilfield water and broaden the application of ICP-AES.

References

[1] Bethany L. Alley, Ben Willis, John Rodgers Jr., James W. Castle, Seasonal performance of a hybrid pilot-scale constructed wetland treatment system for simulated fresh oil field-produced water, Water, Air, & Soil Pollution. 224 (2013) 1639-1640.

[2] Grażyna Jarzyńska, Jerzy Falandysz, The determination of mercury in mushrooms by CV-AAS and ICP-AES techniques, Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering. 46 (2011) 569-573.

[3] Iva Juranović Cindrić, Michaela Zeiner, Michaela Kröppl, Gerhard Stingeder, Comparison of sample preparation methods for the ICP-AES determination of minor and major elements in clarified apple juices, Microchemical Journal. 99 (2011) 364-369.

[4] Sitki Baytak, Fahmida Zereen, Zikri Arslan, Preconcentration of trace elements from water samples on a minicolumn of yeast (*Yamadazyma spartinae*) immobilized TiO_2 nanoparticles for determination by ICP-AES, Talanta. 84 (2011) 319-323.

[5] Vladislav G. Torgov, Tamara M. Korda, Marina G. Demidova, Elena A. Gus'kova, Georgy L. Bukhbinder, ICP AES determination of platinum group elements and gold in collective extract and strip product solution in analysis of geological samples, Journal of Analytical Atomic Spectrometry. 24 (2009) 1551-1557.

[6] Thomas L. Eberhardt, Hui Pan, Analysis of the fly ash from the processing of wood chips in a pilot-scale downdraft gasifier: Comparison of inorganic constituents determined by PIXE and ICP-AES, Biomass and Bioenergy. 51 (2013) 163-168.

[7] Mehmet Musa Özcan, Fahad Y. AL Juhaimi, Determination of heavy metals in bee honey with connected and not connected metal wires using inductively coupled plasma atomic emission spectrometry (ICP–AES), Environmental Monitoring and Assessment. 184 (2012) 2373-2375.

[8] Domingos D. Afonso, Sitki Baytak, Zikri Arslan, Simultaneous generation of hydrides of bismuth, lead and tin in the presence of ferricyanide and application to determination in biominerals by ICP-AES, Journal of Analytical Atomic Spectrometry. 25 (2010) 726-729.

[9] Nancy Lewen, Dennis Nugents, The use of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in the determination of lithium in cleaning validation swabs, Journal of Pharmaceutical and Biomedical Analysis. 52 (2010) 652-655.

[10] G. A. Zachariadis, E. Sahanidou, Multi-element method for determination of trace elements in sunscreens by ICP-AES, Journal of Pharmaceutical and Biomedical Analysis. 50 (2009) 342-348.

[11] Homayon Ahmad Panahi, Hossein Sid Kalal, Elham Moniri, Mahshid Nikpour Nezhati, Mahnaz Taheri Menderjani, Somayeh Ranjbar Kelahrodi, Faranak Mahmoudi, Amberlite XAD-4 functionalized with m-phenylendiamine: Synthesis, characterization and applications as extractant for preconcentration and determination of rhodium (III) in water samples by Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES), Microchemical Journal. 93 (2009) 49-54.

[12] S. Boussetta, F. Bassinot, A. Sabbatini, N. Caillon, J. Nouet, N. Kallel, H. Rebaubier, G. Klinkhammer, L. Labeyrie, Diagenetic Mg-rich calcite in Mediterranean sediments: Quantification and impact on foraminiferal Mg/Ca thermometry, Marine Geology. 280 (2011) 195-204.

[13] Kyeong-nam Park, Sang Yeon Hong, Jin Woo Lee, Kyung Chan Kang, Young Cheol Lee, Myung Gyu Ha, Ju Dong Lee, A new apparatus for seawater desalination by gas hydrate process and removal characteristics of dissolved minerals (Na^+, Mg^{2+}, Ca^{2+}, K^+, B^{3+}), Desalination. 274 (2011) 91-96.

[14] Raquel Sánchez, José Luis Todolí Charles Philippe Lienemann, Jean Michel Mermet, Effect of solvent dilution on the ICP-AES based silicon sensitivity, the aerosol characteristics and the resulting organic solution properties in the analysis of petroleum products, Journal of Analytical Atomic Spectrometry. 25 (2010) 178-185.

[15] Mohammed A. Amin, K. F. Khaled, Monitoring corrosion and corrosion control of iron in HCl by non-ionic surfactants of the TRITON-X series-Part I. Tafel polarisation, ICP-AES and EFM studies, Corrosion Science. 52 (2010) 1762-1770