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Dual-mode chemical vapor generation for simultaneous determination of hydride forming and non-hydride forming elements by atomic fluorescence spectrometry

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Abstract

A dual-mode chemical vapor generation integrating hydride generation and photochemical vapor generation was developed for simultaneous multi-element analysis of hydride forming and non-hydride forming elements by atomic fluorescence spectrometry. Four elements were selected as model elements of hydride forming (As, Cd) and non-hydride forming (Ni, Fe) elements to validate this proposed method. Standard or sample solutions were separately pumped to mix with tetrahydroborate, and concentrated formic acid and ammonia, and then directed to a hydride generator and a photochemical reactor to realize simultaneous hydride generation and photochemical vapor generation, respectively. Optimum conditions for dual-mode chemical vapor generation were carefully investigated. Under the optimized conditions, limits of detection of 0.05, 0.008, 0.8 and 0.1 μg L⁻¹ were obtained for As, Cd, Fe and Ni, respectively. The precisions were 5.0, 5.5, 4.3 and 4.5% (n=6, RSDs) for 2 μg L⁻¹ of As, 1 μg L⁻¹ of Cd, 50 μg L⁻¹ of Fe and 10 μg L⁻¹ of Ni, respectively. This method was validated for accuracy with three certified reference water samples, and applied to the simultaneous determination of these elements in a tap water sample with spike recoveries in the range of 95-99%.
1. Introduction

In common inorganic analytical laboratories, the demand for simultaneous high throughput and sensitive determination of elements has never been greater because a large number of samples have to be determined every day. Atomic spectrometric techniques such as atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) can be used to accomplish the purpose of high throughput because of their capability of simultaneous multi-element analysis\textsuperscript{1,2}. However, the determination of some elements in many environmental samples by these techniques is challenging due to both low content and the serious interferences from sample matrix. Therefore, many efforts have been devoted to improve both sensitivity and throughput\textsuperscript{3-5}. Among these, chemical vapor generation (CVG) provides an elegant example of simultaneously improving sensitivity, sample preparation strategies and throughput. Compared to conventional pneumatic nebulization (PN), CVG provides several unique advantages of higher efficiency of sample introduction (~100%), less matrix and spectral interferences and better sensitivity and selectivity\textsuperscript{5-8}. Hydride generation (HG) is the most used CVG technique because of its high efficiency and simple reaction\textsuperscript{9-12}. Although the scope of elements amenable to HG has expanded from classic hydride forming elements (As, Sb, Bi, Hg, Cd, Ge, Sn, Pb, Zn, Se and Te) to include several transition and noble elements \textit{via} rapid separation of the unstable volatile species from liquid phase or addition of “enhancement” regents and modifiers\textsuperscript{13-17}, their HG efficiencies are too low to be analytically useful. Moreover, different hydride-forming elements have different optimum experimental conditions for hydride generation\textsuperscript{18}. Therefore, simultaneous multi-element analysis using HG is quite limited. Indeed, several sample introduction systems have been developed for simultaneous determination of both hydride forming and non-hydride forming elements\textsuperscript{18}. Sturgeon et al.\textsuperscript{19,20} introduced rapid reaction and gas-liquid phase separation devices to not only retain the sensitivity on the determination of non-hydride forming elements with PN but also improve that of hydride forming elements with HG. McLaughlin and
Brindle\textsuperscript{21} developed a multi-mode sample introduction spray chamber (MSIS), which could introduce analyte to atomizer with either CVG or PN, separately or simultaneously, thereby achieving multielement determination of hydride-forming and non-hydride forming elements. This MSIS chamber was further modified, improved and expanded its application scope\textsuperscript{1,22-27}. However, the sensitivity on the determination of non-hydride forming elements has not yet been improved. Therefore, it is attractive to develop a robust technique for simultaneously sensitive determination of both hydride forming elements and non-hydride forming elements. Photochemical vapor generation (PVG) was firstly reported by Sturgeon et al.\textsuperscript{28-33}, which utilizes UV irradiation to convert analytes ions to volatile species in the presence of low molecular weight (LMW) organic compounds. PVG not only retains the principle advantages of conventional CVG but further offers several unique advantages of elimination of the need for fresh tetrahydroborate solution and minimization of H\textsubscript{2} production\textsuperscript{34-39}. As a result, the instability of plasma arising from H\textsubscript{2} can be significantly alleviated as PVG used as alternative to HG. Most importantly, PVG expanded the CVG application range to determine several non-hydride forming elements including Fe, Co, Ni and I\textsuperscript{2,29,30,32}. Despite of the increased interest in PVG over the past several years, the PVG efficiencies of some hydride forming elements such as Sn, Pb and Cd are too low to be analytically useful for real sample analysis\textsuperscript{40}. The aim of this work is to design a dual-mode chemical vapor generation (DM-CVG) system that integrates HG and PVG to accomplish simultaneous multi-element analysis of hydride forming and non-hydride forming elements by atomic spectrometry. The method not only retains the advantage of high throughput because of its capability of simultaneous multi-element analysis but also offers high sensitivity, and low matrix and spectra interferences for trace elemental analysis.

2. Experimental section

2.1. Instrumentation

The whole instrumental setup is shown in Fig. 1 and mainly consists of a laboratory-built DM-CVG system, two three-channel peristaltic pumps (BT100-02,
Baoding Qili Precision Pump Co., Ltd., Baoding, China) and a commercial four-channel HG non-dispersive atomic fluorescence spectrometer (AFS-9600, Beijing Haiguang Instrumental Co., Beijing, China) fitted with a quartz gas-liquid separator (GLS), a quartz atomizer, the commercial coded high-intensity hollow cathode lamps (HI-HCLs) of As and Cd, and the custom-built HI-HCLs of Fe and Ni. It should be noted that the atomic fluorescence spectrometer is just able to simultaneously determine two elements despite that it retains four channels to fix four HCLs. Therefore, we had to determine one hydride forming element together with one non-hydride forming elements within a run for evaluation of the feasibility of simultaneous multi-elements CVG of hydride forming and non-hydride forming elements.

The DM-CVG system is made of a UV photochemical reactor and a hydride generator. The photochemical reactor was described in our previous works and consisted of a coiled tube (60 cm length × 2.0 mm i.d. × 3.0 mm o.d.) that was wrapped around a 15 W low pressure mercury vapor UV lamp (253.7 nm, Philip, Holland). The photochemical reactor was subsequently wrapped with aluminum foil to prevent the operator from UV irradiation and reflect UV radiation from the lamp to enhance PVG efficiency. The hydride generator is mainly consisted of a polytetrafluoroethylene (PTFE) tube (about 2.4 mL). This DM-CVG system was finally housed in a black box to avoid UV leak.

### 2.2. Reagents and sample preparation

All the used reagents were at least of analytical reagent grade. All solutions were prepared using high purity deionized water (DIW, 18 MΩ cm) produced from a water purification system (Chengdu Ultrapure Technology Co., LTD, China). The standard solutions containing Fe(III), Ni(II), As(III) and Cd(II) were prepared daily by dilution of their 1000 mg L⁻¹ stock solutions from National Research Center of China (NRCC, Beijing, China). Formic acid (88%), ammonia (25% ~ 28%), potassium borohydride (KBH₄) and potassium hydroxide (KOH) were purchased from Kelong Chemical Reagents Co. (Chengdu, China). High purity Ar was obtained from Qiaoyuan Gas Co.
Three Certified Reference water samples (GSBZ50019-90 202308, GBW08607 and GBW(E)080401) from State Environmental Protection Administration of China (SEPAC) or NRCC were used to validate the accuracy of the proposed method. The accuracy was also evaluated by analysis of a tap water sample collected from our laboratory after the tap was opened at full flow for 10 min.

### 2.3. Procedure

The whole procedure of the PVG and the HG was controlled through the pumps. Step 1, the sample or standard solution containing 2% (v/v) formic acid together with 70% (v/v) ammonia was pumped to mix with the 90% (v/v) formic acid with pump 1 at an 8 mL min\(^{-1}\) of flow rate for 20 s, and then exposed to UV irradiation in the photochemical reactor for 220 s. Pump 1 was stopped and Pump 2 was activated to transport 3% (m/v) KBH\(_4\) solution and the sample or standard solution into the hydride generator at about 8 mL min\(^{-1}\) of flow rate for 10 s in step 2. In the third step, the mixtures from the photochemical reactor and the hydride generator were flushed into GLS with Ar carrier gas and/or carrier solution (2% (v/v) formic acid, respectively. Finally, the volatile species of As, Cd, Ni and Fe were separated from liquid phase and transported to AFS for simultaneous multi-element analysis. The fourth step is a 6 s of duration for getting ready for the next measurement. Peak area fluorescence was recorded for quantification and the optimized instrumental factors of AFS were summarized in Table 1.

### 3. Results and discussion

#### 3.1. Experimental condition for hydride generation of As and Cd

In order to validate the feasibility of the proposed method, As, Cd, Fe and Ni were selected as representative elements of the hydride forming elements and the non-hydride forming elements, respectively. As reported previously\(^9,10\), the hydride generation efficiencies of As and Cd were strongly dependent on the acidity of the sample solution. Although HCl or HNO\(_3\) is frequently used for HG, the subsequent
PVG of Fe and Ni was remarkably depressed when inorganic acid such as HNO₃ and HCl was involved. Furthermore, formic acid is the most favorable reaction medium for PVG of Ni and Fe. Considering simultaneous determination of hydride forming and non-hydride forming elements, formic acid was consequently selected as the reaction medium for hydride generation of As and Cd. The effect of formic acid concentration on response is shown in Fig. 2a. The responses from As and Cd are significantly increased in the rage of 0 - 2% (v/v). The response of As remains stable but that of Cd obviously decreases at higher concentration of formic acid. Therefore, 2% formic acid was selected as the reaction medium for subsequent hydride generation.

Various concentrations of KBH₄ containing 0.5% (m/v) KOH was used to investigate its effect on the AFS response, as shown Fig. 3. Both the responses from As and Cd increase throughout the range of 0-3% (m/v), and followed by a plateau at higher concentrations. Low concentration of KBH₄ results in inefficient conversion of As and Cd to their hydrides and/or cannot maintain a stable hydrogen-argon flame for efficient atomization of the hydrides. A 3% (v/v) of KBH₄ was thus used for subsequent experiments.

3.2. Experimental condition for photochemical vapor generation

Although it has been reported that both As and Cd could also be converted to their volatile species by using PVG, their PVG efficiencies are too low to be analytically useful for real sample analysis. Moreover, the conditions for PVG of As and Cd are rather critical. Therefore, only Fe and Ni were used to investigate the effects of experimental conditions on their PVG efficiencies. Initial studies proved that the volatile species of PVG of iron and nickel were Fe(CO)₅ and Ni(CO)₄, respectively, and their efficiencies were significantly influenced by the type and concentration of LWM organic acid. Although acetic acid and propionic acid can also reduce Ni(II) and Fe(III) to their corresponding volatile species with UV irradiation, their efficiencies are too low to be useful for analytical purposes. Therefore, only formic acid was selected to investigate its effect on the PVG efficiencies of Ni and Fe, and
the results are summarized in Fig. 2b. The responses from Ni and Fe were significantly increased with increasing the concentration of formic acid throughout the range of 50 - 80% (v/v), followed by a plateau at higher concentrations. Finally, a concentration of 90% (v/v) of formic acid was used for the subsequent experiments. It should be noted that large blank of iron was observed when analytical grade of formic acid was used. The concentration of Fe in this formic acid was determined by ICP-OES, and about 100 μg L⁻¹ of Fe was found. Therefore, sub-boil distilled or higher purity formic acid was needed for this work.

According to our previous work, pH value was the most important factor for PVG of iron, and the optimum PVG efficiency was obtained within a very narrow pH range of 2.0 – 3.0. Because the HG of As and Cd are accomplished in the presence of 2% (v/v) formic acid, a flow of ammonia was only introduced to neutralize the sample solution in the case of PVG. The effect of pH on the responses from Fe and Ni was investigated using a series of solutions containing 50, 60, 70, 80 and 90% (v/v) ammonia. The pH values of these mixtures measured by a pH meter were 2.58, 2.80, 2.95, 3.15 and 3.31, respectively. The results (Fig. 4) indicate that the PVG of nickel occurred in a wide concentration range of ammonia, whereas the response from Fe is significantly influenced by the concentration of ammonia, and the optimum concentration is 70% (v/v, pH=2.95), which agrees well with our previous work. In order to ascertain that the enhanced response in the presence of ammonia is due to the setting of an optimal pH or possibly the formation of complex of iron and amine, KOH was used as a substitution for ammonia. The results found that the enhanced tendency is similar but the enhancement was much lower than that from optimal pH adjusted by ammonia. Therefore, we think that the pH adjustment using ammonia may not only provide an optimal pH but also offer an amine ligand to form an iron complex that is favorable to PVG. A concentration of 70% ammonia was, therefore, chosen for the subsequent experiments.

The optimum irradiation time was quite different for different elements. The optimum irradiation time for PVG of iron was previously reported to be 250-300 s, which is
much longer than that required for mercury, iodine, selenium and nickel. However, it is necessary to further investigate this parameter for this DM-CVG system because the UV lamp power of the photochemical vapor generator is lower than that used in previous work. A standard solution containing 50 and 10 μg L\(^{-1}\) Fe(III) and Ni(II) was used to investigate the effect of irradiation time on response. The irradiation time was controlled by using an intermittent stop flow method. The results are summarized in Fig. 5 and show that the responses from Fe and Ni increased with increasing the irradiation time within the range of 20 - 160 s. The response from Ni is slightly decreased at longer irradiation time but the response from Fe is still increased to 220 s. Although the UV lamp power is lower than that used in the previous work, the optimum irradiation time is slightly shorter and beneficial to increase throughput. This is probably due to the fact that the mixing of sample with ammonia produced large amount of heat to increase the reaction temperature, which significantly increase reaction speed and reduce the irradiation time. To further support this conclusion, a mercury thermocouple was inserted into the reaction solution and showed the reaction temperature was about 60 °C. The generated Ni(CO)\(_4\) and Fe(CO)\(_5\) would be partly decomposed or excess water vapor would be generated and transported into Ar-H\(_2\) flame atomizer that resulted in the decrease of signal as longer irradiation time used. In consideration of both the intensity and the stability, a 220 s of irradiation time was subsequently selected for the further experiments.

### 3.3. Effect of flow rate of carrier gas

It is well known that the flow rate of Ar carrier gas significantly influenced the overall efficiency of gas-liquid separation and vapor transport, analyte concentration in the carrier gas and its residence time in the Ar-H\(_2\) flame as well as the position of observation height in the AFS spectrometer. Moreover, the carrier gas was also used to simultaneously sweep the PVG and HG reaction solutions to the GLS. Therefore, the influence of the flow rate of argon carrier gas on response was also investigated. The results showed that the response of Fe is increased as flow rate increased from 400 - 500 mL min\(^{-1}\), and then decreased at higher flow rate. Inefficient separation and
low transportation efficiency of the volatile species were occurred at the lower flow rate, while the higher flow rate lead to serious dilution of analyte in the carrier gas. Although the responses of Ni, As and Cd are still increased up to a flow rate of 600 mL min\(^{-1}\), a flow rate of 500 mL min\(^{-1}\) was selected for all the tested analytes in the subsequent experiments because of lower sensitivity of Fe and consideration of the sensitivities for all the analytes and the stability of the measurements.

### 3.4 Figures of merit

Analytical figures of merit were evaluated under optimal experimental conditions. A series of standard solutions containing various concentrations of Fe(III), Ni(II), As(III) and Cd (II), and 2% (v/v) formic acid was used to establish the calibration curves, and the linear correlation coefficients of these calibration curves were better than 0.99. The limits of detection (LODs) defined as the analyte concentration equivalent to 3 s of 11 measurements of a blank solution, were 0.8, 0.1, 0.05 and 0.008 μg L\(^{-1}\) for Fe, Ni, As and Cd. The precision, expressed as relative standard deviation (RSD) of six replicate measurements, were 5.0%, 5.5%, 4.3% and 4.5% (n=6, RSDs) for 50 μg L\(^{-1}\) of Fe, 10 μg L\(^{-1}\) of Ni, 2 μg L\(^{-1}\) of As and 1 μg L\(^{-1}\) of Cd, respectively. Table 2 summarizes figures of merit characterizing the current method and compares its performance to those of similar published analytical methods.

### 3.5. Analytical application

Three Certified Reference water samples from SEPAC and NRCC were analyzed to validate the accuracy of the proposed method. Direct analysis of Fe in GSBZ50019-90 was not successful because of its highly endogenous concentration of nitric acid (5%, v/v), which seriously depressed the PVG of iron. Therefore, 0.2 mL of aliquots of this certified reference sample was evaporated to near dryness on a hot plate in a clean hood and reconstituted to 10 mL using 2% (v/v) formic acid prior to its analysis. Due to the concentrations of nickel and cadmium present in GBW08607 and GBW(E)080401) are higher than their linear range, 0.1 mL of aliquots of these samples were directly diluted to 10 mL using 2% (v/v) formic acid before determination by DM-CVG-AFS. Analytical results are summarized in Table 3. The
t-test results showed that the analytical results obtained by the proposed method had good agreement with the certified values at the confidence level of 95%.

The utility of the proposed method was further demonstrated by the determination of these hydride forming and non-hydride forming elements in tap water. The results are also summarized in Table 3, which shows that excellent recoveries in the range of 95–99% could be achieved for all the four elements by the proposed method.

4. Conclusion

A new DM-CVG system integrating hydride generation and photochemical vapor generation was developed and demonstrated its successful application to the simultaneous multi-element analysis of the classical hydride-forming and non-hydride-forming elements by chemical vapor generation atomic spectrometry. Although the precision was degraded with CVG-AFS, limits of detection were significantly improved compared to that realized with conventional pneumatic nebulization ICP-OES. Moreover, The proposed method not only retains the advantage provided by using HG or PVG along but also offers capability of simultaneous multi-element analysis of hydride forming elements and non-hydride forming elements with high sensitivity and less interference. The analytical performance including LODs, accuracy, sample throughout and the capability of simultaneous multi-element analysis could be significantly improved by coupling this DM-CVG system to ICP-OES/MS instrument for detection.

Acknowledgements

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Reference


Figure caption

Fig. 1. Schematic of the experimental set-up.

Fig. 2. Effect of formic acid on response. (a) hydride generation of As and Cd; and (b) photochemical vapor generation of Ni and Fe.

Fig. 3. Effect of KBH₄ on the responses from HG of As and Cd.

Fig. 4. Effect of ammonia on the responses from PVG of Ni and Fe.

Fig. 5. Effect of irradiation time on the responses from PVG of Ni and Fe.
Fig. 1
Fig. 2

![Graph a: Fluorescence intensity vs. Concentration of formic acid, % (v/v)](image)

- **Graph a**: Comparison of Cd and As fluorescence intensity with varying concentrations of formic acid.

![Graph b: Fluorescence intensity vs. Concentration of formic acid, % (v/v)](image)

- **Graph b**: Comparison of Fe and Ni fluorescence intensity with varying concentrations of formic acid.
Fig. 3

[Graph showing fluorescence intensity against concentration of KBH₄ (% m/v) for As and Cd]
Fig. 4

Fluorescence intensity vs. Concentration of ammonia, % (v/v)
Fig. 5

The graph shows the fluorescence intensity against irradiation time for Fe and Ni. The fluorescence intensity is plotted on the y-axis, ranging from 0 to 7000, while the irradiation time is on the x-axis, ranging from 0 to 250 seconds. Two curves are depicted: one for Fe (black line with grey circles) and one for Ni (red line with red circles). The error bars indicate the variability of the data points.
Table 1. Optimal instrumental parameters for the DM-CVG-AFS

<table>
<thead>
<tr>
<th>Element</th>
<th>Lamp current, mA</th>
<th>Voltage of PMT, V</th>
<th>Observation height, mm</th>
<th>Carrier gas flow rate, mL min⁻¹</th>
<th>Shield gas flow rate, mL min⁻¹</th>
<th>Quantification mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>80</td>
<td>-350</td>
<td>10</td>
<td>600</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>80</td>
<td>-300</td>
<td>10</td>
<td>600</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>80</td>
<td>-350</td>
<td>10</td>
<td>600</td>
<td>1000</td>
<td>Peak area</td>
</tr>
<tr>
<td>Ni</td>
<td>80</td>
<td>-300</td>
<td>10</td>
<td>600</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

PMT, photomultiplier tube.

Table 2 Analytical figures of merit in comparison with those of other methodologies

<table>
<thead>
<tr>
<th>Element</th>
<th>This Method</th>
<th>MSIS-ICP-AES (ref.21)</th>
<th>MSIS™-ICP-AES (ref.25)</th>
<th>PN-MSIS-PE-ICP-AES (ref.26)</th>
<th>USN-MSIS-PE-ICP-AES (ref.26)</th>
<th>USN-PET-ICP-OES (ref.27)</th>
<th>MSIS-MSIP-P-AES (ref.23)</th>
<th>MSIS-ICP-MS (ref.22)</th>
<th>TMSIS-ICP-AES (ref. 24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As: LOD, µg L⁻¹</td>
<td>0.05</td>
<td>0.2</td>
<td>0.7</td>
<td>0.2</td>
<td>0.2</td>
<td>1</td>
<td>0.07</td>
<td>7</td>
<td>0.3</td>
</tr>
<tr>
<td>Cd: LOD, µg L⁻¹</td>
<td>0.008</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.07</td>
<td>0.1</td>
<td>-</td>
<td>30</td>
<td>0.53</td>
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<tr>
<td>Element</td>
<td>LOD, μg L⁻¹</td>
<td>Precision, % RSD</td>
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<tr>
<td>Fe</td>
<td>0.8</td>
<td>5.0ᵃ 2.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni</td>
<td>0.1</td>
<td>3.6ᵇ 1.4</td>
<td></td>
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<td></td>
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<tr>
<td>As</td>
<td>5.0ᵃ 2.24</td>
<td>4.1 1.6 1.4 10</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>5.5ᵇ -</td>
<td>1.4 1.4 0.3 0.3</td>
<td>0.3~6.7</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Fe</td>
<td>4.3ᶜ -</td>
<td>1.6 1.4 2.1 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>4.5ᵈ 3.6ᵈ</td>
<td>1.1 0.7 1.8 0.3</td>
<td>0.3~6.7</td>
<td></td>
<td></td>
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</tbody>
</table>

ᵃ 2 μg L⁻¹,ᵇ 1 μg L⁻¹; ᶜ 50 μg L⁻¹; ᵈ 10 μg L⁻¹; ᵉ μg g⁻¹; ᶠ ng L⁻¹. PET, pre-evaporation tube; USN, Ultrasonic nebulization; MIP, Microwave induced plasma; and TMSIS, triple mode sample introduction system.
Table 3. Analytical results of As, Cd, Fe and Ni in water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Certified value, mg L$^{-1}$</th>
<th>Added, μg L$^{-1}$</th>
<th>Found, mg L$^{-1}$</th>
<th>Recovery, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSZ50019-90</td>
<td>Fe</td>
<td>2.49 ± 0.14</td>
<td>-</td>
<td>2.57 ± 0.01</td>
<td>-</td>
</tr>
<tr>
<td>202308</td>
<td>Ni</td>
<td>0.521 ± 0.006</td>
<td>-</td>
<td>0.525 ± 0.008</td>
<td>-</td>
</tr>
<tr>
<td>GBW08607</td>
<td>Cd</td>
<td>0.104 ± 0.002</td>
<td>-</td>
<td>0.104 ± 0.001</td>
<td>-</td>
</tr>
<tr>
<td>GBW(E) 080401</td>
<td>Cd</td>
<td>0.100 ± 0.004</td>
<td>-</td>
<td>0.109 ± 0.002</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>22.79 ± 0.92</td>
<td>50</td>
<td>70.51 ± 0.72</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>ND</td>
<td>1</td>
<td>0.99 ± 0.35</td>
<td>99</td>
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<tr>
<td>Tap water</td>
<td>As</td>
<td>ND</td>
<td>10</td>
<td>9.49 ± 0.25</td>
<td>95</td>
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<tr>
<td></td>
<td>Cd</td>
<td>ND</td>
<td>0.5</td>
<td>0.42 ± 0.01</td>
<td>99</td>
</tr>
</tbody>
</table>

*Mean and standard deviation (n = 3); $^b$ μg L$^{-1}$; $^c$ detected value; ND, not detected.
A dual-mode chemical vapor generation integrating hydride generation and photochemical vapor generation was developed for simultaneous multi-element analysis.
Graphic abstract

A dual-mode chemical vapor generation system has been developed for simultaneous multi-element analysis of hydride forming and non-hydride forming elements.