

Integration of Hydrogen Evolution Reaction and Microplasma Induced Vapor Generation: A Strategy for Improving Safety and Sensitivity of Microplasma Optical Emission Spectrometry

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ABSTRACT: Microplasma-induced vapor generation (μ PIVG), particularly using only hydrogen, has attracted increasing attention in the field of atomic spectrometry. However, its application for field analysis of environmental samples remains limited owing to the difficulty of hydrogen storage and transportation. Herein, a non-noble metal electrode-based hydrogen evolution reaction (HER) was utilized as a safe and environment-friendly hydrogen supply method for the efficient μ PIVG of Hg, Cd and Zn. Subsequently, HER- μ PIVG was used for the sensitive field detection of Hg, Cd and Zn in environmental samples via miniature point discharge optical emission spectrometry (μ PD-OES). In contrast to conventional hydrogen-enhanced μ PIVG, hydrogen was produced in situ and in real time using a superior cathode composed of cobalt-phosphorous nanomaterial, eliminating the storage and transport of hydrogen requirements and improving the safety, sensitivity, and feasibility of μ PIVG- μ PD-OES. Under the optimized conditions, the limits of detection (LODs) were 0.8, 10, and 14 $\mu\text{g L}^{-1}$ for Hg, Cd, and Zn, respectively, with relative standard deviations (RSDs) of $< 4.7\%$. The accuracy and practicability of the proposed method were validated through Hg, Cd, and Zn determinations in two certified reference materials (CRMs) and several water samples with satisfactory results.

INTRODUCTION

Miniature optical emission spectrometers (OES) fabricated with various microplasmas have demonstrated good potential for the field detection of metallic and non-metallic elements due to their compact setup, cost-effectiveness, portability, and low gas and power consumption.¹⁻⁵ To reduce matrix interference and energy consumption by sample desolvation, chemical vapor generation (CVG) has been frequently adopted for sample introduction in atomic spectrometry.^{6,7} As a common CVG technique, hydride generation (HG) requires large amounts of toxic/unstable reagents (e.g. mineral acids and NaBH_4), which can interfere with the detection of transition metals and produce significant amounts of hydrogen, which is sufficient to deteriorate the excitation efficiencies and microplasma stability (a small amount of

hydrogen does not interfere with the microplasma normally).⁸⁻¹¹ Microplasma-induced vapor generation (μ PIVG), highlighted as a novel and promising CVG technique, exhibits the advantages of high vapor generation efficiency, fast reaction speed, simple device configuration, and easy construction.¹²⁻¹⁵ Therefore, it has become a suitable sample introduction technology in the development of portable and miniaturized spectrometers. Leng et al. developed a compact mercury analyzer for mercury determination in water samples by integrating a thin film dielectric barrier discharge (DBD)- μ PIVG reactor and a DBD-OES into a small polymethyl methacrylate plate.¹⁶ Recently, methanol was added to the sample solution to enhance the μ PIVG efficiency of Hg, Cd and Zn, achieving highly sensitive and simultaneous determination by atomic fluorescence spectrometry (AFS).¹⁷ Although the μ PIVG technique does not require unstable chemical

reduction/oxidation reagents, additional hydrogen is needed to efficiently generate volatile species for hydride-generating elements (As, Sb, Cd, and Zn).¹⁸⁻²² It is well-known that hydrogen is a flammable and explosive gas that requires special considerations for storage and transportation. Consequently, the development of a safe and convenient method for hydrogen generation is necessary for the field detection of elements by hydrogen-enhanced μ PIVG atomic spectrometry.

The electrochemical reduction of water is a desirable pathway for hydrogen production. Recently, many low-cost non-noble metal materials have been successfully used as alternatives to conventional noble metal electrodes for the hydrogen evolution reaction (HER), including transition metal dichalcogenides, phosphides, carbides, and nitrides.^{23, 24} In particular, transition metal phosphides contain proton-acceptor and hydride-acceptor centers similar to the active site of hydrogenase, thus exhibiting great potential as effective HER catalysts.²⁵⁻²⁸ Dang et al. integrated modified ultrathin and three-dimensional holey nanostructures to produce the cobalt-phosphorous (Co-P) phase on the carbon cloth as a HER electrocatalyst at pH 0–14, demonstrating the preparation of binder-free HER electrodes for renewable energy applications.²⁹ Different Co-P nanostructures, including films,²⁸ nanowires,³⁰ and nanosheets³¹ have been developed as bifunctional catalysts for water splitting with electrocatalytic properties that compare favorably with Pt.

Because it is easy to control with low cost, high efficiency, and an excellent safety profile, the HER was utilized herein as a safe and convenient hydrogen supply for liquid electrode discharge microplasma-induced vapor generation (LED- μ PIVG) and further

coupled with μ PD-OES for the field detection of Hg, Cd, and Zn. To improve the generation efficiency of H₂, a Co-P nanomaterial was deposited on a titanium mesh as a superior cathode material for the HER. The proposed method overcomes the need for hydrogen storage and transportation while maintaining a high vapor generation efficiency for the tested elements and significantly reducing chemical consumption, alleviating environmental pollution concerns. Finally, the newly proposed HER- μ PIVG- μ PD-OES was successfully applied for analyzing water samples with satisfactory recoveries (92–108%), showing great potential for the field analysis of metal ions.

EXPERIMENTAL

Instrumentation. The experimental setup details are shown in Fig. 1, including an electrolytic cell for HER (GaossUnion Technology Co., Wuhan, China) and a 3D printed LED- μ PIVG- μ PD-OES device (10 cm length \times 2.5 cm width \times 10 cm height). The electrolytic cell includes two single cells (25 mL), a Co-P nanomaterial cathode, a graphite anode, and a perfluorosulfonic acid proton membrane. Two gas tubes at the top of the cathode cell served as the Ar inlet and the outlet for the gas mixture of Ar and H₂. H₂ was generated from the surface of the Co-P cathode and consequently separated from the condensed liquid phase by Ar purging and introduced to the μ PIVG device from the outlet tube. The LED- μ PIVG- μ PD-OES device consists of a LED- μ PIVG reactor, a gas-liquid separator (GLS), and a point discharge microplasma optical emission spectrometer (μ PD-OES) with a commercial handheld inductively coupled device (CCD)

Fig. 1 Schematic diagram of the HER-LED- μ PIVG- μ PD-OES setup.

spectrometer (USB 4000, Ocean Optics, USA). The main part of the LED- μ PIVG reactor is a discharge chamber (1.0 cm length \times 1.0 cm width \times 3.0 cm height), wherein tapered tungsten electrode (0.16 cm diameter \times 3.0 cm length) and stainless-steel tube electrodes (0.06 cm i.d. \times 0.14 cm o.d. \times 5.0 cm length) were inserted face-to-face from the holes (0.15 cm diameter \times 1.0 cm length) drilled on the ends of the chamber. The mixed gas from the electrolytic cell was used as both the carrier and discharge gas and was introduced through a side hole in the chamber. The microplasma was ignited and maintained between the tungsten electrode and the sample solution when a high voltage was supplied by an AC neon sign electric transformer power supply (NGB408BL, Electronic Equipment Factory of Jinshi, Guangzhou, China). A hole (0.2 cm diameter \times 1.0 cm length) on the rear side of the chamber was used for waste solution effluent. The GLS consisted of two hollow columns (3.0 cm diameter \times 5.0 cm height) and their connecting lines (0.2 cm diameter). The μ PD-OES device was connected at the outlet of the GLS, which contains four holes, the large hole directly in front as the discharge chamber (1.0 cm length \times 1.0 cm width), two electrode holes at the top and bottom for the tungsten and nozzle electrodes, respectively, and an exhaust waste gas hole at the rear. The PD microplasma was ignited between the tungsten and nozzle electrodes, and a quartz sheet was attached to the front of the large hole to ensure gas tightness, from which the characteristic emission signals were collected by the CCD spectrometer.

Characterization. X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (TD-3500, Dandong Tongda Technology Co., China). Scanning electron microscopy (SEM) images were recorded using an XL30 scanning electron microscope (FEI Co., USA). X-ray photoelectron spectroscopy (XPS, AXIS Supra, Shimadzu, Japan) was used to characterize the Co-P nanomaterials. Electrochemical experiments were performed using an electrochemical workstation (CHI 660E, Chenhua Instrument Co., China) at room temperature. The electrochemical performance of the prepared Co-P nanomaterial was tested by the conventional three-electrode system. The prepared Co-P nanomaterial was directly used as the working electrode, a graphite film as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All the potentials reported herein were converted from vs. Ag/AgCl to vs. RHE using the equation of $E(\text{RHE}) = E(\text{Ag/AgCl}) + 1.023 \text{ V}$ (1.0 M KOH). The experimental data were calibrated using iR compensation.

Reagents and materials. Titanium mesh (150 mesh), stainless steel mesh (150 mesh), and copper foam (1 mm thick) cut to 1.5 cm length \times 1.5 cm width were used as substrates to synthesize Co-P nanomaterials. All reagents were of analytical grade. High-purity (18.25 M Ω -cm) deionized water (DIW) produced from a water purification system (Chengdu Ultrapure Technology Co., China) was used throughout this study. Hg, Cd, Zn, Fe, Co, Ni, Cu, Pb, K, Ca, Na, and Mg were purchased from the National Standard

Material Center of China (NSMCC, Beijing, China). Standard solutions of Hg, Cd, and Zn were prepared daily by diluting stock solutions with DIW. Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), potassium hydroxide (KOH), and sodium acetate (NaOAc) were purchased from Kelong Chemical Reagent Co. (Chengdu, China). Sodium hypophosphite (NaH_2PO_2) was purchased from Aladdin Co., Ltd. (Shanghai, China). CRMs for water samples (GBW08603 and GBW08607) were obtained from the China National Reference Material Center (NSMCC, Beijing, China). Water samples were also collected from the local rivers, lakes, and groundwater in Chengdu, China. After being transported to the laboratory, the samples were filtered through a 0.22 μm membrane filter and immediately analyzed.

Preparation of Co-P nanomaterials. Herein, the Co-P nanomaterials were obtained by facile potentiodynamic electrodeposition using common cobalt and phosphorous reagents according to a previous report.²⁸ The titanium mesh was immersed in HCl and boiled at 90 $^\circ\text{C}$ for 20 min until the solution turned green. The titanium mesh was cleaned thoroughly in ultrapure water and ethanol before being stored in ethanol. The stainless-steel mesh and copper foam used for comparison were ultrasonically cleaned sequentially in ethanol, ultrapure water, HCl (3 M), ultrapure water, and ethanol to remove surface residues and the oxide layer, and stored in ethanol before use. Subsequently, the pretreatment substrate was fixed on the electrode clamp and exposed to the deposition solution (50 mM CoSO_4 , 0.5 M NaH_2PO_2 , and 0.1 M NaOAc in water). A graphite film was used as the counter electrode and Ag/AgCl (sat. KCl) as the reference electrode. The potential of consecutive linear scans was cycled 15 times between -0.3 and -1.0 V vs. Ag/AgCl at a scan rate of 5 mV/s. After deposition, the Co-P nanomaterial electrode was removed from the deposition bath and rinsed gently with excess water before drying in an oven at 60 $^\circ\text{C}$ for 12 h.

Analytical procedure. The prepared Co-P nanomaterial electrode was used as the cathode, a graphite film as the anode, and a 1.0 M KOH solution as the electrolyte. When a voltage of -4 V was applied to the electrodes, hydrogen was immediately continuously, and stably generated from the cathode. Ar was used to purge the headspace of the cathode cell and mixed with the generated hydrogen to form an Ar-H₂ mixed carrier/discharge gas, which was blown into the LED- μ PIVG reactor. A standard or sample solution was injected into the 1 mL sample loop of the six-way valve with a syringe and flushed into the stainless-steel tube outlet by DIW with a peristaltic pump. The discharge microplasma spontaneously ignited between the sample solution and tungsten electrode when a 90 V input voltage was supplied. The volatile analytes Hg, Cd, and Zn were immediately generated, separated from the liquid phase through GLS, and blown into the μ PD-OES chamber for excitation and detection. Characteristic emission signals were collected using a handheld CCD spectrometer. All experiments were conducted in an adequate ventilation/exhaust

Fig. 2 (a) LSV polarization curves of copper (blk-Cu), stainless-steel mesh (blk-Ss), titanium mesh (blk-Ti), platinum sheet (Pt), and Co-P film on copper (Co-P/Cu), stainless-steel mesh (Co-P/Ss), and titanium mesh (Co-P/Ti) in 1 M KOH at a scan rate of 5 mV s^{-1} ; (b) corresponding Tafel plots of Co-P/Cu, Co-P/Ss, Co-P/Ti, and Pt; (c) low- and (d) high-magnification SEM images of the Co-P nanomaterials on titanium mesh.

system due to the toxicity of the Hg, Cd, and Zn products generated from the system.

RESULTS AND DISCUSSION

Electrocatalytic performance. To achieve satisfactory electrocatalytic performance, the HER activities in a strongly alkaline solution obtained using Co-P nanomaterials deposited on the titanium mesh (Ti), copper foam (Cu), and stainless-steel mesh (Ss) substrate were evaluated, as shown in Fig. 2a. The blank titanium mesh, copper foam, and stainless-steel mesh did not exhibit any HER catalytic activity. The cathodic current of Co-P/Ti increases rapidly when the voltage exceeds -60 mV , and a current density of 10 mA cm^{-2} was achieved with an overvoltage of -133 mV . In addition, Co-P/Ss and Co-P/Cu demonstrated good catalytic activity for the HER, reaching a current density of 10 mA cm^{-2} at overvoltages of -135 and -176 mV , respectively. Tafel curves (Fig. 2b) were further calculated, and Tafel slopes of 57.9 , 59.0 , 60.1 , and 46.0 mV dec^{-1} were obtained for Co-P/Ti, Co-P/Ss, Co-P/Cu, and Pt sheets (Pt), respectively, showing better HER activity for Co-P/Ti compared to Co-P/Ss and Co-P/Cu (smaller Tafel slopes indicate higher kinetic catalytic rates).²⁴ Additionally, the Co-P nanomaterial stability in a strong alkaline solution was investigated by continuous electrolysis for 10 h at a full electrolysis voltage of -4 V . Fig. S1 shows that charge accumulation increased linearly with time, maintaining a stable

current over the entire electrolysis process (Fig. S1 inset). Moreover, the Co-P/Ti current was more stable than those of Co-P/Ss and Co-P/Cu, indicating better HER activity. Therefore, Co-P/Ti was selected as the HER electrode for the subsequent experiments.

Characterization of the Co-P nanomaterials. The morphology of the Co-P nanomaterials deposited on the titanium mesh was characterized using SEM. As shown in Figs. 2c and 2d, a spherical Co-P nanomicrosphere film was observed on the titanium mesh substrate, and the generated Co-P nanomicrospheres on the mesh surface were approximately $3 \mu\text{m}$ in diameter with smaller fine structures on their surfaces, which may expose more active adsorption centers that can facilitate electrolytes and gas diffusion.³² Furthermore, elemental mapping analysis of Co-P/Ti indicated Co and P were distributed evenly over the entire film (Fig. S2). To characterize the crystalline structure of the generated Co-P nanomaterials, as well as analyze their composition and chemical valence, the Co-P/Ti nanomaterials were further characterized by XRD and XPS, as shown in the “XRD results of the Co-P/Ti” (Fig. S3) and “XPS results of the Co-P/Ti” sections in the Supporting Information (Figs. S4 and S5), respectively.

Feasibility of integrating HER-LED- μ PIVG- μ PD-OES. Previous reports have indicated that auxiliary hydrogen used in LED- μ PIVG could significantly improve the CVG efficiency of Hg, Cd, and Zn.¹⁸⁻²² To achieve a safe and convenient hydrogen supply in the field, a miniaturized electrocatalytic HER device was

Fig. 3 The atomic emission spectrum (a: 180–400 nm, b: 200–260 nm) of HER-LED- μ PIVG- μ PD-OES with a blank or sample solution. Injection volume: 1 mL; injection flow rate: 2 mL min⁻¹; carrier gas flow rate: 100 mL min⁻¹; HER voltage: -4 V; LED input voltage: 90 V; PD input voltage: 90 V.

Fig. 4 Atomic emission signal profile (a, b, and c) and calibration curves (d, e, and f) of standard solutions of Hg (a and d), Cd (b and e), and Zn (c and f) using HER-LED- μ PIVG- μ PD-OES.

applied as an alternative to provide the necessary auxiliary hydrogen. The feasibility of the proposed portable HER device integrated with LED- μ PIVG- μ PD-OES for the analysis of Hg, Cd, and Zn was investigated using a standard solution containing 100 μ g L⁻¹ of Hg, Cd, and Zn. As shown in Fig. 3, the distinct atomic emission lines at 253.7, 228.8, and 213.9 nm were observed compared to the blank solution, which were attributed to Hg, Cd, and Zn, respectively, indicating the feasibility of the proposed method for Hg, Cd, and Zn analysis. It should be noted that large

amounts of hydrogen would be generated in the presence of tetrahydridoborate salts (NaBH₄, KBH₄), which inevitably affect excitation efficiencies and can even extinguish the microplasma owing to the dilution of analytes and microplasma destabilization by excess hydrogen.^{16, 33} Herein, the amount of hydrogen generated by the portable HER device (8 mL min⁻¹) integrated with LED- μ PIVG- μ PD-OES was smaller than that of HG, which is conducive to the microplasma stability. Additionally, a small amount of hydrogen can effectively decrease the Ar background

Table 1. Analytical results for Hg, Cd, and Zn in CRMs (N=3, $\mu\text{g L}^{-1}$)

| CRMs | Elements | Certified | HER-LED- μ PIVG- μ PD-OES |
|----------|----------|---------------|-----------------------------------|
| GBW08603 | Hg | 10 \pm 0.4 | 10.2 \pm 0.4 |
| GBW08607 | Cd | 106 \pm 2 | 103.7 \pm 5.2 |
| GBW08607 | Zn | 5230 \pm 50 | 5173.0 \pm 75.0 |

Table 2. Analytical results for Hg, Cd, and Zn in water samples (N=3, $\mu\text{g L}^{-1}$)

| Sample | Elements | HER-LED- μ PIVG- μ PD-OES (This method) | | | ICP-MS |
|-------------|----------|---|----------------|------------------|-----------------|
| | | Added | Found | Recovery, % | |
| Pond water | Hg | 0 | ND | | 0.06 \pm 0.01 |
| | | 5 | 4.7 \pm 0.2 | 93 | |
| | | 10 | 9.9 \pm 0.6 | 99 | |
| | Cd | 0 | ND | | ND |
| | | 50 | 47.9 \pm 3.7 | 96 | |
| | | 100 | 92.3 \pm 6.4 | 92 | |
| Zn | 0 | ND | | 0.90 \pm 0.09 | |
| | 100 | 93.0 \pm 5.7 | 93 | | |
| | 200 | 207.3 \pm 5.5 | 104 | | |
| Groundwater | Hg | 0 | ND | | 0.06 \pm 0.01 |
| | | 5 | 4.6 \pm 0.6 | 92 | |
| | | 10 | 10.7 \pm 0.9 | 107 | |
| | Cd | 0 | ND | | ND |
| | | 50 | 47.5 \pm 1.7 | 95 | |
| | | 100 | 95.8 \pm 2.6 | 96 | |
| Zn | 0 | ND | | 13.50 \pm 0.07 | |
| | 100 | 104.5 \pm 6.8 | 105 | | |
| | 200 | 208.6 \pm 4.8 | 104 | | |
| River water | Hg | 0 | ND | | 0.06 \pm 0.01 |
| | | 5 | 4.6 \pm 0.4 | 92 | |
| | | 10 | 10.8 \pm 0.7 | 108 | |
| | Cd | 0 | ND | | 0.02 \pm 0.01 |
| | | 50 | 48.0 \pm 1.3 | 96 | |
| | | 100 | 96.5 \pm 1.2 | 97 | |
| Zn | 0 | ND | | 7.16 \pm 0.29 | |
| | 100 | 97.9 \pm 4.9 | 98 | | |
| | 200 | 204.4 \pm 3.8 | 102 | | |

emission peaks (e.g. NO and OH), which is beneficial for the sensitive detection of analytes using μ PD-OES.^{34,35}

Optimization of experimental parameters. The integration of HER-LED- μ PIVG with μ PD-OES required the optimization of experimental parameters including HER voltage, sample flow rate, carrier gas flow rate, LED input voltage, and PD input voltage, which were carefully investigated using standard solutions containing 50 $\mu\text{g L}^{-1}$ of Hg^{2+} , 100 $\mu\text{g L}^{-1}$ of Cd^{2+} , and 200 $\mu\text{g L}^{-1}$ of Zn^{2+} to obtain the optimal HER-LED- μ PIVG efficiency and μ PD-OES detection sensitivity (see “Optimization of experimental parameters for HER-LED- μ PIVG- μ PD-OES” in the Supporting Information, Fig. S6). A 4 V HER voltage, 2 mL min^{-1} sample flow rate, 100 mL min^{-1} Ar flow rate and 90 V input discharge voltage of the LED and PD were selected for subsequent experiments. In addition, referring to our previous work,¹⁷ a discharge gap of 3 mm and a pH of 6 (the natural pH of DIW) were chosen as the optimal experimental conditions.

Interferences. To evaluate the anti-interference capability of the

proposed system, the effects of 11 ionic interferences (Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , K^+ , Ca^{2+} , Na^+ , Mg^{2+} , NO_3^- , and Cl^-) on the responses of Hg, Cd, and Zn were investigated, and the results are summarized in Table S1. Satisfactory recoveries (between 85 and 110%) were obtained for Hg, Cd, and Zn at coexisting ion concentrations of 10 mg L^{-1} , indicating no significant interference. Therefore, it can be concluded that the proposed method exhibits a satisfactory anti-interference capabilities.

Analytical performance. The analytical figures of merit of the proposed system were evaluated by analyzing a series of standard solutions of Hg, Cd, and Zn under optimized experimental conditions. The atomic emission signal profiles and typical calibration curves of Hg, Cd, and Zn are shown in Fig. 4. The obtained linear ranges for Hg, Cd, and Zn were 5–1000, 50–1000, and 50–1000 $\mu\text{g L}^{-1}$ with a coefficient of determination (R^2) \geq 0.99, respectively. The limits of detection (LODs) were 0.8, 10, and 14 $\mu\text{g L}^{-1}$ for Hg, Cd, and Zn, calculated as three times the standard deviation of 11 measurements of a blank solution divided by the calibration curve slope. The precision, expressed as the relative

standard deviations (RSDs), was obtained via 20 replicate measurements of 50 $\mu\text{g L}^{-1}$ Hg, 100 $\mu\text{g L}^{-1}$ Cd, and 200 $\mu\text{g L}^{-1}$ Zn standard solutions, with RSDs of $\leq 4.7\%$, as shown in Fig. S7. The analytical figures of merit obtained using the proposed system and other similar μPIVG systems are summarized in Table S2. It can be concluded that the LOD of Hg obtained using the proposed system is comparable to or superior to those of other microplasma OES systems. The LODs for Cd and Zn are comparable to those of most similar systems but worse than those of solution anode glow discharge microplasma (SAGD) and membrane desolvation (MD)-atmospheric pressure glow discharge-OES, possibly due to the different plasma chemical reaction mechanisms of SAGD³⁶ and effective sample introduction of MD, respectively. The obtained LODs of Hg, Cd, and Ni were worse than those of $\mu\text{PIVG-AFS}$, which was attributed to the enhanced capacity in the presence of methanol and the good detection ability of AFS.¹⁷ However, the proposed method has better potential for instrumental miniaturization than the commercial AFS and hydrogen generator and does not require dangerous hydrogen transport for field analysis. Moreover, many studies have shown that the presence of formic acid is beneficial for improving Hg response signals.¹³ Therefore, to further improve the analytical performance of the portable LED- $\mu\text{PIVG-}\mu\text{PD-OES}$ for Hg determination, a series of standard solutions of Hg containing 1% formic acid without the introduction of hydrogen (HER voltage not applied) were analyzed, as shown in Fig. S8. A lower LOD (0.3 $\mu\text{g L}^{-1}$) was obtained in the presence of 1% formic acid, meeting the requirements for field analysis of lower Hg concentrations.

Sample Analysis. The accuracy and practicability of the proposed system were first validated by the determination of Hg, Cd, and Zn in CRMs (GBW08603 and GBW08607), and the results are summarized in Table 1. The *t*-test results show no significant difference between the obtained and certified values at a confidence level of 95%, demonstrating the accuracy of the newly proposed method. To further verify the practicability of the proposed system, Hg, Cd, and Zn in three water samples were analyzed using HER-LED- $\mu\text{PIVG-OES}$ and ICP-MS. Because of the low contents of Hg, Cd, and Zn in the environmental water samples, 5 $\mu\text{g L}^{-1}/10 \mu\text{g L}^{-1}$ of Hg, 50 $\mu\text{g L}^{-1}/100 \mu\text{g L}^{-1}$ of Cd, and 100 $\mu\text{g L}^{-1}/200 \mu\text{g L}^{-1}$ of Zn standard solutions were spiked into the water samples for spiked recovery experiments, respectively. As summarized in Table 2, the spike recoveries ranged from 92 to 108%, indicating good accuracy and practicality of HER-LED- $\mu\text{PIVG-}\mu\text{PD-OES}$ for the determination of Hg, Cd, and Zn in environmental water samples.

CONCLUSION

This work integrates a portable electrocatalytic hydrogen

evolution device with a liquid electrode discharge microplasma-induced vapor generation-tip discharge emission spectrometer (HER-LED- $\mu\text{PIVG-}\mu\text{PD-OES}$) to detect Hg, Cd, and Zn in environmental water samples. This method retains the unique advantages of μPIVG (high vapor generation efficiency, fast reaction speed, simple device structure, and easy construction) and microplasma emission spectroscopy (compact setup, cost-effectiveness, portability, and low power consumption), while eliminating the need for chemical reductive reagents and avoids dangerous hydrogen storage and transportation. The Co-P nanomaterials with stable and excellent catalytic hydrogen precipitation performance provide a hydrogen supply for field analysis using miniaturized equipment for the practical analysis of metal ions using $\mu\text{PIVG-}\mu\text{PD-OES}$.

ASSOCIATED CONTENT

The supporting information (Figs. S1–S7, Table S1–S2) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

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