JAAS

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *J. Anal. At. Spectrom.*, 2022, 37, 1876

Sensitive determination of chromium by inductively coupled plasma mass spectrometry using chelate-enhanced nebulized film dielectric barrier discharge vapor generation†

Qian He, *[ab] Chenchen Li,[b] Xiangyu Kong,[b] Minggang Zhao [c] and Jing Zhang*[de]

Received 7th July 2022
Accepted 20th July 2022

DOI: 10.1039/d2ja00235c

rsc.li/jaas

In this work, a novel and sensitive procedure for Cr determination by inductively coupled plasma mass spectrometry (ICP-MS) with a chelate-enhanced nebulized film dielectric barrier discharge (NFDBD) vapor generation sampling system was developed. Using sodium diethyldithiocarbamate (DDTC) as a chelating reagent, the sensitivity of Cr(VI) was specifically increased 10.5-fold by the DDTC-enhanced NFDBD sampling system compared with pneumatic nebulization. The enhancement mechanism and the experimental parameters for Cr(VI) determination such as the DDTC concentration, the solution pH, the input discharge voltage and the argon (DBD plasma gas) flow rate were evaluated in detail. The interferences from the sample matrix at 10–100 mg L^{-1} level were found negligible for trace Cr(VI) determination in the NFDBD sampling system. Under optimized conditions, the relative standard deviation for Cr(VI) was 1.4% at the concentration of 5 μg L^{-1} and the detection limit for Cr(VI) was 0.023 μg L^{-1}. After oxidation of the Cr species to Cr(VI), the total Cr in environmental and biological samples could be sensitively determined by this DDTC-enhanced NFDBD-ICP-MS system. The determined values of the total Cr (29.8 ± 0.3 ng g^{-1} and 402.8 ± 18.8 ng g^{-1}) in the standard reference materials of the simulated natural water sample (GBW08608) and biological tissue sample (GBW10210) agreed well with the certified values (30 ± 2 ng g^{-1} and 0.4 ± 0.08 μg g^{-1}), respectively. It is also worth noting that this is the first report to use DBD induced vapor generation of Cr. Compared with other sampling techniques such as chemical vapor generation and electrothermal vaporization, this proposed technique has a competitive detection limit for trace Cr determination. Furthermore, it eliminates the additional reducing agent for vapor generation, and could operate with low cost and low power (≤65 W).

1. Introduction

Chromium in environmental and biological systems has both essential and toxic properties.[1] The toxicity, bioavailability, and reactivity of chromium not only depend on its chemical form (Cr(VI) and Cr(III)), but also depend on its concentration.[2] Accordingly, except for developing various speciation analysis methods of chromium, it is also of importance to develop a more practical and sensitive method for the determination of chromium concentration in complicated environmental and biological samples.

Inductively coupled plasma mass spectrometry (ICP-MS) has been used for the routine determination of trace metal elements in environmental and biological samples, due to its low detection limit and wide linearity range.[3] However, the determination of four isotopes of chromium (^{50}Cr, ^{52}Cr, ^{53}Cr, ^{54}Cr) by ICP-MS with pneumatic nebulization sampling not only suffers from the low introducing efficiency, but also is susceptible to interferences from sample matrices (*e.g.*, $^{34}S^{16}O^+$, $^{35}Cl^{16}O^1H^+$ and $^{37}Cl^{16}O^+$). Even after column separation, carbonates, chlorides and sulfates would still interfere with the ICP-MS detection of chromium.[4] Thus, developing a high efficiency sampling introduction technique instead of pneumatic nebulization is a meaningful improvement for the sensitive determination of chromium.

Chemical vapor generation (CVG), especially hydride generation (HG) with $Na(K)BH_4$, is adopted as an alternative sample introduction technique to pneumatic nebulization for atomic

---

[a] *Frontiers Science Center for Deep Ocean Multispheres and Earth System, and Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China. E-mail: heqian@ouc.edu.cn*

[b] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China*

[c] *Department of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China*

[d] *Faculty of Science, University of Toyama, Toyama 930-8555, Japan. E-mail: jzhang@sci.u-toyama.ac.jp*

[e] *Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China*

† Electronic supplementary information (ESI) available. See https://doi.org/10.1039/d2ja00235c

and mass spectrometry.[5,6] Non-volatile metal ions such as Zn^{2+}, Pb^{2+}, and Hg^{2+} in solution can be easily transformed into volatile gaseous hydride or atomic vapor through the HG process reacted with Na(K)BH_4,[7–9] which not only greatly increases the sample introduction efficiency, but also significantly reduces the matrix interferences. However, the volatile species of chromium was very difficult to form by the HG process with Na(K)BH_4, as its vapor generation efficiency did not exceed 0.23%.[10–12] Therefore, it is necessary to develop another practical vapor generation technique for chromium determination with high sampling efficiency and low matrix interference.

Dielectric barrier discharge (DBD) plasma induced vapor generation is another sampling introduction technique with high vapor generation efficiency and low matrix interference for element determination.[13–15] Different from the HG technique, it utilizes free radicals and electrons generated by plasma chemical reactions to produce the volatile species of analyte, thus eliminating the usage of Na(K)BH_4. Combining pneumatic nebulization with DBD plasma (as NFDBD), the vapor generation efficiency of elements such as rare earth elements (REEs) could be improved to 20–30%,[16] as the REEs were also very difficult to be vaporized in the HG process similar to chromium. Moreover, our group further found that with the addition of chelate such as 2,2,6,6-tetramethyl-3,5-heptanedione (DPM), the REEs vapor generation efficiency in the NFDBD system could be further increased to 50–60%.[17] Considering that some chelating agents such as diethyldithiocarbamate (DDTC),[4,18,19] ammonium pyrrolidine dithiocarbamate (APDC),[20,21] and 8-hydroxyquinoline (8-Ox)[22] had also been reported to enhance the volatility of chromium, it is of significance to investigate the feasibility of chelate-enhanced chromium vapor generation by NFDBD plasma in order to sensitively determine the amount of chromium in complicated environmental and biological samples.

In this work, a sensitive procedure for chromium determination by ICP-MS with a chelate-enhanced NFDBD vapor generation sampling system was developed. To the best of our knowledge, this is the first report on the generation of volatile chromium species using DBD plasma. Several experimental parameters for chromium determination including the type and concentration of chelating agents, the concentration of carrier solution, the input discharge voltage and the argon flow rate, as well as the potential interference by matrix elements were studied. Finally, the developed chelate-enhanced NFDBD vapor generation sampling system was applied to determine the amount of chromium in environmental and biological samples for method validation.

2. Experimental

2.1. Instrumentation

The setup of the chelate-enhanced NFDBD vapor generation coupled with ICP-MS (Fig. S1†) for Cr determination was similar to that reported in our previous work.[17] The NFDBD vapor generator was composed of a commercial concentric nebulizer for pneumatic nebulization and a cylindrical DBD discharge reactor for vapor generation. The DBD discharge reactor consisted of an inner glass tube (1.4 mm inner diameter, 3 mm outer diameter, 92 mm length) with an inserted copper rod electrode, and an outer glass tube (10 mm inner diameter, 12 mm outer diameter, 110 mm length) with a piece of copper foil (40 mm length) wrapped outside as the other electrode. The two electrodes were connected by a commercial ozone generator power supply (Anhui Tianze Electronic Technology Co. Ltd, China) with a maximal power output of 65 W, an alternating current frequency of 28 kHz and an output voltage of 25 kV at 220 V input. A Thermo iCAP Q ICP-MS (Thermo Fisher Scientific, Bremen, Germany) was used for Cr determination throughout the experiments. To decrease the interference of the plasma gas-containing species for Cr^+ determination, kinetic energy discrimination (KED) with a constant helium stream was used throughout the experiments.[23,24] The instrument conditions of ICP-MS for Cr determination, such as the isotope of Cr, RF power and helium gas flow rate, were optimized as shown in Fig. S2a–c† based on the maximized ratio of signal-to-noise (S/N). The optimized parameters in ICP-MS are listed in Table S1.† A tandem set of two gas–liquid separators (GLS1 and GLS2) connected NFDBD and ICP-MS were used to remove the solvent as much as possible. A flow injection (FI) valve (Rheodyne 7725i, 200 μL, USA) was also used coupled with NFDBD as a whole sample introduction system (FI-NFDBD) in this work for reduced sample consumption and high sample throughput.

2.2. Reagents, solutions and samples

All chemicals used in the experiments were at least analytical reagent grade. The chelating agents of sodium diethyldithiocarbamate (DDTC), ammonium pyrroldinedithiocarbamate (APDC) and 8-hydroxyquinoline (8-Ox) were all purchased from Adamas (Shanghai, China). Nitric acid and hydrochloric acid with trace elemental level purchased from Merck Drugs & Biotechnology (Germany) were used for Cr(VI) and Cr(III) solution pH adjustment, respectively. Hydrogen peroxide (Sinopharm Chemical Reagent Co., Ltd, China) was used as an oxidizing agent for the total Cr analysis. The following solid chemicals of NaCl, Na_2CO_3, $NaNO_2$, KH_2PO_4, $BaCl_2\cdot2H_2O$, $CaCl_2$, $MgSO_4\cdot7H_2O$, $Co(NO_3)_2\cdot6H_2O$, $Fe_2(SO_4)_3\cdot xH_2O$, $Al_2(SO_4)_3\ldots18H_2O$, $ZnSO_4\cdot7H_2O$ and $PbSO_4$ (Sinopharm Chemical Reagent Co., Ltd, China) were employed for the matrix interference study.

Ultrapure deionized water (18.2 MΩ cm, obtained from the Milli-Q ELIX advantage system, Millipore, USA) was used throughout the experiments as the solvent. A stock standard solution of Cr(VI) (Cr^{6+}, SRM-C11Y1AAO, 1000 mg L^{-1}) was purchased from Bolinda (Shenzhen, China). A stock standard solution of Cr(III) (Cr^{3+}, GSB 04-1723-2004e, 1000 mg L^{-1}) was purchased from the National Center of Analysis and Testing for Non-Ferrous Metal & Electronic Materials (Beijing, China). The working standard solution of Cr(VI) and Cr(III) were prepared freshly by diluting the stock standard solution with Milli-Q water. The complexing agents of DDTC and APDC were all dissolved in Milli-Q water, while the complexing agent of 8-Ox was dissolved in 10% (v/v) ethanol–water solution.

One certified reference material of simulated natural water sample (GBW08608) sourced from the National Institute of Metrology (Beijing, China) and one certified reference material of freeze-dried salmon powder (GBW10210) from Tanmo Quality Inspection Technology Co., Ltd (Changzhou, China) were used for method validation. Spike-recovery tests were carried out from one rainwater sample collected at our university campus (Qingdao, China), one river water sample collected from Dagu River (Qingdao, China), one seawater sample collected from Shilaoren Beach (Qingdao, China), one biological tissue sample of *Nibea albiflora* from Sanggou Bay (Weihai, China) and one sediment sample from Sanggou Bay (Weihai, China). The detailed pretreatment processes of these environmental and biological tissue samples for the total Cr determination were shown in ESI.†

2.3. Analytical procedure

In this FI-NFDBD vapor generation sampling system, the aqueous solution of Cr mixed with chelating agent was first injected into the sample loop, and then carried away by carrier solution into the concentric nebulizer with a peristaltic pump. Then, the fine droplets from the nebulizer would spray onto the outside surface of the inner tube of the DBD discharge reactor to form a thin film. Once the thin film was formed, the DBD plasma could be turned on, and then some volatile Cr-containing species would be formed immediately in the thin film area. Subsequently, the volatile Cr species were introduced to a tandem set of two gas–liquid separators (GLS1 and GLS2). After achieving two-stage gas–liquid separation from the solvent as much as possible, the volatile Cr species were directly introduced into ICP-MS for determination. The wastes from the DBD discharge reactor and GLS2 were discharged out of this system by another peristaltic pump.

3. Results and discussion

3.1 Feasibility of Cr vapor generation by the FI-NFDBD sampling system

The vapor generation behavior of Cr with different chemical forms (Cr(VI) and Cr(III), 5 μg L^{-1}) by the FI-NFDBD sampling system with Milli-Q water as a carrier without the assistance of any chelating reagent was investigated first. The temporal profiles of Cr(VI) and Cr(III) that changed with DBD plasma off and on are shown in Fig. 1a and b. It could be seen that although the signals of Cr(VI) and Cr(III) all appeared in the nebulization process with the DBD plasma off, an enhancement of 2.4-fold and 1.9-fold for the Cr(VI) and Cr(III) signals respectively were found when the DBD plasma was on. Our previous work[25] had reported that the DBD plasma did not affect the nebulization efficiency. Therefore, the enhancement results for Cr(VI) and Cr(III) were mainly caused by the volatile species of Cr produced by the DBD induced vapor generation process. These results also indicate that although the FI-NFDBD sampling system can not be used for speciation analysis of Cr(VI) and Cr(III), it is suitable for the sensitive determination of the total Cr after the valence states of Cr are unified.

3.2 Enhancement effect of chelating agents on Cr vapor generation by FI-NFDBD sampling system

The enhancement effect of chelating agents (such as DDTC, APDC and 8-Ox) with the same concentration (0.02%, v/v) on Cr(VI) (5 μg L^{-1}) vapor generation by the FI-NFDBD sampling system with Milli-Q water as the carrier was further investigated. As show in Fig. 2a, compared with the peak area of Cr(VI) with no chelating agents, DDTC presented the highest enhancement effect (4.0-fold) for Cr(VI) determination by the FI-NFDBD sampling system. To further validate whether the enhancement effect with DDTC for Cr(VI) determination was related to the nebulization process or not, the effect of DDTC on the Cr(VI) determination in FI-PN sampling mode (*i.e.*, FI-NFDBD with DBD plasma off) was also investigated. As shown in Fig. 2b, only a slight enhancement (1.9-fold) was found for Cr(VI) with DDTC compared with Cr(VI) with no chelating agents in FI-PN sampling mode, indicating that the enhancement effect with DDTC for Cr(VI) determination was mainly caused by the increased vapor generation efficiency in the DBD process.

The enhancement mechanism of DDTC in the FI-NFDBD vapor generation sampling system for Cr(VI) determination might be attributed to the kinetic thermal temperature of 300 K–1000 K in DBD plasma,[26] which was beneficial to promote the vaporization of the Cr(VI)-DDTC chelate, as the vaporization temperature of this chelate was less than the temperature of 1000 °C reported in the ETV sampling system.[19] Besides this, the addition of chelating reagents might also change the plasma chemical reactions in the DBD plasma and thus enhance the vapor generation efficiency. Meanwhile, the vaporization temperature of the Cr(VI)-APDC chelate was less than 1500 °C;[21] thus, the enhancement of APDC was not obvious. At the same time, no enhancement was found with 8-Ox for Cr(VI) determination. This might be due to the specific reaction between 8-Ox and Cr(III),[22] not Cr(VI), at pH 4.0 used in this chelation test.

Besides Cr(VI), the enhancement effect of chelating agents such as DDTC, APDC and 8-Ox with the same concentration (0.02%, v/v) for Cr(III) (5 μg L^{-1}) vapor generation by the FI-NFDBD sampling system with Milli-Q water as the carrier was also studied (Fig. 2c). However, only 8-Ox presented an obvious enhancement (2.3-fold) for Cr(III) determination compared with Cr(III) with no chelating agents. The enhancement effect with 8-Ox for Cr(III) determination was also mainly caused by the increased vapor generation efficiency in DBD process since only 1.3-fold enhancement with 8-Ox for Cr(III) determination by the FI-PN sampling system (Fig. 2d) was found. The other two chelates of DDTC and APDC all showed no enhancement for Cr(III) determination, which might also be due to the specific reaction between DDTC[19] or APDC[27] with Cr(VI), rather than Cr(III), at pH 4.0 used in this chelation test.

Considering that the enhancement of Cr(VI) with DDTC was much higher than that of Cr(III) with 8-Ox, Cr(VI) with DDTC enhancement was finally selected for procedure optimization and sample analysis for the sensitive determination of the total Cr in the following studies.

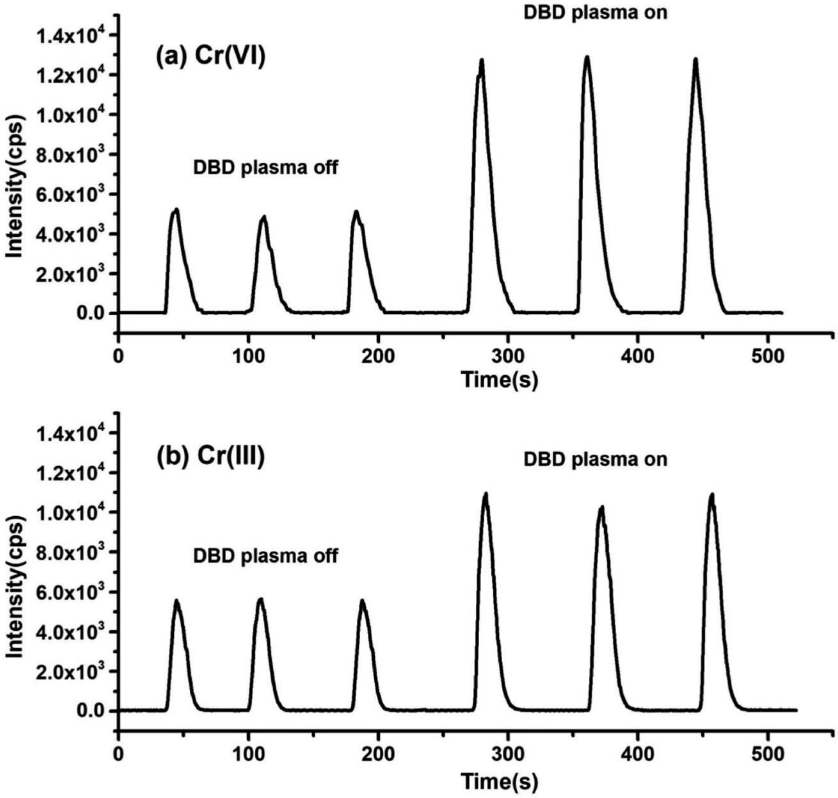

Fig. 1 Temporal profiles of 5 µg L^{-1} Cr(VI) (a) and Cr(III) (b) solution using FI-NFDBD sampling systems changed with DBD plasma off and on.

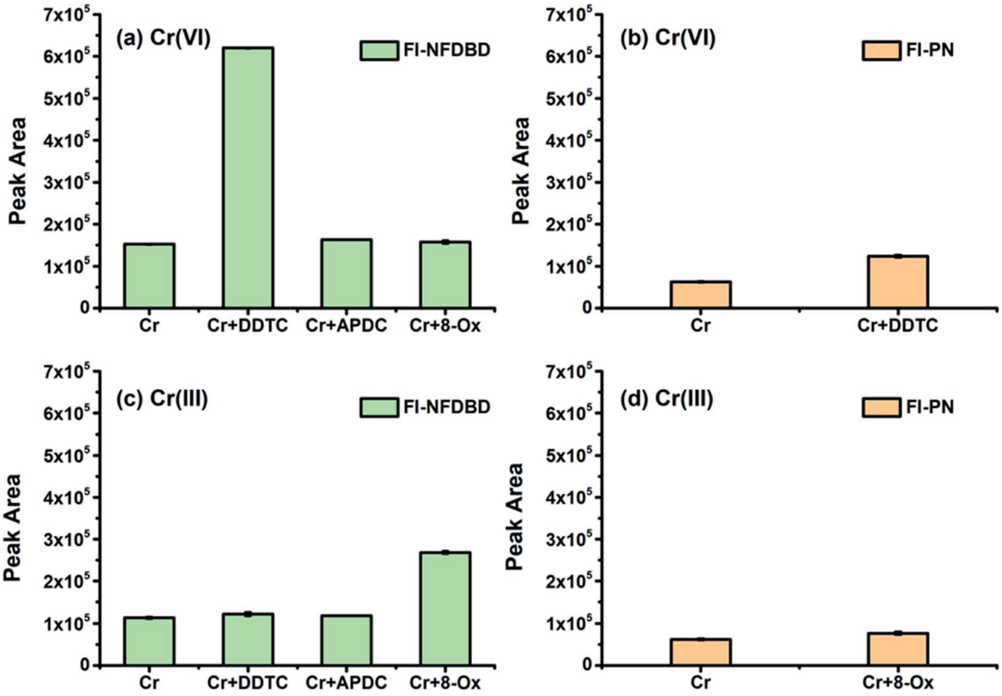

Fig. 2 (a) Effect of chelating agents of DDTC, APDC and 8-Ox (0.02%, v/v) on the Cr(VI) (5 µg L^{-1}) peak area in the FI-NFDBD sampling mode; (b) effect of DDTC (0.02%, v/v) on the Cr(VI) (5 µg L^{-1}) peak area in the FI-PN sampling mode; (c) effect of chelating agents of DDTC, APDC and 8-Ox (0.02%, v/v) on the Cr(III) (5 µg L^{-1}) peak area in the FI-NFDBD sampling mode; (d) effect of 8-Ox (0.02%, v/v) on the Cr(III) (5 µg L^{-1}) peak area in the FI-PN sampling mode. Each datum is the average of three measurements ($n = 3$). Error bars are defined as ± standard deviation (SD).

Table 1 The variation range and optimum value of the experimental parameters

Experimental parameter	Variation range	Optimum value
DDTC concentration	0.001–0.02% (v/v)	0.005% (v/v)
Solution pH	2.0–5.5	4.0
Input discharge voltage	50–250 V	250 V
Argon flow rate	0.8–1.3 L min^{-1}	1.1 L min^{-1}
Chelation reaction time	0–60 min	30 min

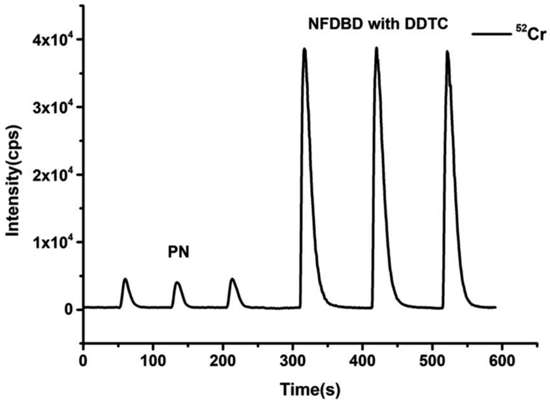

Fig. 3 The temporal profile of Cr(VI) (5 μg L^{-1}) using FI-PN sampling mode and DDTC-enhanced FI-NFDBD vapor generation sampling mode. (DDTC: 0.005%, v/v).

3.3 Optimization of the experimental parameters

To obtain the maximum sampling efficiency of Cr(VI) by this chelate-enhanced NFDBD vapor generation approach, the effects of the experimental parameters including DDTC concentration, solution pH, input discharge voltage, argon flow rate and chelation reaction time on the Cr(VI) sensitivity were investigated with univariate optimization method. The results are shown in Fig. S3 in ESI†.

Under the optimum experimental parameters as shown in Table 1, the temporal profile of Cr(VI) (5 μg L^{-1}) using the FI-PN sampling mode and DDTC-enhanced FI-NFDBD vapor generation sampling mode were compared (Fig. 3). The sensitivity for Cr(VI) by DDTC-enhanced FI-NFDBD sampling mode was increased by 10.5-fold compared with that for the FI-PN sampling mode. The vapor generation efficiency for Cr(VI) in this DDTC-enhanced NFDBD sampling system was also estimated from a comparison of the Cr(VI) signal in the Cr(VI) standard solution (5 μg L^{-1}) mixed with DDTC (0.005%, v/v) and its waste solution. The waste solution was collected from the waste of the DBD setup, the GLS 1 and the GLS 2 after the standard solution was submitted to NFDBD system using continuous flow mode. The signals of the Cr(VI) standard solution and its waste solution were all determined by ICP-MS using the FI-PN sampling mode. The mass spectrometry peak area for Cr(VI) waste was 46.6 ± 0.2% of the feed values, resulting in a vapor generation efficiency of Cr(VI) at 53.4 ± 0.2%.

3.4 Evaluation of the matrix interference

To investigate the influence of the coexisting matrix in environmental samples for Cr(VI) determination, the effect of some alkaline, alkaline earth, transition metal ions and anions on the recovery of the Cr(VI) peak area by this DDTC-enhanced FI-NFDBD vapor generation sampling system was studied, as shown in Table 2. The recoveries of Cr(VI) at 5 μg L^{-1} were all found in the range of 90.7 ± 0.4% to 104.3 ± 1.4% from the coexisting matrix of NaCl, Na_2CO_3, $NaNO_2$, KH_2PO_4, $MgSO_4$, $Co(NO_3)_2$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $ZnSO_4$ and $PbSO_4$ presented at 10 or 100 mg L^{-1}. However, slightly lower recoveries of 85.3 ± 0.5% and 81.8 ± 0.8% for $CaCl_2$ and $BaCl_2$, respectively, at a concentration of 100 mg L^{-1} were observed. This might be due to the mass spectral interference of Cl^-.[28] Besides these, considering that the DDTC degradation products may present as another potential source of spectral interferences for Cr(VI) determination, the blank signal profiles of Cr(VI) by only DDTC (0.005%, v/v) using the FI-NFDBD sampling system was also investigated, as shown in Fig. S4.† The peak area of Cr(VI) in the DDTC blank was about 1.5% of Cr(VI) at 5 μg L^{-1}. Thus, to reduce the influence of the matrix interference by DDTC, the signal of Cr(VI) in the DDTC blank was subtracted in the linear analysis and sample determination process.

3.5 Analytical characteristics

The analytical performance of Cr(VI) determined by ICP-MS using this DDTC-enhanced FI-NFDBD vapor generation sampling system was also investigated under the optimized

Table 2 Influence of the coexisting matrix ions on the recovery of Cr(VI) (5 μg L^{-1}) determined by the DDTC-enhanced FI-NFDBD vapor generation sampling system. Each datum is the average of three measurements (n = 3). The uncertainty is defined as ±SD

Matrix	Concentration (mg L^{-1})	Recovery (%)
NaCl	10	95.2 ± 1.3
	100	90.7 ± 0.4
Na_2CO_3	10	92.2 ± 0.6
	100	91.5 ± 0.3
$NaNO_2$	10	96.6 ± 0.6
	100	94.8 ± 1.1
KH_2PO_4	10	99.4 ± 0.2
	100	97.3 ± 0.2
$CaCl_2$	10	95.3 ± 0.2
	100	85.3 ± 0.5
$BaCl_2$	10	99.0 ± 1.5
	100	81.8 ± 0.8
$MgSO_4$	10	97.3 ± 0.4
	100	90.8 ± 0.4
$Co(NO_3)_2$	10	97.1 ± 1.1
	100	96.2 ± 0.7
$Fe_2(SO_4)_3$	10	97.7 ± 0.8
	100	94.5 ± 0.2
$Al_2(SO_4)_3$	10	102.8 ± 0.8
	100	104.3 ± 1.4
$ZnSO_4$	10	95.7 ± 1.4
	100	94.8 ± 0.2
$PbSO_4$	10	94.9 ± 1.1
	100	92.9 ± 1.3

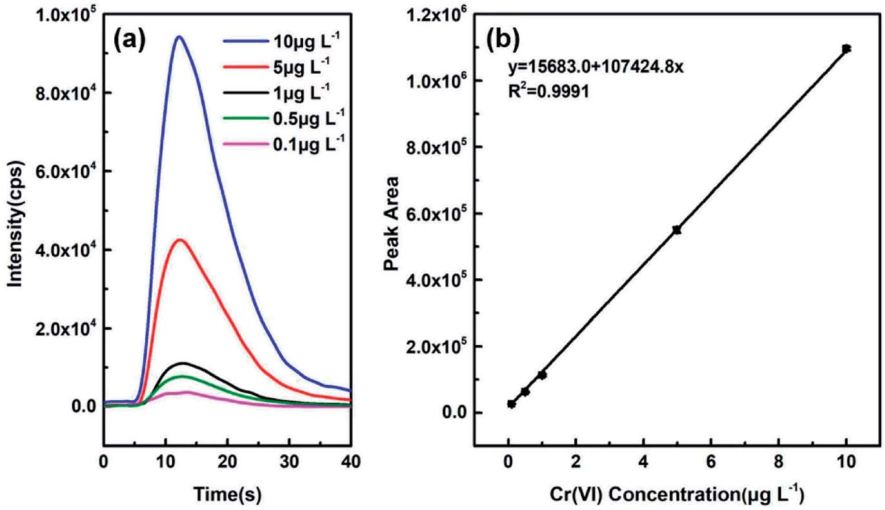

Fig. 4 Temporal profile (a) and calibration curve (b) of Cr(VI) determined by ICP-MS using this DDTC-enhanced FI-NFDBD vapor generation sampling system. Peaks were obtained with Cr(VI) standard solutions between 0.1 and 10 μg L^{-1}. Error bars are defined as ± SD.

Table 3 Comparison of the detection limit (LOD) of Cr determined by ICP-MS with different sampling techniques

Sampling technique	LOD (μg L^{-1})	Ref.
DDTC-enhanced CVG	0.2	4
DDTC-enhanced electrothermal vaporization	0.045	19
Hydraulic high-pressure nebulization	0.1	29
Ultrasonic nebulization	0.011	30
Dual mode with nebulization and CVG	0.017	31
DDTC-enhanced NFDBD vapor generation	0.023	This work

conditions. Calibration curve (R^2 = 0.9991) was obtained between the peak area and different Cr(VI) concentrations in the range of 0.1 μg L^{-1} to 10 μg L^{-1}, as shown in Fig. 4. The relative standard deviation (RSD, $n = 5$) of Cr(VI) determined at 5 μg L^{-1} was calculated as 1.4%. The detection limit (LOD) of Cr(VI), using the definition of $3sm^{-1}$ (where s is the standard deviation, corresponding to 11 blank measurements, and m is the slope of the calibration graph), was calculated as 0.023 μg L^{-1}. Comparing the LOD of Cr with those of other sampling techniques as shown in Table 3, this proposed DDTC-enhanced FI-NFDBD vapor generation technique was very competitive for trace Cr determination.

3.6 Sample application

To evaluate the accuracy of the proposed procedure, the total Cr concentration in the certified reference materials of the simulated natural water sample (GBW08608) and freeze-dried salmon powder (GBW10210) were first analyzed by ICP-MS with this DDTC-enhanced FI-NFDBD vapor generation sampling system. With the standard curve method, the concentrations of the total Cr determined by the proposed procedure all agreed well with the certified values as shown in Table 4, suggesting the good accuracy of this DDTC-enhanced FI-NFDBD vapor generation sampling system for Cr determination.

To further evaluate the application of the proposed procedure, the total Cr concentrations and recoveries were analyzed in three environmental water samples, including rainwater, river water, seawater, and one biological tissue sample of *Nibea albiflora*, and one bay sediment sample. After pretreatment, oxidation and chelation, the rainwater sample, river water sample, *Nibea albiflora* tissue sample and bay sediment sample were analyzed with

Table 4 Analytical results of the total Cr concentration and recovery in water, biological and sediment samples by ICP-MS using the DDTC-enhanced FI-NFDBD sampling system. Each datum is the average of five measurements ($n = 5$). The uncertainty is defined as ± SD

		This work		
Sample	Certified value	Found	Spiked	Recovery (%)
GBW08608	30 ± 2 ng g^{-1}	29.8 ± 0.3 ng g^{-1}	—	—
GBW10210	0.4 ± 0.08 μg g^{-1}	402.8 ± 18.8 ng g^{-1}	—	—
Rainwater	—	0.38 ± 0.01 μg L^{-1}	1 μg L^{-1}	100.1 ± 1.9
River water	—	0.20 ± 0.01 μg L^{-1}	1 μg L^{-1}	95.8 ± 3.1
Seawater	—	0.85 ± 0.02 μg L^{-1}	1 μg L^{-1}	97.5 ± 1.8
Nibea albiflora	—	83.5 ± 2.7 ng g^{-1}	80 ng g^{-1}	92.4 ± 3.9
Bay sediment	—	275.5 ± 5.6 ng g^{-1}	400 ng g^{-1}	95.0 ± 1.6

standard curve method, while the seawater sample was analyzed with standard addition method due to the matrix effect. From Table 4, the concentrations of total Cr in these samples were all detectable by our procedure, especially for the three water samples at sub μg L^{-1} level. In addition, the recoveries in these samples were all found between 92.4 ± 3.9% and 100.1 ± 1.9%, which were satisfactory. All of these results indicated that our proposed DDTC-enhanced FI-NFDBD vapor generation sampling system with ICP-MS detection can reliably determine trace Cr in complicated environmental and biological samples.

4. Conclusion

In this work, a novel and sensitive procedure was developed for Cr determination in environmental and biological samples by ICP-MS with a DDTC-enhanced FI-NFDBD vapor generation sampling system. To the best of our knowledge, this is the first report on vapor generation of Cr by DBD plasma. A 10.5-fold enhancement in sensitivity of Cr(VI) was realized using DDTC-enhanced FI-NFDBD vapor generation compared to the conventional pneumatic nebulization. This procedure also tolerated 10–100 mg L^{-1} matrix interference, thus enabling analysis of environmental freshwater samples, sediment and biological tissue samples with just the standard curve method. Moreover, this procedure is sensitive and simple in operation with low cost and low power, thus serving as a useful alternative to other sampling techniques such as electrothermal vaporization and ultrasonic nebulization for trace Cr determination. Future research can further identify the volatile product of Cr in the DDTC-enhanced NFDBD vapor generation system and develop a speciation method of Cr(VI) and Cr(III) by this chelate-enhanced DBD vapor generation sampling system.

Author contributions

Qian He: conceptualization, methodology, writing – original draft, writing – review & editing. Chenchen Li: investigation. Xiangyu Kong: investigation. Minggang Zhao: fund acquisition. Jing Zhang: resources, supervision, fund acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [No. 41890801], Fundamental Research Funds for the Central Universities of Ocean University of China [No. 202042009], and the JSPS KAKENHI [No. 20H04319].

References

1 Y. Ogawa, S.-i. Yamasaki and N. Tsuchiya, *Anal. Sci.*, 2010, **26**, 867–872.
2 S. Chen, S. Zhu and D. Lu, *At. Spectrosc.*, 2011, **32**, 90–94.
3 K. Benkhedda, H. G. Infante, F. C. Adams and E. Ivanova, *TrAC, Trends Anal. Chem.*, 2002, **21**, 332–342.
4 W. Zou, C. Li, J. Hu and X. Hou, *Talanta*, 2020, **218**, 121128.
5 A. R. Kumar and P. Riyazuddin, *Anal. Sci.*, 2005, **21**, 1401–1410.
6 Z. Long, Y. Luo, C. Zheng, P. Deng and X. Hou, *Appl. Spectrosc. Rev.*, 2012, **47**, 382–413.
7 M. A. P. da Costa, D. L. Franca da Silva, F. d. S. Dias, A. d. F. Santos Junior and W. N. Lopes dos Santos, *Anal. Methods*, 2020, **12**, 1711–1719.
8 J. X. Li, F. Lu, T. Umemura and K. Tsunoda, *Anal. Chim. Acta*, 2000, **419**, 65–72.
9 X. Guo, C. G. Zheng, Z. X. Jin and Z. Y. Tang, *Microchim. Acta*, 2004, **148**, 221–225.
10 T. Wickstrom, W. Lund and R. Bye, *Analyst*, 1996, **121**, 201–204.
11 P. Pohl and W. Zyrnicki, *Anal. Chim. Acta*, 2001, **429**, 135–143.
12 M. Welna, J. Lasowska and W. Zyrnicki, *J. Braz. Chem. Soc.*, 2011, **22**, 1164–1169.
13 Q. He, Z. Zhu and S. Hu, *Rev. Anal. Chem.*, 2014, **33**, 111–121.
14 P. Pohl, K. Greda, A. Dzimitrowicz, M. Welna, A. Szymczycha-Madeja, A. Lesniewicz and P. Jamroz, *TrAC, Trends Anal. Chem.*, 2019, **113**, 234–245.
15 X. Liu, Z. Zhu, P. Xing, H. Zheng and S. Hu, *Spectrochim. Acta, Part B*, 2020, **167**, 105822.
16 Q. He, X. Wang, H. He and J. Zhang, *Anal. Chem.*, 2020, **92**, 2535–2542.
17 Q. He, Y. Qiao, M. Zhao and J. Zhang, *Spectrochim. Acta, Part B*, 2022, **191**, 106396.
18 Z. F. Fan, B. Hu, Z. C. Jiang and L. Pan, *Microchim. Acta*, 2006, **153**, 211–217.
19 S. Chen and D. Lu, *At. Spectrosc.*, 2012, **33**, 9–13.
20 Y.-Z. Yi, S.-Y. Wu, S.-J. Jiang and A. C. Sahayam, *At. Spectrosc.*, 2013, **34**, 39–47.
21 Z. F. Fan, B. Hu and Z. C. Jiang, *Talanta*, 2006, **68**, 1359–1365.
22 X. S. Zhu, H. Bin, Z. C. Jiang, Y. L. Wu and S. Xiong, *Anal. Chim. Acta*, 2002, **471**, 121–126.
23 C. D. Quarles Jr, D. R. Jones, J. M. Jarrett, G. Shakirova, Y. Pan, K. L. Caldwell and R. L. Jones, *J. Anal. At. Spectrom.*, 2014, **29**, 297–303.
24 M. Carmen Barciela-Alonso, M. Castrelo Otero, M. R. Dominguez Gonzalez, E. Pena-Vazquez and P. Bermejo-Barrera, *At. Spectrosc.*, 2016, **37**, 91–95.
25 Q. He, X. Wang, H. He and J. Zhang, *J. Anal. At. Spectrom.*, 2020, **35**, 2704–2711.
26 K. Kunze, M. Miclea, G. Musa, J. Franzke and K. Niemax, *Spectrochim. Acta, Part B*, 2002, **57**, 137–146.
27 V. Orescanin, L. Mikelic, S. Lulic and M. Rubcic, *Anal. Chim. Acta*, 2004, **527**, 125–129.
28 Y. C. Sun, C. Y. Lin, S. F. Wu and Y. T. Chung, *Spectrochim. Acta, Part B*, 2006, **61**, 230–234.
29 C. Barnowski, N. Jakubowski, D. Stuewer and J. A. C. Broekaert, *J. Anal. At. Spectrom.*, 1997, **12**, 1155–1161.
30 B.-H. Chen and S.-J. Jiang, *J. Anal. At. Spectrom.*, 2021, **36**, 142–149.
31 M. Mulugeta, G. Wibetoe, C. J. Engelsen and A. Asfaw, *Anal. Bioanal. Chem.*, 2009, **393**, 1015–1024.