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The choice of conditions for the determination of vanadium, chromium and arsenic concentration in waters by ICP-MS using collision mode

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Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) is a popular method for the analysis of waters with various matrices and salinity. One of the difficulties of routine measurements by ICP-MS is spectral interferences conditioned by polyatomic ion formation in the plasma. The detection of the background concentration of such elements as vanadium, chromium and arsenic in natural waters by ICP-MS is complicated because of the polyatomic interferences, having the same mass-to-charge ratio. Thus, the purpose of this article is to determine the optimal rate of helium flow for the effective correction of polyatomic interferences of vanadium, chromium and arsenic and the reduction of their detection limits in Cl-rich waters. This research has been carried out using an inductively coupled plasma mass spectrometer NexION 300D with a universal cell technology (UCT) (PerkinElmer, USA) and three model solutions. For the detection of vanadium, chromium and arsenic content in chloride matrix water by ICP-MS, a collision mode is preferable for polyatomic interference correction. The optimal helium flow rate for this purpose is 2.5 ml/min. Under these conditions, the detection limit of vanadium, chromium and arsenic decreases by order of two.

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Keywords: Inductively coupled plasma mass spectrometry; collision mode; standard mode; polyatomic interferences; detection limits; chloride matrix water; vanadium, chromium and arsenic content; analytical signal intensity

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a popular method for the analysis of numerous

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objects in diverse scientific areas including geochemistry for the analysis of waters with various matrices and salinity^{1,2}. In spite of the undeniable advantages of this method, namely, a low detection limit, high-precision, a stable analytical signal, high productivity and simultaneous determination of more than 60 chemical elements, this method has disadvantages. One of them in carrying out routine measurements by ICP-MS is spectral interferences conditioned by polyatomic ion formation in the plasma³. In water solutions such polyatomic ions as oxides, argides, hydroxides, hydrides, etc. are widely spread. Polyatomic interferences can significantly influence the detection limit of some elements^{3,4}. The detection of the background concentration of such elements as vanadium, chromium and arsenic in natural waters by ICP-MS is complicated due to the polyatomic interferences, having the same mass-to-charge ratio.

At present in analytical procedures using ICP-MS, the kinetic energy discrimination (KED) in a collision cell is applied for the correction of polyatomic interferences⁵. Ions lose their energy in collisions with inert gas (helium) molecules in a collision cell. Large polyatomic ions, in contrast with the analysis element ions, collide with helium molecules and cannot overcome the potential barrier leaving the cell^{3,5,6}. Thus, only the analysis element ions remain leaving the cell. The helium flow rate is a significant characteristic for the effective correction of polyatomic interferences⁷. The disadvantage of this approach is decreasing an analytical signal for all analysis elements^{8,9}.

Thus, the purpose of this article is to determine the optimal rate of helium flow for the effective correction of polyatomic interferences of vanadium, chromium and arsenic and the reduction of their detection limits in Cl-rich waters.

2. Methods

The research was carried out using an inductively coupled plasma mass spectrometer NexION 300D with a universal cell technology (UCT) (PerkinElmer, USA) and model solutions. The main ICP-MS instrumental operating conditions are presented in Table 1.

Table 1. ICP-MS instrumental operating conditions

Component/Parameter	Type/Value/Mode
Nebulizer	Cross flow GemTip
Spray Chamber	Ryton Scott
Triple Cone Interface Material	Platinum/Aluminium
Plasma Gas Flow	16.0 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Gas Flow	0.86 – 0.88 L/min
Sample Uptake Rate	0.75 mL/min
RF Power	1150 W
Integration Time	600 ms
Replicates per Sample	3
Mode of Operation	Standard; Collision (using He gas)

The model solutions were prepared using standard solutions (PerkinElmer, USA) and deionized water. Three types of solutions were prepared. In the first model solution the chromium, arsenic, vanadium concentration was 0.1 µg/L, the chloride ion concentration was 500 mg/L. The second solution was clear deionized water without any solutes (blank solution). The third model solution was the chloride ion solution with a concentration of 500 mg/L.

The analytical signal intensity of analysis elements was measured in standard and collision modes. The choice of the effective correction conditions of the polyatomic interferences was made by the determination of the optimal helium flow rate in the range from 1.3 to 3.2 ml/min.

3. Results and discussion

The measurement of the vanadium, chromium and arsenic concentration is complicated at the presence of chloride [2, 10]. Chloride is the major matrix component of the natural brines belonging to a chloride-sodium type. The detection limit of the studied elements in such type of waters can be higher due to the polyatomic interferences. The possible polyatomic interferences for the studied elements are shown in Table 2.

Table 2. The vanadium, chromium and arsenic polyatomic interferences

Element	Possible polyatomic interferences
V (51 amu)	$^{35}\text{Cl}^{16}\text{O}^+$, $^{34}\text{S}^{16}\text{OH}^+$
Cr (52 amu)	$^{40}\text{Ar}^{12}\text{C}^+$, $^{35}\text{Cl}^{16}\text{OH}^+$, $^{34}\text{S}^{18}\text{O}^+$, $^{36}\text{Ar}^{16}\text{O}^+$
As (75 amu)	$^{40}\text{Ar}^{35}\text{Cl}^+$, $^{38}\text{Ar}^{37}\text{Cl}^+$, $^{40}\text{Ca}^{35}\text{Cl}^+$

The study of the analytical signal intensity of vanadium, chromium and arsenic (51, 52, 75 amu, respectively) in chloride matrix was carried out in standard and collision modes (Table 3). According to Table 3 the analytical signal intensity decreases when increasing the helium flow rate. Possibly, this fact is conditioned by the correction of the polyatomic ion-interferences, having the same mass-to-charge ratio [11]. Nevertheless, at a helium flow rate more than 2.5 ml/min, the analytical signal intensity decreases to the level which seems not to be analytically unrepresentative.

Table 3. Analytical signal intensity in the masses 51, 52, 75 amu in the first model solution at the various rate of helium flow ($C_V=0.1 \mu\text{g/L}$, $C_{Cr}=0.1 \mu\text{g/L}$, $C_{As}=0.1 \mu\text{g/L}$, $C_{Cl}=500 \text{ mg/L}$)

Mode	Helium flow rate, ml/min	Analytical signal intensity, imp/sec		
		51 amu	52 amu	75 amu
Standard	0	93200	14400	5770
	1.3	88300	8250	3680
	1.6	62100	5240	2620
	1.9	36000	3410	1670
Collision	2.2	19400	2040	888
	2.5	11800	1440	527
	2.8	6200	998	315
	3.1	3100	450	170
	3.4	1590	33.4	78

The intensity of the analytical signal was measured in deionized water (the blank solution) and in the chloride ion solution (the third model solution) for the influence detection of ion-interferences containing chlorine. When helium was absent and the helium flow rate was low (less than 2 ml/min), the high analytical signal intensity in the masses 51, 52 and 75 amu was obtained (Figure 1).

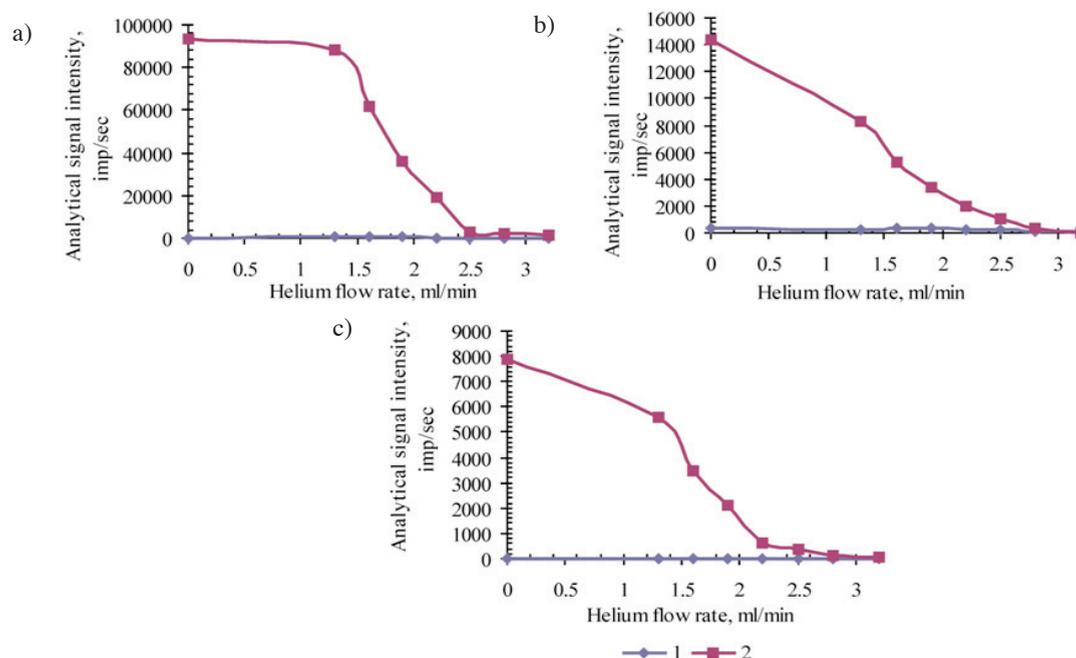


Fig.1. Analytical signal intensity vs. helium flow rate in the masses 51 amu (a), 52 amu (b) and 75 amu (c) in the model chloride ion solution (1) and in deionized water (2)

It was conditioned by the presence of the great polyatomic interferences. At the helium flow rate more than 2.5 ml/min, the intensity of the analytical signal in those masses was similar in the model chloride ion solution and in deionized water. That witnessed the effective correction of polyatomic interferences. Thus, the optimal helium flow rate was 2.5 ml/min.

The detection limit of vanadium, chromium and arsenic was calculated at the various helium flow rate. Figure 2 shows that the highest detection limit of the studied elements is obtained in the standard mode. In the collision mode the detection limit of the studied elements decreases by order of two when helium flow rate increases. At the rise of the helium flow rate more than 2.5 ml/min, the changes of the detection limit are marginal (by order of one). In spite of the fact that maximum reduction of the detection limit of the studied elements is obtained at the helium flow rate of 3.2 ml/min, the intensity of the analytical signal is the lowest.

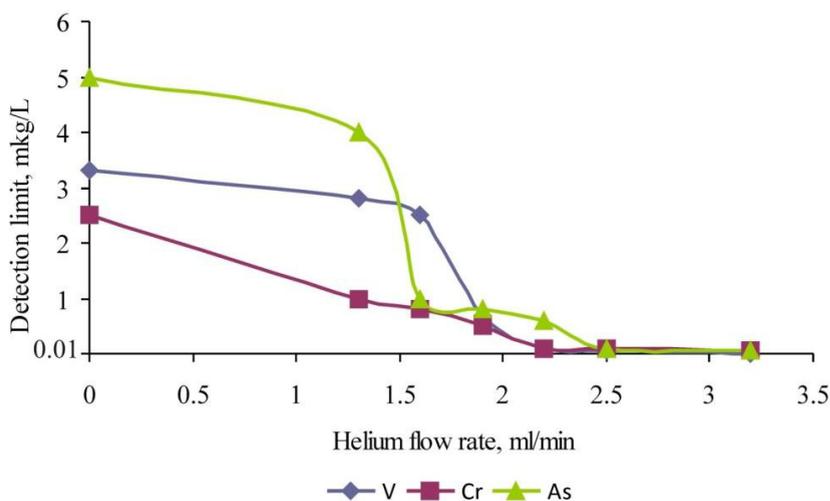


Fig.2. Detection limit of V, Cr, As vs. helium flow rate

4. Conclusions

The detection of the trace element content in brines of a chloride-sodium type by using ICP-MS is complicated because of the numerous reasons including polyatomic interferences. Using various modes (collision mode) of the trace element detection and the choice of the optimal analytical conditions (for example the helium flow rate) allow us to overcome these difficulties and to reduce the detection limit of numerous chemical elements.

The influence of the helium flow rate, standard and collision mode on the detection limit of vanadium, chromium and arsenic in Cl-rich brines has been investigated. For the detection of vanadium, chromium and arsenic content in chloride matrix water by ICP-MS, the collision mode is preferable for the polyatomic interference correction. The optimal helium flow rate for this purpose is 2.5 ml/min. Under these conditions the detection limit of vanadium, chromium and arsenic decreases by order of two and is 10^{-5} mg/L.

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