Direct Mass Spectrometric Analysis of Zinc and Cadmium in Water by Microwave Plasma Torch Coupled with a Linear Ion Trap Mass Spectrometer

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ABSTRACT

Microwave plasma torch (MPT) is a simple and low power-consumption ambient ion source. When MPT Mass spectrometry is applied in the detection of some metal elements, the metallic ions exhibit some novel features which are different with traditional ICP Mass spectrometry and may be helpful for the metal element analysis. Zinc and cadmium both are important transition metals with wide applications in modern industry. Here, we presented the research results about the MPT mass spectra of zinc and cadmium elements by a linear ion trap mass spectrometer (LTQ) both in positive and negative mode. Without any sample pretreatment, the aqueous samples were pneumatically nebulized and generated the aerosols. The dried aerosols were introduced into the plasma through the central tube of the MPT to generate the complex metallic ions. For the positive composite ions of zinc and cadmium, the general forms are the hybrid of $M(NO_3) \cdot nOH \cdot mH_2O$, thus the MPT mass spectra are extremely complicated and unsuitable for the quantitative monitoring. However, the MPT negative ionic of zinc and cadmium are quite regular in the forms of $M(NO_3)$. We also showed the limit of detection (LOD) for zinc and cadmium in negative mode can achieve at the level of $10\mu g/L$ (ppb). Therefore, the negative mode MPT mass spectrometry can be used as one of alternative supplements of ICP-MS applied in on-line monitoring of zinc and cadmium metal ions in water at trace levels, which will be promising in the field analysis of metal elements and the rapid water quality inspection.

Keywords: microwave plasma torch; linear ion trap mass spectrometry; zinc; cadmium; water inspection

INTRODUCTION

Zinc and cadmium are both the metal elements of IIB group in the period table and have extensive applications in modern industries. Their chemical properties are similar and so zinc and cadmium always associated in the natural world. Zinc is one of indispensable trace elements in living body, and plays a very important role in human metabolism [1]. Indeed, zinc deficiency in human body may have effects on almost all parts of the human immune system [2] and then lead to a series of diseases [3], such as maldevelopment, hyp immunity, mental retardation, and so on. However, cadmium is a famous toxic heavy metal element [4, 5]. The extensive use of cadmium can contaminate seriously the environment and damage the health of human being [6, 7]. Some researches showed that cadmium mainly affects the enzyme system zinc contained [8, 9]. On the other hand, zinc has also buffer effect on cadmium toxic for many crops, for example, wheat and corn [10, 11]. Currently, scientists are increasingly aware of the index of zinc cadmium ratio in biological system, which is more important rather than the content of single cadmium element [12]. Developing the rapid and direct method for the quantitative measurement of zinc and cadmium will be an efficient approach.

The analytical methods for zinc and cadmium elements are mainly traditional. Recently, Liu et al. [13] developed a high sensitive fluorescent probe technique which can monitor cadmium in aqueous solutions and living cells with low detection limit of 20 nM. But this method is highly selective and may be not suitable for the detection of zinc. Inductively coupled plasma mass spectrometry (ICP-MS) [14-16] is quite sensitive element analysis method and can determine the contents of zinc and cadmium [17]. Nevertheless, in the current field analytical sense, ICP-MS is yet limited due to the general essential, tedious chemical pretreatment, expensive and cumbersome equipments. The microwave plasma torch (MPT) mass spectrometry [18-22] is one of lately developed ambient mass spectrometric techniques with multi-advantages, including low-power consumption, easy operation, simple

construction, strong excitation ability, and so on. More early, MPT had been used as a powerful light source and applied widely in spectrometric instruments [23, 24]. Our previous studies [25] have showed that the MPT ion source coupled with a mass spectrometer can be a promising analytical tool in various fields. Adopting the desolvation unit, and injecting aqueous samples through the central-tube of MPT, the MPT mass spectrometry can be used to detect directly sensitively many kinds of metal elements in water, without tedious sample pretreatment. Thus the MPT mass spectrometry can be used as the supplementary of ICP MS and has potential applications in field analysis.

To expand further the applications of MPT-MS in metal element analysis in water, especially in the detection of zinc and cadmium, the in-depth studies about the feature MPT mass spectra of zinc and cadmium are necessary. This article presented the MPT mass spectra of zinc and cadmium both in positive mode and negative mode of linear ion trap (LTQ) mass spectrometer. The cations and anions of zinc and cadmium complexes were characterized by multistage collision induced dissociation (CID) experiments. Moreover, primer results showed that the LOD for the detection of zinc and cadmium in water are at the levels of 10 μ g/L. These results established the basic of the practical applications of MPT mass spectrometry in the fields of environment controlling and the water quality inspection for zinc and cadmium elements.

EXPERIMENTAL

Materials and Reagents

Aimin Yu's group at Jilin University of China provided the MPT for this experimental research. The 2450 MHz microwave generator (YY1-50 W-2450) with maximum power 50 W and the coaxial line (SFCJ-50-9) were purchased from the Nanjing Electronic Technology Co., Ltd. (Nanjing, China). High purity argon (99.999%) (the Guoteng Special Gas Ltd., Nanchang, China) is used as the MPT assisted gas. Zinc and cadmium standard solution (1.0

g/L Zn or Cd in 1.0mol/L HNO₃) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used was deionized water provided by the chemistry facilities in the East China Institute of Technology (ECIT).

Instrumental Setup

A commercial linear ion trap (LTQ XL) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) combined with a MPT as the ion source was employed in this study. To detect efficiently the metal ion in solution, a desolvation unit was combined with the MPT ion source and the LTQ mass spectrometer. The experimental schematic was shown in Fig. 1a).

The desolvation unit Water samples, without any pretreatments, were pneumatically nebulized and generated the aerosols. The aerosols flow by carrying gas through a desolvation system to reduce microwave energy absorption by water as far as possible before the samples were introduced into the MPT central tube. The desolvation system comprised a heated tube and a dessication chamber. The heated tube is 25cm long and is wrapped with heating tape monitored by a thermocouple and a heater controller (XMT61X, Beijing Huibang Science Technology Co. Ltd., China). The heater controller was set at $140^{\circ}\text{C} \pm 5^{\circ}\text{C}$. A 500-mL flask was filled with concentrated sulfuric acid (98%) to further remove the H₂O molecules from the aerosol. Finally, the dry aerosols were introduced into the plasma through the central tube of the MPT.

The MPT ion source The MPT was described previously as shown in Fig.1b) [23, 26], in brief, a central tube and the intermediate tube are concentric, with the central tube inside the intermediate tube. The supporting gas flow in the intermediate tube and the working gas flows in the central tube. This dual-flow structure is proved to be beneficial for the optimization of jet shape and plasma stabilization [27]. The central tube is made of copper with an outer diameter of 3 mm and inner diameter of 2 mm. The outer tube (26 mm o.d and

22 mm i.d) and the intermediate tube (5.5 mm o.d and 4.5 mm i.d.) are made of brass. The argon gas flowing from the argon cylinder is separate into two routes. One is directly introduced into the intermediate tube at a flow rate of about 500 mL/min, and another one is introduced into the pneumatic nebulizer with 800 mL/min flow rate. The argon in the nebulizer creates the aerosols of the sample solution and carries the dried aerosol into the central tube. Two adjustable rotameters (100– 1000ml/min) are used to control the two argon flow rates. A 2450-MHz voltage with a maximum power of 50W is applied to the intermediate tube by the center conductor of a coaxial cable. The shielding ground of the coaxial cable is connected to the outer tube. The microwave field propagates in the annulus between the intermediate tube and the outer tube. The plasma is started with a spark, which is created manually by a short circuit between the intermediate tube and the inner tube. By optimizing these parameters, a stable visible cone-shaped plasma jet is generated on the top opening of the MPT. During the experiments, the MPT was fixed on a translate-stage with a coaxial distance d about 1 cm from the ion inlet of LTQ mass spectrometer to the tip of the plasma.

The mass spectrometer The LTQ mass spectrometer coupled with the MPT source is set for the analysis of zinc and cadmium both in positive mode and negative mode with mainly parameters including the capillary voltage of $\pm(0-24)$ V and the tube lens voltage of ± 52 V. The temperature of the heated capillary was 150°C. The mass spectra were collected with an average time of 0.5 min. Ions of interest were isolated with a mass-to-charge window width of 0.6 units for collision-induced dissociation (CID) experiments by applying a collision energy (CE) of about 35% (arbitrary unit defined by the MS manufacturer). The commercial software Xcalibur is inherent used for LTQ control and data processing.

RESULTS AND DISCUSIONS

Previous studies had shown that the excitation temperature of the MPT plasma is relatively high, about 800-2000K [28, 29], but the ionization degree is low, only 0.01%, far less than that of ICP, 0.2% [30]. Moreover, the MPT plasma expose to the ambient surrounding, hence there are some characteristic groups, for instance, NO_3^- , NH_2^- , H_2O and OH etc., which can be used as reagent ions to make the MPT mass spectra of metal elements easy assignment [20]. In general, the metal ions come into being a regular forms of $\text{M}(\text{NO}_3)_n$ pulsing several H_2O molecules or OH groups in MPT plasma, here M represents a metal element, since the NO_3^- is electrophilic while metal ions are general electron donor. Usually, the nitrate radical comes from the air surroundings, but not the sample solutions [25, 31]. Moreover, depending on the number n, the result group $\text{M}(\text{NO}_3)_n$ can be a cation or anion, which provides an opportunity for the detection of metal elements in both positive mode and negative mode.

The MPT Mass Spectra of Zinc and Cadmium in Positive Mode

Zinc Zinc has five main isotopes, ^{64}Zn with a natural abundance 48.6%, ^{66}Zn with a natural abundance 27.9%, ^{67}Zn with a natural abundance 4.1%, ^{68}Zn with a natural abundance 18.8 %, and ^{70}Zn with a natural abundance 0.6 %. Fig.2 showed the MPT mass spectra of zinc in positive mode collected in the range of 50-250Th with a 500 $\mu\text{g/L}$ zinc standard solution. Obviously, there are three similar mass spectral bands, with main peaks at m/z 146, 162 and 180, respectively. Each spectral band comprises more than five peaks, which seems to conflict with the natural isotopic distribution of zinc. However, thinking about that there are abundant OH group in the plasma and the generation of zinc nitrate OH group is as easy as that of zinc nitrate H_2O group, these spectral bands in Fig. 2 can be unambiguously assigned. For instance, the band of m/z 162 is hybrid $\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$, $\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, as well as the band of m/z 146 is analogous to that of m/z 162 merely with NO_2 replacing NO_3 . The band of m/z 180 seems that the band of m/z 162 attach a H_2O

molecule. The detail assignment of these bands was summarized in Table 1. It is interesting to determine the mixing ratio, here then a simple algorithm is need. For the band of m/z 162, without loss of generality, supposing the yielding of $\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$, $\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ in the MPT plasma are constant, and adopting the theoretical isotopic distribution values of zinc, then a linear equation set can be derived. By regression testing this algebraic system, the mixing ration of $\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$, $\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ can be determined as 1: 3.401: 3.239, as shown in Fig. 3a), b) and c). Then simulating results, i.e. the summation of that in Fig. 3a), b) and c), was shown in Fig. 3d) and was compared with the experimental data. As shown, at low mass side, the simulating results match well with the experimental data, but there is a certain deviation in high mass side, maybe due to the relatively low intensities. For the band of m/z 146 and 180, same algorithm was employed and the simulating results were also summarized in Table 1. It was worth noting that the group containing triple OH was excluded in the assignment of the spectral band of m/z 180, because m/z 177, should be assigned to $^{64}\text{Zn}(\text{NO}_3)\cdot 3\text{OH}$, disappear in this spectrum. Presumably triple-OH group is difficult to produce in the MPT plasma.

Furthermore, the above qualitative analysis can be supported by the tandem mass spectrometry procedure. As a representative, Fig. 4 showed the MS^n mass spectra of the ions of m/z 145 and 146. Fig.4a) is the MS^2 mass spectrum, the precursor ions of m/z 145 produce fragments at m/z 127, 128, 117 and 82 by the lost of H_2O , OH, a 28-Da group and a 63-Da group, respectively. The 28-Da group had been found frequently in the collision induced dissociation processes of nitrate complexes of many transition metal elements in positive mode [25, 31]. The 63-Da group may be $\text{NO}_2\cdot \text{OH}$. The fragments of m/z 127 and 128 can be further dissociated both to generate mainly the sub-fragment at m/z 110, as shown in Fig. 4b) and c). Finally, $^{64}\text{Zn}^+$ is yielded from the sub-precursor ion of m/z 110 in MS^4 mass spectrum by throwing out the NO_2 group (Fig. 4d). This dissociation series show that the ions of m/z

145 is $[^{64}\text{Zn}(\text{NO}_2)\cdot\text{OH}\cdot\text{H}_2\text{O}]^+$. The precursor ions of m/z 146 have the same fragment pattern, as shown in Fig. 4e), and the main fragment ions of m/z 128 dissociated along the route as shown in Fig. 4c) and d). The minor fragment of m/z 129 dissociated further along the similar way to yield the ultimate ions ^{66}Zn by losing consecutively the second OH group and NO_2 group (Fig. 4f and g). Consequently, these experimental data approve that the ions of m/z 146 is the hybrid of $[^{64}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}]^+$ and $[^{66}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}]^+$.

Cadmium Analogously, the cadmium nitrate cation exhibits similar pattern. Fig. 5 showed the MPT mass spectrum of cadmium collected in the interval of m/z 100-240 Th. Three clear spectral bands, located at m/z 195, 211 and 230 were also assigned to the hybrid of $\text{Cd}(\text{NO}_3)\cdot n\text{OH}\cdot m\text{H}_2\text{O}$, $m=0,1$ and $n=0, 1, 2$. A direct identification by using the tandem mass spectrometry is necessary. For simple, only the MPT MS^2 mass spectrum of m/z 212 and 211 were exhibited. Fig. 6 a) is that of the precursor ion of m/z 212, which mainly lost a H_2O to produce the peak at m/z 194. In the MS^3 mass spectrum (Fig. 6 b), the sub-precursor ion of m/z 194 was isolated and then lost a second H_2O molecule to produce the primary ions of m/z 176 and a 28-Da group to obtain the signal at m/z 166. The ions of m/z 176 can be further dissociated in MS^4 experiments to generate the ultimate ions at m/z 114, i.e. ^{114}Cd , with the lost of NO_3 group, as shown in Fig. 6 c). In Fig. 6 d), e) and f), the parallel fragmentation patterns with the corresponding fragment peaks shifting right 1-Th comparing to that of m/z 211 were watched, which give obvious isotopic characteristics. Therefore, these CID processes verify that the signal in Fig.5 belong to the ions cadmium contained.

The MPT Mass Spectra of Zinc and Cadmium in Negative Mode

For zinc and cadmium elements, the positive MPT spectra are extremely complex since a lot of spectral lines of the metallic H_2O groups and the metallic OH groups as well as their isotopes overlap, which prevents the exactly quantitative analysis using the positive mass

spectrometry signal. However, relative to the complexity in positive mode, the negative MPT mass spectra show more concise.

Fig. 7 showed the MPT spectra of zinc and cadmium in negative mode. As shown in Fig. 7 a), the spectral band at m/z 250 comprises five peaks, according with the five natural isotopes of zinc. Moreover, the intensity ratio of peaks at m/z 250, 252, 253, 254, 256 is 1:0.563: 0.0975: 0.367:0.017, which is quite close to the theoretical value 1: 0.574: 0.084: 0.387: 0.012. The spectral band can be assigned to $\text{Zn}(\text{NO}_3)_3^-$, according with the rule aftermentioned. Similarly, the spectral band at m/z 300 in Fig. 7 b) can be also assigned to $\text{Cd}(\text{NO}_3)_3^-$, where the experimental intensity ratio of peaks at m/z 292, 294, 296, 298, 299, 300, 302 is 0.026: 0.023: 0.446: 0.455: 0.839: 0.411:1:0.245, almost according with the natural isotopic distribution of cadmium: ^{106}Cd with a abundance 1.22%, ^{108}Cd with a abundance 0.88%, ^{110}Cd with a abundance 12.39%, ^{111}Cd with a abundance 12.75%, ^{112}Cd with a abundance 24%, ^{113}Cd with a abundance 12.2%, ^{114}Cd with a abundance 28.86%, ^{116}Cd with a abundance 7.56%,. More important, the signal-noise ratio is high enough so that the minimum distribution of natural isotopes, for instance, ^{70}Zn , ^{106}Cd and ^{108}Cd , were all determined clearly in such negative MPT mass spectra. In addition, the negative MPT tandem mass spectra of zinc and cadmium are also regular, i.e. the zinc or cadmium nitrate anion will cast gradually away NO_2 and NO_3 group in CID processes, similar to other common transition metal elements. Fig. 8 showed the representative MS^n mass spectra of $[\text{}^{64}\text{Zn}(\text{NO}_3)_3]^-$. In the first dissociated step, the main product is the ions of m/z 204 by losing a NO_2 group (Fig. 8a), and the fragment ions of m/z 204 will further generate the ions of m/z 172 and m/z 142 with the lost of O_2 and NO_3 , respectively (in Fig. 8 b). For cadmium, parallel fragment pattern can also be obtained (not shown). These characteristic fragments in MS^n mass spectra are used to monitor quantitatively the concentrations of zinc and cadmium elements in water.

Semi-quantitative analysis of zinc and cadmium in negative mode

Nonambiguous mass spectral structure and low background noise make us adopt the negative mode to test the analysis capacity for zinc and cadmium. We measured the limit of detection (LOD) values for zinc and cadmium by using m/z 250 and 300 in the negative MPT mass spectra of zinc and cadmium as monitoring signal and reducing the concentrations down until the signal decayed to 3 times of noise level. The results were 15 μ g/L for zinc and 5 μ g/L for cadmium, respectively. Although these values are much larger than those got in ICP-MS (Table 2), they are almost close to the results obtained in ICP-AES and can meet the real requirement in detection of metal elements in water [32]. In addition, the analysis of a single water sample can be finished in 5~6 minutes. Thus this novel MPT mass spectrometry method provides an alternative approach for field analysis of water inspection.

CONCLUSIONS

Over all, we developed a MPT-MS method for the analysis of zinc and cadmium metal elements in water. We studied the MPT mass spectra of zinc and cadmium in both positive and negative modes, and found that the positive MPT mass spectra are complicated owing to the hybrid of metal nitrate OH group and metal nitrate H₂O group, thus the positive mode is not suitable for the analysis of zinc and cadmium. However, the negative mode is regular and the sensitivity can achieve at about the levels of 10 μ g/L. Therefore, this method will have highly potential applications in quality monitoring of zinc and cadmium ions in water. More promisingly, MPT-MS can be used as the supplement of ICP-MS for the detection of trace metal elements in water.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest and no conflicts of interest.

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Table 1 The Assignment of MPT Mass Spectrum of Zinc in Positive Mode

Band (<i>m/z</i>)	Peak (<i>m/z</i>)	Assignment	Relative Intensity (%)	Simulating Values (%)
146	144	$^{64}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}$	2.384	2.384
	145	$^{64}\text{Zn}(\text{NO}_2)\cdot \text{OH}\cdot \text{H}_2\text{O}$	11.080	11.080
	146	$^{64}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}$, $^{66}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}$	14.306	14.306
	147	$^{66}\text{Zn}(\text{NO}_2)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}$	8.766	6.562
	148	$^{66}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_2)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{68}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}$	8.766	9.283
	149	$^{68}\text{Zn}(\text{NO}_2)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}$	4.418	5.377
	150	$^{68}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}$, $^{70}\text{Zn}(\text{NO}_2)\cdot 2\text{OH}$	4.698	5.034
	151	$^{70}\text{Zn}(\text{NO}_2)\cdot \text{OH}\cdot \text{H}_2\text{O}$	--	0.137
	152	$^{70}\text{Zn}(\text{NO}_2)\cdot 2\text{H}_2\text{O}$	--	0.159
	160	$^{64}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$	26.227	26.198
	161	$^{64}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$	89.201	89.189
	162	$^{64}\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, $^{66}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$	100.000	100.000
	163	$^{66}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$	61.431	53.411
	164	$^{66}\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{68}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$,	73.492	66.432
162	165	$^{68}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$	48.107	41.669
	166	$^{68}\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, $^{70}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}$	38.780	33.189
	167	$^{70}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot \text{H}_2\text{O}$	5.259	1.1011
	168	$^{70}\text{Zn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$	3.787	1.0489
	177	$^{64}\text{Zn}(\text{NO}_3)\cdot 3\text{OH}$	--	--
	178	$^{64}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}\cdot \text{H}_2\text{O}$	5.260	5.260
	179	$^{64}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot 2\text{H}_2\text{O}$	18.654	18.654
	180	$^{64}\text{Zn}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$, $^{66}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}\cdot \text{H}_2\text{O}$	51.332	51.332
180	181	$^{66}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot 2\text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}\cdot \text{H}_2\text{O}$	16.339	11.153
	182	$^{66}\text{Zn}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$, $^{67}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot 2\text{H}_2\text{O}$, $^{68}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}\cdot \text{H}_2\text{O}$	34.712	31.343
	183	$^{67}\text{Zn}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$, $^{68}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot 2\text{H}_2\text{O}$	12.553	11.292
	184	$^{68}\text{Zn}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$, $^{70}\text{Zn}(\text{NO}_3)\cdot 2\text{OH}\cdot \text{H}_2\text{O}$	23.352	18.754
	185	$^{70}\text{Zn}(\text{NO}_3)\cdot \text{OH}\cdot 2\text{H}_2\text{O}$	3.787	0.230
	186	$^{70}\text{Zn}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$	2.595	0.596

Table 2 Comparing the LOD of MPT-MS with ICP-MS and ICP-AES for detection of zinc and cadmium in water (µg/L)

	Zn	Cd
LOD in MPT-LTQ MS in negative mode	15	5
LOD in ICP-MS[17]	0.8	0.06
LOD in ICP-AES[17]	1	4
Ref.32	1000	5

Figure

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