

# A Novel Tungsten Coil Electrothermal Vaporizer with Composite Structure Coupled with Dielectric Barrier Discharge Optical Emission Spectrometer for Direct Determination of Trace Mercury

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**ABSTRACT:** In this study, a small platinized tungsten coil (TC) with a composite structure was utilized for the first time in a liquid sampling electrothermal vaporizer (ETV) setup. A novel direct sampling mercury (Hg) analyzer coupled with a dielectric barrier discharge (DBD) and a miniature fiber optic spectrometer (FOS) as an optical emission spectrometer was fabricated for the sensitive determination of Hg in environmental water. This ETV setup displayed a maximum sample volume of 100  $\mu\text{L}$  and fulfilled the task of sequestering Hg during the dehydration and ashing processes under high temperature due to the formation of a platinum (Pt) and Hg amalgam. Under optimized conditions, the limit of detection (LOD) of Hg was  $0.1 \mu\text{g L}^{-1}$  for a 100  $\mu\text{L}$  liquid sample and the relative standard deviation (RSD) of 11 repeated measurements of Hg standard solution was 3.2%; the linearity ( $R^2$ ) was  $> 0.999$  in the range of  $0.4\text{--}100 \mu\text{g L}^{-1}$ . The results for the GBW08063 sample ( $9.89 \mu\text{g L}^{-1}$ ) agreed with the certified values of certified reference materials (CRMs) ( $10 \mu\text{g L}^{-1}$ ), and the spiked recoveries were 94–100%, which proved favorable analytical accuracy and precision. The total analysis time was observed to be less than 3 min, and this small-sized ETV-DBD-OES system consumes only  $\sim 100$  W of power while weighting less than 12 kg. Therefore, the proposed ETV-DBD-OES method demonstrates simplicity, suitable sensitivity, precision, and robustness, with promising application in the field for rapid water analysis for Hg.

## INTRODUCTION

Mercury (Hg)<sup>1</sup> has been utilized by human for millennia across various fields, but its distinct physicochemical properties allow for its widespread distribution and deposition on various substrates in different environmental media, resulting in significant environmental and biological pollution concerns. Hg have ultimately ended up in one of its final sinks, such as incorporation into deep sediment or bioaccumulation, especially in water systems.<sup>2,3</sup> Though Hg in drinking water is always considered to be present at an ultra-trace level, long-term exposure to low dose Hg remains a potential threat to biological health.<sup>4</sup> To guarantee

human and animal health, it is crucial to monitor the concentration of trace Hg in environmental waters quickly and precisely.

Currently, atomic and inorganic mass spectrometric methods are commonly used for Hg analysis, such as cold atomic absorption spectrometry (CAAS),<sup>5</sup> atomic fluorescence spectrometry (AFS)<sup>6</sup> and inductively coupled plasma mass spectrometry (ICP-MS),<sup>7</sup> which use a nebulizer or peristaltic pump for sample introduction. The instrumental approaches mentioned above require complex sample digestion processes that use strong acids or alkaline reagents before detecting. The process is not only time-consuming and environmental harmful, which

makes it impossible to achieve rapid Hg detection.<sup>8</sup> To achieve fast and in situ analysis, a direct-sampling Hg analyzer based on ETV or chemical vapor generation (CVG) coupled with catalytic pyrolysis and gold amalgamation was developed. This system has since become one of the most successful commercialized ETV instruments, allowing for the direct analysis of Hg in various matrices, including water, liquid, and solid samples with LOD below 0.1 ng mL<sup>-1</sup>. However, ETV designs using a quartz tube and a catalytic pyrolysis furnace, with both wrapped with heating Ni/Cr coils, commonly consume > 1000 W of power, and weight more than 30 kg, making field deployment impractical. Thus, it is necessary to design a portable Hg analyzer for the field analysis of environmental water.

Recently, the miniaturization of atomic spectrometers has mainly focused on optical emission spectrometry (OES) using microplasma as an excitation source and a fiber optic spectrometer (FOS) as a detector. Typical low-temperature plasmas, such as dielectric barrier discharge (DBD),<sup>9, 10</sup> point discharge (PD),<sup>11, 12</sup> solution cathode/anode glow discharge (SCGD/SAGD),<sup>13, 14</sup> and atmospheric pressure glow discharge (APGD)<sup>15, 16</sup> are characterized by their low cost, small size, and low power consumption. Among them, DBD consists of two metallic electrodes with one or both encased with a dielectric material, and typically requires only a few to dozens of watts of power. Thus, DBD has become a promising excitation source for portable OES. Unfortunately, ultra-trace Hg analysis using microplasma OES additionally suffers from insufficient sensitivity and vulnerable plasmas. To accommodate vulnerable microplasma, CVG is frequently chosen as a sample introduction approach, but it requires dangerous and inconvenient chemicals such as strong acids and stannous chloride or potassium borohydride (PBH), which are not suitable for portable analysis and field deployment. Thus, direct sampling and analysis without the use of chemicals are urgently required for microplasma OES.

To enable direct sampling, ETV has emerged as an efficient and versatile method for atomic spectrometry, which includes ETV-OES. Among the different ETV setups available, the tungsten coil (TC) is one of the most widely utilized due to its high melting temperature (> 3000 °C), rapid heating, affordability, and low energy consumption. To date,<sup>17, 18</sup> ETV-OES analyzers with DBD excitation sources have been frequently developed, demonstrating great potential for the field analysis of toxic elements such as Hg, Cd, Pb, and As in environmental investigations.<sup>10, 17</sup> However, controlling the loss of Hg analytes presents a challenge due to its low melting and vaporization points, as well as the need to protect the microplasma against moisture interference *via* dehydration at high temperatures.<sup>10, 18</sup> To the best of our knowledge, Hg analysis using TC-ETV combined with microplasma OES has not been reported.

To address this issue, the concept of amalgamation suggests that an alloy of Hg + metal may enhance the vaporization of Hg

analytes during ETV process.<sup>20</sup> In essence, this principle is in accordance with the permanent chemical modifiers previously used in atomizers such as Ir, Pd, Rh, and Re<sup>19</sup>. Hg trapping and Au is widely used as an amalgamating agent in commercialized Hg analyzers,<sup>20</sup> in which Hg must be heated under > 600 °C to release from the amalgamator, and 600 °C is higher than the initial vaporization temperature (from >100 °C to 800 °C) of Hg analytes without amalgamation. Other than Au, other noble metals such as Pt can also fulfill the amalgamation process, with Pt being more inert than gold. Therefore, if Pt is coated on the surface of the TC, then the modified ETV might be capable of increasing Hg vaporization during dehydration and ashing at high temperatures because of amalgamation, while also protecting W from the formation of tungsten oxides (WO<sub>x</sub>)<sup>21</sup>. In terms of analytical sensitivity, a microplasma-based OES is usually inferior to AAS, AFS, or ICPMS. Limited by loading capacity, the traditional TC is able to accommodate a sample size of 10 - 20 μL at maximum.<sup>22</sup> <sup>23</sup> If the loading capacity of TC is increased to some extent, the absolute LOD of the Hg analyzer can be further reduced.

In this study, a miniature ETV-DBD-OES instrument was developed for the direct detection of Hg in environmental water. To load a larger size of water sample, a TC featuring a secondary helical structure was selected, allowing for a maximum sampling size of 100 μL. The TC was platinized using chloroplatinic acid to coat Pt onto the tungsten surface. A miniature FOS was then coupled to DBD to form a microplasma-based OES detector for Hg. Under the optimized conditions, a method LOD of 0.1 ng mL<sup>-1</sup> was achieved for Hg with a total analysis time of under 3 min. With its demonstrated robustness, low LOD, affordability, low power and gas consumption, small size and weight, and ease of operation, this miniature and portable OES Hg analyzer allowed for the fast field analysis of Hg in environmental water.

## EXPERIMENTAL

**Instrumentation.** As illustrated in Fig. 1, a direct-sampling Hg analyzer setup was built in our laboratory, which mainly consisted of a TC with a composite helical structure as the ETV and sample carrier, a DBD reactor as the excitation resource, an FOS as the OES detector, and a power supply. This composite TC device (which was processed by Tianjin Dongfang Qiyun Auto Body Manufacturing Co., Ltd.) was composed of the first and second helical structure coils, of which Φ0.1 mm tungsten wire was coiled into 0.8 mm diameter coils as the first helical structure, with the first helical coils coiled 8 times (around 7.0 mm length) into a 2.5 mm diameter composite coil forming the secondary helical structure. A quartz cover chamber with a gas inlet was employed to seal and accommodate the TC-ETV and connect to the DBD reactor. The ETV system was powered by a direct-current (DC) power supply (DC-01, Beijing Ability Technology, Beijing,

**Fig. 1** Schematic of direct sampling Hg analyzer and fine structure of TC.

**Table 1.** Programs of the proposed direct sampling Hg analysis

Steps	Voltage (V)	Time (s)	Power (W)	Atmosphere
Dry	2.9 (ETV)	42	3.5	Air at ambient
Ash	1.2 (ETV)	110	0.6	Air at ambient
Vaporization	6.9 (ETV) 24 (DBD)	10	/	Ar+0.1%H <sub>2</sub>
Clean	9.0 (ETV)	10	/	Ar+0.1%H <sub>2</sub>

China). The DBD reactor consisted of two concentric quartz tubes with a silver bar as the inner electrode and silver foil as the outside electrode. The inner electrode was inserted into the inner quartz tube as a high-voltage electrode, and the outside electrode was wrapped tightly around the outer tube as the ground electrode. The DBD system was powered by a high-voltage 33 kHz pulsed power source (MeV 40 kV, Beijing Ability Technology, Beijing, China). An Ar/H<sub>2</sub> mixture (0.1% H<sub>2</sub>, v/v) was used to transport the Hg analytes from the ETV to the DBD unit. To further reduce the manufacturing cost, a cheap commercial hand-held CCD spectrometer (USB 2000+, Ocean Optics Inc., Dunedin, FL, USA) covering a range of 186 – 418 nm with 100 μm slit width was utilized to acquire the atomic emission signals of Hg in DBD microplasma. The fabricated direct sampling Hg analyzer is shown in Fig. S1, with dimensions of 0.57×0.42×0.19 m, a weight <12 kg, and a power consumption of ~100 W.

**Reagents and materials.** All chemicals were of reagent grade and were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China), unless otherwise stated. The purity of the Ar/H<sub>2</sub> mixture was 99.99% (v/v) and H<sub>2</sub> accounted for 0.1% (v/v). Standard stock solutions of Hg (1000 mg L<sup>-1</sup>) and simulated natural water certified reference materials (CRM) (GBW 08603) were purchased from the National Research Center for Certified Reference Materials (Beijing, China). Working solutions were prepared by serial dilution with deionized (DI) water. DI water (18 MΩ) was obtained using a Milli-Q purification system (Millipore, Billerica, MA, USA). Mineral water was purchased from a local

supermarket and tap and snow-water samples were collected within the city of Beijing.

**Analytical procedure.** The analytical procedures using this proposed direct-sampling Hg analyzer can be summarized as follows: (1) A water sample (100 μL) was injected and remained on the TC; (2) The TC was heated by a 2.9 V output voltage for 42 s at ambient temperature until no moisture was retained, and the heating voltage was declined to 1.2 V lasting for 110 s to complete the ashing and control the additional loss of Hg caused by overheating. At this point, the Hg analytes remains in the TC; (3) Following the insertion of the TC into the quartz cover chamber, the TC was heated at 6.9 V for 10 s to vaporize Hg analytes into the DBD reactor under 1.2 L/min carrier Ar/H<sub>2</sub>. Meanwhile, the DBD was powered by 24 V input voltage under Ar/H<sub>2</sub> atmosphere to form microplasma to atomize Hg and emit the characteristic spectrum of Hg while simultaneously, the USB2000+ FOS detector was used to measure the OES signal of Hg with 10 s integration windows; (4) Following the vaporization of Hg analytes, DBD microplasma atomization and detection, the TC was heated at 9 V for 10 s for clean the impurities in TC and quartz cover chamber. The programs of the proposed direct sampling Hg analysis are listed in Table 1.

**Platinization of tungsten coil.** Pt was deposited on the TC using electrochemical plating at room temperature under ambient conditions. Hydrogen hexachloroplatinate (IV) hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) was utilized as the Pt source, and then the TC was platinized with the detailed procedure as follows: the TC was placed in a cell with 0.1% of H<sub>2</sub>PtCl<sub>6</sub> solution (100 mL) as the cathode, and a titanium mesh (80 mm × 150 mm, Chan Kwong Kee Hk Co., Ltd. Hk, China) was used set as the anode, followed by electroplating at 0.006 A for 1h (each side for 30 min). The electrochemical plating instrument used in this study is illustrated in Fig. S2.

**Fig. 2** The comparison of TC and platinized TC on Hg trapping and the effect of platinized TC with different H<sub>2</sub>PtCl<sub>6</sub> concentrations on Hg trapping (n=3). (A) Hg solution with the same concentration and volume was loaded on to TC or platinized TC connected AFS, then the vaporization program was carry out (a) 1 V, (b) 2 V and (c) 5 V heating for 3 s. The Hg intensity was normalized with the high group set as 100. (B) 100 μL Hg solution was loaded in TC-ETV device, then introduced into ETV-DEB-OES. The intensity of Hg was normalized with signal at 10 μg L<sup>-1</sup> Hg and 0.1% H<sub>2</sub>PtCl<sub>6</sub> concentration.

**Statistical analysis.** Experimental data were statistically analyzed using Excel software (Microsoft, Redmond, WA, USA), OriginLab 2021 (Originlab, Northampton, MA, USA) and SAS 9.4 (SAS Institute Inc, NCSU, USA). Statistical significance of the differences between the proposed and standard methods was evaluated using a t-test. A probability of 0.05, or lower ( $p < 0.05$ ), was considered significant.

## RESULTS AND DISCUSSION

**Design of platinized TC-ETV with composite structure.** The tungsten coil is one of the most commonly used ETV devices for liquid and slurry sampling. However, the maximum loading size of the TC is only 10-20 μL depending on its limited specific surface area.<sup>22</sup> To increase the TC sample size to improve sensitivity, a TC with a composite helical structure was fabricated. Herein, the first helical coils were coiled by 0.8 mm to retain the liquid *via* surface tension with the specific surface area enlarged to absorb more liquid than prior designs. As a result,<sup>23</sup> a larger sampling size of up to 100 μL was achieved using the proposed TC device.

Referring to the permanent chemical modifiers previously used in atomizers, such as Ir, Pd, Rh, and Re, we attempted to platinize the tungsten coil to form an amalgamator to control Hg loss during

dehydration and ashing at high temperatures, as well as to protect tungsten against oxidization.<sup>24</sup> According to the previous study, a composite tungsten coil was immersed into 0.1% of H<sub>2</sub>PtCl<sub>6</sub> solutions for 0.5 h and then air dried to platinize the TC surface<sup>23</sup>. Therefore, this platinized TC was selected as the ETV for subsequent experiments. TC or platinized TC with a composite structure was directly employed to vaporize an Hg solution with the same concentration and volume under different vaporization intensities. As shown in Fig. 2A (a, b, c), using 1 V and 2 V heating, the intensity of the Hg signal in TC was ~98% higher than that using the platinized TC, but after increasing to 5 V for heating, the intensity of Hg in platinized TC was ~92% higher than that in TC, indicating that Hg more easily evaporated from the TC surface than platinized TC at a low vaporization temperature. After platinization, the loss temperature of Hg during the vaporization process improved significantly, effectively reducing the vaporization loss of Hg.

Subsequently, the platinized TC by different H<sub>2</sub>PtCl<sub>6</sub> concentrations on Hg trapping were investigated. A TC with a composite structure was directly employed to vaporize a 100 μL standard solution containing 10 μg L<sup>-1</sup> Hg using 2.9 V heating. After ~42 s heating, the 100 μL solution was evaporated to dryness. At this moment, if the vaporization program of 6.9 V heating for 20 s, the Hg signal acquired by OES was ~99% lower than that using the proposed platinized TC-ETV (Fig. 2B), indicating an unacceptable loss of Hg analyte during the dehydration process. As shown in Fig. 2B, when a 0.05% H<sub>2</sub>PtCl<sub>6</sub> solution was employed, only 17.8% Hg was measured, while when a 0.1% H<sub>2</sub>PtCl<sub>6</sub> solution was employed, the measured Hg was the highest, indicating an effective remaining effect of Hg on the ETV. Finally, when a 0.3% H<sub>2</sub>PtCl<sub>6</sub> solution was employed, the intensity of Hg was not different from that the 0.1% H<sub>2</sub>PtCl<sub>6</sub> solution. Therefore, a 0.1% H<sub>2</sub>PtCl<sub>6</sub> solution was chosen to platinize the TC. The platinized TC will normally vaporize Hg in water after ~100 times repeated testing. However, after that, due to exposure to O<sub>2</sub>-containing (air) atmosphere during ashing and drying process, platinization uncovered region on the surface of the TC was oxidized to tungsten oxides (WO<sub>x</sub>) via observation to impact the following detection. So, after 100 times use, the platinized TC need be reduced in Ar/H<sub>2</sub> mixture (10% H<sub>2</sub>, v/v) under 6.9 V heating (~1000 °C) for 60 s, where WO<sub>x</sub> can be removed and then the TC recovered for the next use.

**Spectral characteristics.** To monitor the Hg signal intensity, the Hg spectrum of the OES was investigated and optimized. A blank solution (100 μL) of DI water and a standard solution (100 μL) containing 10 μg L<sup>-1</sup> Hg were measured using the fabricated ETV-OES to obtain the background and emission spectrum signals (Fig. 3). The molecular peaks of OH (309 nm), N<sub>2</sub> (316 nm), and NH (337 nm) were observed in both the blank and standard solutions. The baseline signal exhibited a significantly high intensity, likely due to a higher degree of H<sub>2</sub> excitation in the Ar/H<sub>2</sub> microplasma.

**Fig. 3** Optical emission spectra of blank and mercury standard solutions before/after background correction. (A) Optical emission spectra of blank solution; (B) Optical emission spectra of 10  $\mu\text{g L}^{-1}$  Hg standard solution before background correction; (C) Optical emission spectra of 10  $\mu\text{g L}^{-1}$  Hg standard solution after background correction. Hg signal is collected at 253.8 nm.

**Fig. 4** Effect of ETV ashing time on Hg signal ( $n=3$ ). 100  $\mu\text{L}$  Hg solution (10  $\mu\text{g L}^{-1}$ ) was introduced into the ETV-DBD-OES and the Hg intensity was normalized with the signal at 120 s set as 100.

In addition, fluctuations in baseline signals without correction would severely compromise the reproducibility of Hg analysis. A fitting algorithm (in the Supplementary Information) was used for data processing to obtain a smoother baseline.<sup>25</sup> Characteristic atomic emission lines of Hg are clearly identified at 253.8 nm.<sup>24</sup>

**Dehydration and ashing.** In a real fresh water sample, the presence of moisture and a small amount of organic substances might interfere with the excitation of Hg in the DBD owing to vulnerable microplasma. To ensure analytical precision and accuracy, it is necessary to remove moisture and organic substances before introducing Hg by ETV. In this work, dehydration and ashing processes were performed in air *via* heating the TC; subsequently, the TC was inserted into a quartz

cover chamber to completely vaporize the Hg. At first, a 100  $\mu\text{L}$  solution containing 10  $\mu\text{g L}^{-1}$  Hg was loaded on the TC and heated *via* the application of 2.9 V to remove moisture. After approximately 42 s of heating, no residual water was observed. To control Hg signal loss caused by overheating, the electrothermal voltage was reduced to 1.2 V to fulfill complete ashing. The effect of the ashing time on the Hg signal intensity was investigated using a standard solution (100  $\mu\text{L}$ ) containing 10  $\mu\text{g L}^{-1}$  Hg, and the results are shown in Fig. 4. The Hg signals changed slightly in the 105-120 s range, and declined significantly beyond 125 s. Among them, 110 s of ashing ( $\sim 340$   $^{\circ}\text{C}$  measured by a K-type thermocouple inside) was sufficient, with an RSD of 3.2%, indicating an appropriate level of precision. To compromise, 1.2 V heating for 110 s was chosen for ashing.

**Vaporization of Hg and working gas.** Following the ashing step in air, the TC with the ashed residue was transferred into a quartz cover chamber for the subsequent vaporization of Hg by ETV. The vaporization of Hg mainly depends on the heating temperature; therefore, the temperature of the TC at 6.9 V heating was measured using a K-type thermocouple. When heated for 10 s, the temperature reached  $> 1000$   $^{\circ}\text{C}$ . According to the previous heating condition of amalgamator used in a commercial Hg analyzer,  $> 800$   $^{\circ}\text{C}$  is sufficient for Hg release from Au trap.<sup>20</sup> Therefore, 1000  $^{\circ}\text{C}$  is enough for Hg vaporization from the platinized TC, and higher temperature (1500 $^{\circ}\text{C}$ ) cannot release more Hg for measurement. As a result, 6.9 V heating for 10 s was chosen for the complete vaporization of Hg for the following DBD excitation.

For atmospheric composition, Ar is a commonly used working gas that supports a stable and strong plasma and H<sub>2</sub> is crucial for elemental atomization and excitation by DBD microplasma owing to the effect of H radicals.<sup>9</sup> In addition, H<sub>2</sub> can protect TC from oxidation in air at high temperatures. In this study, a carrier Ar/H<sub>2</sub> mixture was used as the working gas to transport the vaporized Hg analytes. However, the H background severely impacts the Hg signal peak, and excessive H<sub>2</sub> consumes microplasma energy and is thereby adversely affected by Hg excitation.<sup>25</sup> The dependence of the Hg signal intensity on H<sub>2</sub> presence in the Ar/H<sub>2</sub> mixture is shown in Fig. 5A. The Hg signal decreased significantly with an increase in H<sub>2</sub> in the 0-10% range, with the Ar atmosphere showing the best Hg signal response, but after several tests, the TC was WOx, which reduced the service life of TC (Fig. S3). Addition of 0.1% H<sub>2</sub> showed an acceptable Hg signal intensity with a favorable RSD (3%). Therefore, 0.1% H<sub>2</sub> in the Ar/H<sub>2</sub> mixture was considered optimal in this step. As shown in Fig. 5B, the Ar/H<sub>2</sub> flow rate was investigated, and the Hg signal intensity reached a maximum at 0.6 L/min, with higher flows causing the signal to decline due to the dilution effect. Finally, a 0.6 L/min Ar/H<sub>2</sub> mixture was chosen as the working gas.

**Excitation of Hg by DBD.** DBD is regarded as a miniature excitation source for OES and was utilized to excite Hg vaporized

**Fig. 5** Effect of H<sub>2</sub> percentage in Ar/H<sub>2</sub> mixture and Ar/H<sub>2</sub> flow rate on Hg signals (n=3). Herein, 100 µL Hg solution (10 µg L<sup>-1</sup>) was introduced into the ETV-DBD-OES; (A) The Hg intensity was normalized with the signal at 0% H<sub>2</sub> set as 100; (B) the Hg intensity was normalized at 0.5 L/min set as 100.

**Fig. 6** Effect of discharge current on Hg signal (n=3). Herein the Hg intensity was normalized with the signal at 0.34 A set as 100.

**Table. 2** Effect of potential inorganic ions in water on Hg measurement by this proposed method (n=3)

Interfering elements	Concentration (mg L <sup>-1</sup> )	Recovery (%)
Cd <sup>2+</sup>	0.5	103±2
Pb <sup>2+</sup>	0.5	94±12
Cu <sup>2+</sup>	1	99±2
Co <sup>2+</sup>	10	93±6
Zn <sup>2+</sup>	10	83±3
Fe <sup>3+</sup>	10	105±4
Mn <sup>2+</sup>	10	108±1
Mg <sup>2+</sup>	10	95±2
Ni <sup>2+</sup>	10	102±6
K <sup>+</sup>	100	99±5

from TC-ETV for OES measurements in this work.<sup>26</sup> Here, a coaxial DBD device based on a quartz tube was employed, and the effect of the discharging current was investigated for Hg excitation.<sup>9, 27</sup> As shown in Fig. 6, with increase of discharging

current, the Hg signal intensity increasing in the range of 0.11 A to 0.34 A due to the intensified microplasma, and reaches a plateau. As a result, 0.34 A was an inflection point and set as the optimized discharging current for Hg by DBD-OES.

**Interference study.** The susceptibility of the ETV-DBD-OES method to interference was tested. Various concentration of macro-and-micro elements (Mg<sup>2+</sup> and K<sup>+</sup>), and transition metals (Cu<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>) were mixed with the 10 µg L<sup>-1</sup> Hg standard, and the results are shown in Table. 2. The recoveries ranged from 83% to 108%, indicating no significant interference from inorganic ions in the water at these levels.

**Analytical performance and real sample analysis.** Analytical figures of merit were evaluated under optimal conditions. Using USB 2000+ CCD, >0.999 regression coefficients (R<sup>2</sup>) were achieved in the 0.4-100 µg L<sup>-1</sup> range by measuring a series of Hg standard solutions as shown in Fig. S4. The Hg LOD was 0.1 µg L<sup>-1</sup> (introduction volume = 100 µL), which was calculated by taking three times the standard deviation of the blank solution from 11 measurements divided by the slope. The RSD of the 10 µg L<sup>-1</sup> Hg standard solution from the 11 measurements was 3.2%, demonstrating high analytical precision (Fig. S5).

To verify the feasibility of the proposed TC-ETV-OES method, simulated natural water CRM samples (GBW08063), mineral water, tap water, and snow water were analyzed. As shown in Table. 3, the Hg results for the GBW08063 sample agree with the certified values, and for real water samples, the mean spiked recoveries ranged from 95% to 100%, which proved a high analytical accuracy.

## CONCLUSION

In this study, a novel miniature ETV-DBD-OES instrument was fabricated to detect ultra-trace Hg in water samples. The platinumized tungsten coil with composite structure was for the first time utilized as an ETV setup for Hg, of which the maximum sample volume reaches 100 µL and loss of Hg signal during dehydration and ashing processes is effectively controlled. This new design ETV-OES fulfills the direct sampling analysis of Hg, with LODs of 0.1 µg L<sup>-1</sup> in water samples and total analysis time of less than 3 min. The proposed direct sampling Hg analyzer weighs less than 12 kg and draws approximately 100 W when in operation, indicating power consumption, indicating excellent miniaturization and portability, and when coupled with a USB 2000+ CCD, provides an affordable alternative to currently available instrumentation. In summary, the proposed ETV-DBD-OES method demonstrates simplicity, high sensitivity, precision, and robustness, with promising applicability in field use for rapid Hg analysis.

**Table 3** Spiked recoveries and measured values of Hg in real water sample (n=3)

Sample	Certified ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Spiked ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	RSD (%)
Mineral water	/	0.38±0.2	10	10.1±0.2	99	2
Tap water	/	n.d	10	9.49±0.2	95	2
Snow water	/	n.d.	10	10.0±0.1	100	1
GBW08063	10	9.89±0.1	/	/	99	1

## ASSOCIATED CONTENT

The supporting information (Figs. S1–S5) is available at [www.at-spectrosc.com/as/home](http://www.at-spectrosc.com/as/home).

## AUTHOR INFORMATION



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### Notes

The authors declare no competing financial interest.

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