

Influence Factors and Elimination on Iron Content Using ICP-AES Method in Oilfield Produced Water

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Abstract. ICP-AES method can be used to determine multiple metallic elements simultaneously, and has the advantages of high sensitivity, good repeatability and high accuracy. In the paper, the detection limit of iron content was determined by stepwise dilution method. The influence of the cationic concentration on the determination of iron element was studied, and the matrix matching method was proposed to eliminate the influence. The results show that, the determination limit of Iron element is 0.01 mg·L⁻¹. Because the other cationic content is several times or even tens of times as much as iron ions, it has a great influence on the determination results of Iron element. The effects of cationic concentration can be effectively eliminated by establishing a standard curve using matrix matching. After digestion pretreatment on the oil and gas field produce water, The standard adding recovery rate was between 95% and 105%, and the RSD is less than 4%. Compare this method with o-phenanthroline spectrophotometry, its relative error is within 5%. Therefore, ICP-AES method can fully meet the requirements of determination of iron content in oil field produce water, and greatly improves the efficiency and accuracy of the laboratory analysis of oil and as field wastewater.

1. Introduction

In the process of oil and gas water injection mining and gathering and transportation, the iron ion content of the water extracted from oil and gas fields is an important indicator[1] for monitoring injection water quality and gathering pipeline corrosion. At present, the main methods for determining the concentration of iron ions in water are: o-phenanthroline spectrophotometry[2-5], graphite furnace atomic absorption spectrometry[6], EDTA ligand titration[7-9], reversed-phase high performance liquid chromatography[10] and so on. These methods have their own characteristics: spectrophotometry and EDTA ligand titration can only determine the content of iron ions in water alone; atomic absorption spectrometry and reversed-phase high performance liquid chromatography are mainly suitable for the quantitative[11-13] analysis of trace and trace inorganic elements in samples, reversed-phase high performance chromatography requires six organic reagents for the complex pretreatment[10] of samples. The methods for the determination of iron content in oilfield water are specified in the Oilfield Water Analysis[14] Method (SY/T 5523-2016), including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP) and o-phenanthroline spectrophotometry. The ICP-AES method is widely[23-25] used for the determination of metal

elements due to its high sensitivity, reproducibility and accuracy[15-22], as it can be used for the simultaneous analysis of multiple elements.

The water quality of oil and gas field produced water is characterised by high mineralisation, high SS and high oil concentration. However, the standard method[26] of SL394.1 used in the ICP method recommended in SY/T 5523-2016 does not address the interference of other components contained in oil and gas field produced water on the determination results and the methods to eliminate them. Therefore, according to the quality characteristics of produced water of oil and gas fields, the influence of cation concentration in produced water on the determination of iron content by ICP-AES is studied, and the corresponding elimination method is proposed to achieve the rapid and accurate determination of iron ion concentration.

2. Experimental section

2.1 Apparatus and reagents

Main instruments: HK-8100 inductively coupled plasma emission spectrometer(Beijing Huake Yi Tong Analytical Instruments Co., Ltd.), TU-1901 double-beam UV-Visible spectrophotometer (Unocal (Shanghai) Instruments Co., Ltd.), analytical balance, heating plate.

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Main reagents: NaCl (sodium chloride), CaCl₂ (calcium chloride anhydrous), MgCl₂(magnesium chloride anhydrous), Na₂SO₄ (sodium sulphate), NaHCO₃ (sodium bicarbonate), FeCl₃·6H₂O (ferric chloride), HNO₃ (concentrated nitric acid), H₂O₂ (hydrogen peroxide, 30%), all analytically pure, Fe standard stock solution (500mg·L⁻¹), weigh 0.6050g (accurate to 0.0001g) FeCl₃·6H₂O, dissolved in 5mL of concentrated hydrochloric acid and fixed to 250mL with ultra-pure water.

The water used for the experiments was ultra-pure water.

2.2 Experimental methods

2.2.1 Analytical conditions of the ICP-AES instrument

High frequency generator power: 1KW, carrier gas flow: 20L·h⁻¹, carrier gas pressure: 0.2MPa, working gas flow: 700 L·h⁻¹, working gas: high purity argon (99.99% purity).

2.2.2 Establishment of the standard curve

Produced water from oil and gas fields contains cations such as Ca²⁺, Mg²⁺, Na⁺ and K⁺ from the formation, which at high levels may affect the accurate determination of iron concentrations. Therefore, it is necessary to establish an ICP-AES standard curve using the matrix matching method (simulating the mineralisation of formation water). The method was as follows 1.1 Prepared Fe standard stock solution was taken in a 250mL volumetric flask, 5 mL of concentrated hydrochloric acid was added l. The matrix mineralisation solution (see Table 1 for the basic formulation) was added to simulate formation water to make three mineralisation series of 5000 mg·L⁻¹(series 1), 10000 mg·L⁻¹ (series 2) and 15000 mg·L⁻¹ (series 3), and ultrapure water was used to fix the volume. The samples were diluted 10 times for determination, i.e. 50,000 mg·L⁻¹ (series 1), 100,000 mg·L⁻¹ (series 2) and 150,000 mg·L⁻¹ (series 3) for the three standard series of mineralisation. The standard mass concentrations of each series of elemental Fe are 0, 5, 10, 20 and 50mg·L⁻¹, while a standard mass concentration of 0, 5, 10, 20 and 50 mg·L⁻¹ is used to make a standard line of Fe without matrix using ultrapure water.

Tab. 1 Composition of simulated formation water

Reagents	NaCl	CaCl ₂	MgCl ₂	Na ₂ SO ₄	NaHCO ₃	Mineralization
Mass concentration/(mg·L ⁻¹)	12019.2	961.5	480.8	1442.3	96.2	15000

2.2.3 Elimination of the effect of oil on the determination of iron ion concentration

When the produced water of oil and gas fields contains organic matter such as oil, ICP-AES method is used for determination. The change of physical properties of water samples will affect the injection of ICP atomizer, so that

the flame cannot ignite normally[27], which will affect the Fe content determination results, therefore, the water sample from oil and gas fields needs to be pre-treated by digestion. 1mL of HNO₃ and 2 mL of H₂O₂ were added to the sample, and the sample was heated on a hotplate to about 1 mL, cooled and then fixed to 10mL with ultrapure water.

3. Results and Discussion

3.1 Standard curves

Stock solutions of Fe prepared with ultrapure water and simulated formation water, respectively, were used to determine Fe by ICP-AES in the range of 0.01 to 50 mg·L⁻¹. The standard curves for Fe content established at different mineralisation series are shown in Table2.

Tab. 2 Correlation parameters of Standard curve

λ/nm	To add or not to add a substrate	Regression equation	R ²	Detection limit/(mg·L ⁻¹)
259.940	No (ultrapure water)	y=0.9993x + 0.0008	0.9999	/
	Yes (Series 1)	y=0.9996x + 0.0032	0.9999	0.01
	Yes (Series 2)	y=0.9995x + 0.0063	0.9999	0.01
	Yes (Series 3)	y=0.9997x + 0.0048	0.9999	0.01

As can be seen from Table2, the linear correlation coefficient R² ≥ 0.999 of the regression equation. The detection limit of the ICP-AES method was determined to be 0.01 mg·L⁻¹ by stepwise dilution, indicating that the method has a high sensitivity.

3.2 Effect of cations on the determination of iron content and their elimination

3.2.1 Effect of cations on the determination of iron content

Samples with different cation mass concentrations and containing elemental Fe were prepared separately according to the proportions of simulated formation water, and the Fe concentration in the samples was 50 mg·L⁻¹, which was determined by ICP-AES using a calibration line established with ultrapure water. The results of the determination of elemental Fe content at different cation concentrations are shown in Figure1.

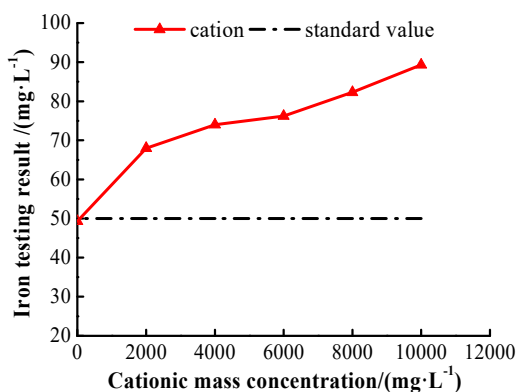


Fig. 1 Influences of cationic mass concentration on the determination of iron mass concentration by ICP-AES method As can be seen from Figure 1, for cations such as Na^+ , Ca^{2+} and Mg^{2+} concentrations of more than 40 times the iron content produce serious interference with the determination of iron, with increasing cation concentrations the interference is also greater.

3.2.2 Cation influence elimination method

In order to eliminate the influence of cations in water on the determination, the matrix matching method was used for the determination. The mass concentrations of cations were $2000 \text{ mg}\cdot\text{L}^{-1}$, $4000 \text{ mg}\cdot\text{L}^{-1}$ and $6000 \text{ mg}\cdot\text{L}^{-1}$. The standard concentration of Fe in the samples was $50 \text{ mg}\cdot\text{L}^{-1}$. The solutions prepared were determined using three matrix series of markers, and the results are shown in Figure 2.

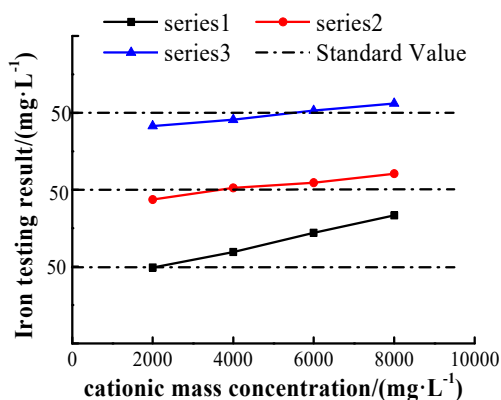


Fig. 2 Iron content determination by matrix matching series at different cationic concentrations

As can be seen from Figure 2, the results of the three matrix-matched series of series 1, series 2 and series 3 are very close to the true value of Fe ion concentration. Compared with Figure 1, the measurement error is significantly reduced, indicating that all three series are well adapted to the corresponding mineralisation level of the water sample, and that the influence of cations on the determination can be well eliminated by matrix matching. The range of suitable cation concentrations for matrix series 1 is $1721\sim 2560 \text{ mg}\cdot\text{L}^{-1}$, matrix series 2 is $3208\sim 5060 \text{ mg}\cdot\text{L}^{-1}$ and matrix series 3 is $4558\sim 6558 \text{ mg}\cdot\text{L}^{-1}$. The corresponding

mineralisation ranges are $4540\sim 6860 \text{ mg}\cdot\text{L}^{-1}$, $8500\sim 13350 \text{ mg}\cdot\text{L}^{-1}$ and $12030\sim 17300 \text{ mg}\cdot\text{L}^{-1}$. Under these conditions, the relative error of the iron content determination results is within 5%.

3.3 Determination of Fe content in oil and gas field produced water

3.3.1 Results of elemental Fe determination at different oil contents

Simulated water with Fe content of 5 and $50 \text{ mg}\cdot\text{L}^{-1}$ was prepared using ultrapure water, different amounts of condensate were added and stirred well at high speed. After disintegration of the water samples according to method 1.2.2, the Fe content in the water samples was determined according to the standard curve established by ultrapure water, and the results are shown in Table 3.

Tab. 3 Determination results of iron content at different oil content

oil content/(mg·L ⁻¹)	0		157.68		348.44	
	Measured values	Error/%	Measured values	Error	Measured values	Error
50 mg·L ⁻¹	49.00	2.00	49.55	0.90	50.13	0.26
5 mg·L ⁻¹	4.93	1.40	5.02	0.40	5.04	0.80

As can be seen from Table 3, the determination results of the water samples after the ablation treatment all meet the error range (<5%), indicating that the ablation method used can better eliminate the influence of oil on the determination results and has a good adaptability to a certain content of oil substances in the water samples.

3.3.2 Comparison of the results of the determination of Fe content in oil and gas field produced water

Extracted water samples from oil and gas fields were selected and their conductivity was determined. Salinity was estimated from $y = 0.866x - 7.79$ [28] (x is conductivity, $\mu\text{s}\cdot\text{cm}^{-1}$. y is salinity, $\text{mg}\cdot\text{L}^{-1}$), and the wastewater samples were pretreated and then the Fe content was [29] determined by ICP-AES and o-phenanthroline spectrophotometry respectively, and the results are shown in Table 4.

Tab. 4 Fe content Comparison of the determination results in oil field produced water

Serial number	Conductivity/(ms·cm ⁻¹)	Salinity/(mg·L ⁻¹)	ICP-AES		Spectrophotometry	Relative error of the two methods/%
			Substrate Series Markers	Measurement value/(mg·L ⁻¹)	Measurement value/(mg·L ⁻¹)	
Waste water sample 1	56.23	48687.39	Seri es 1	12.40	12.17	1.89
Waste water sample 2	67.22	58204.73	Seri es 1	115.38	117.44	1.75
Waste water sample 3	135.44	117283.25	Seri es 2	155.29	152.28	1.98
Waste water sample 4	182.92	158400.93	Seri es 3	84.19	82.35	2.23

As can be seen from Table 4, the relative errors of the two assays were <5%, indicating that the differences were not significant.

3.3.3 Accuracy and precision analysis of the determination method

After the oil and gas field recovered water samples were digested and treated, the accuracy of the method was investigated by determining the spiked recoveries of iron using the standard addition method. The spiked values in the samples are shown in Table 5, and the results were determined for each sample five times consecutively using matrix-matched markers.

Tab. 5 Iron standard addition recovery rate and relative standard deviation using ICP-AES determination(n=5)

Serial number	Sample value/(mg·L ⁻¹)	Substrate Series Markers	RSD/%	Spiked value/(mg·L ⁻¹)	Measurement value/(mg·L ⁻¹)	Recovery rate/%
water sample 1	12.40	Series 1	2.5	50	60.28	95.8
water sample 2	115.38	Series 1	0.9	50	166.4	102.0
water sample 3	155.29	Series 2	0.4	50	204.88	99.2
water sample 4	84.19	Series 3	1.1	50	132.79	97.2

As can be seen from Table 5, the spiked recoveries of Fe determined by ICP-AES matrix-matched series after pretreatment of water samples ranged from 95% to 105%, indicating that the method is accurate. The relative standard deviation (RSD) is used to indicate the degree of dispersion of the data in the model. The smaller the value, the less dispersion of the data, the higher the precision of the analytical results. The RSDs in this study were all less than 4%, indicating that the data had a high degree of precision and the tests were reproducible.

4. Conclusion

- (1) The lower limit of detection of iron was 0.01 mg·L⁻¹ by ICP-AES. The method is sensitive and the error is within 5% compared to O-phenanthroline spectrophotometry.
- (2) Cations such as Na⁺, Ca²⁺ and Mg²⁺ have a large influence on the determination results, and the matrix matching method can effectively reduce the interference caused by cations.
- (3) The standard curve established by ICP-AES matrix matching series can be used to determine Fe in water samples. The standard recovery rate is 95%~105%, and RSD is less than 4%, indicating that the method is suitable for the accurate determination of Fe in gas field water.

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