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A miniature and efficient colorimetric system assisted by the microplasma jet array for Cr (VI) detection

Cheng Yao^a, Yi Cai^{a,*}, Yali Gong^a, Yong Zhao^{a,b}, Qing Chen^{c,**}

^a School of Control Engineering, Hebei Key Laboratory of Micro-Nano Precision Optical Sensing and Measurement Technology, Northeastern University at Qinhuangdao, Qinhuangdao, 066004, China

^b College of Information Science and Engineering, Northeastern University, Shenyang, 110819, China

^c School of Pharmacy, Liaoning Province Key Laboratory for Phenomics of Human Ethnic Specificity and Critical Illness (LPKL-PHESCI), Shenyang Medical College, Shenyang, 110034, China

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ABSTRACT

Microplasma jet (MPJ), serving as excitation sources in miniaturized systems, has been widely used for contaminant detection. However, the employment of the MPJ is conditioned due to the limit generation of the radicals. Here, a novel 4-channel microplasma jet array (MPJA) is designed for 3,3,5,5-tetramethylbenzidine (TMB) rapid oxidation without oxidizing reagents and catalysts. The jet array, generated from a ceramic tube, allows direct contact with the sample. A colorimetric system containing the MPJA has been developed for the detection of hexavalent chromium. Compared to the MPJ, the employment of MPJA significantly makes the detection system effective and sensitive. Under optimal operating condition, the system exhibits a linear response for Cr (VI) detection within the range of $0.3-1.2 \ \mu$ mol L⁻¹, with a detection limit (LOD) of $0.11 \ \mu$ mol L⁻¹. The practicality of the system is validated through the analysis of real-world samples. The system can be packed into a case with 40 cm in length, 30 cm in width and 30 cm in height. The power consumption is 0.052 W. The system provides a potential method for samples determination in emergency.

1. Introduction

Microplasma can be generated at a minimum breakdown voltage under atmospheric pressure according to the theory of Paschen's law. It typically features a micron-scale discharge gap, significantly smaller than that of conventional plasma [1]. Microplasma possesses distinct advantages, including cost-effectiveness, compact size, and low power consumption [2]. The high-energy electrons, ions, and radicals generated by microplasma play significant roles in chemical reactions [3]. Therefore, microplasma technology has gained high recognition in various fields, including environmental monitoring [4], biomedicine [5], clean energy [6], surface treatment [7] etc. The microplasma jet (MPJ), a highly promising form of microplasma, offers the inherent advantages associated with microplasma, and facilitates precise positioning and delicate manipulation [8]. The MPJ also contains a variety of reactive species (·OH, H₂O₂, ·HO₂, O₃, O₂, ·H, ·O, etc), and can be used as a prospective tool for detection. In 2012, an argon MPJ was employed for rapid desorption and atomization of the mercury species on the thin-layer chromatography sheet. Before being introduced to the detector, the inorganic Hg²⁺, methylmercury (MeHg), and phenylmercury (PhHg) in the sample was separated by the MPJ [9]. The investigation of trace 3-NPA determination with MPJ was conducted by Zhou et al. MPJ was used for luminol oxidation and chemiluminescence induction instead of the reagent of hydrogen peroxide [10].

However, the diameter of MPJ is usually confined within a small scale, making it difficult for its widespread application in efficient treatment [11,12]. The microplasma jet array (MPJA), which is ordered arrangements of multiple jets, is gradually gaining prominence. Designing of MPJA is an excellent solution for effective sample processing [13]. The study conducted by Park et al. demonstrated the high efficiency of a low-temperature MPJA in the treatment of Candida albicans infections, while also highlighting its capability to cover an expanded surface area of at least 10 square centimeters [14]. Some researchers also designed various types of MPJA to investigate the properties [15]. Wu et al. developed a photonic crystal fiber-based MPJA. The electron density of this jet array was measured to reach a maximum

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^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: caiyi@qhd.neu.edu.cn (Y. Cai), chenqing0906@symc.edu.cn (Q. Chen).

value of 8 \times 10¹⁶ cm⁻³, which significantly exceeds the typical range observed in general plasma jets (10¹¹–10¹⁵ cm⁻³) [16]. The electron and gas temperatures of the jet array were 0.85 eV and 500 K, respectively. Although the MPJA exhibits such advantages, there exists a lack of research regarding their practical applications for hazardous substances detection.

For some colorimetric method, such as 3,3',5,5'-tetramethylbenzidine (TMB) -based system, oxidants play a key role in the reaction [17-19]. With the presence of specific oxidants (e.g., hydrogen peroxide, bovine serum albumin, etc.) and catalysts (e.g., catalase, graphene oxide, etc), the TMB solution turns blue and oxTMB is formed [20-24]. 8-HQ (C9H7NO), a kind of organic compound, is usually employed as complexing agent. In this work, a 4-channel MPJA is designed for the colorimetric detection of Cr (VI). No oxidant or catalyst is used in the system. The oxidation property of the proposed MPJA is confirmed by Cr (VI) detection through the colorimetric reaction of TMB and 8-HQ. The MPJA has excellent capacity for oxTMB formation. Compared to the MPJ, the electronic excitation temperature of MPJA is improved. After a dozen seconds treatment with MPJA, the absorption spectrum at 652 nm obtained by the system is quantitatively enhanced upon the addition of Cr (VI). The detection is rapid. Through some water samples determination with the proposed system, the reliability and practicality are demonstrated. In this study, the MPJA is utilized as a fundamental component of the detection system, and its performance is deemed satisfactory.

2. Experimental section

2.1. Reagents and chemicals

All chemicals and reagents were of analytical grade and used directly without further purification. The reagents of 8-Hydroxyquinoline (8-HQ, C₉H₇NO), 3,3',5,5' -tetramethylbenzidine (TMB, C₁₆H₂₀N₂), sodium acetate anhydrate (NaAc), CH₃COOH (HAc), hydrogen peroxide (H₂O₂) and dimethyl sulfoxide (DMSO) were purchased from Aladdin Reagents Co, Ltd (Shanghai, China). The stock solution of Cr (VI), with a concentration of 1000 mg L⁻¹ (19.23 mmol⁻¹), was provided by the National Research Centre for Standard Materials (Beijing, China) and contains nitrate ions as anions. Prior to the experiment, solutions of 5 mmol L⁻¹ TMB and 10 mmol L⁻¹ 8-HQ in DMSO were prepared, respectively, for convenient utilization. High-purity argon (Ar, 99.99 %) was used to sustain the microplasma. Throughout the experiments, solutions were prepared using deionized water with a resistivity of ${\geq}18$ M\Omega cm.

2.2. Experimental set-up

The experimental system designed for Cr (VI) detection is exhibited in Fig. 1. This system comprises a MPJA generator, a sample injection unit and an optical detection unit. The MPJA is generated from a 4-channel ceramic tube. As shown in the inset of Fig. 1, there are 2×2 rectangular arrangement holes (0.5 mm in diameter) in the ceramic bar (3 mm in diameter and 40 mm in length). The high-purity argon is used to maintain the microplasma and blow the plume out of the tube. The argon flow rate is regulated by a flowmeter (FL-802, Flow Method Measure & Control Co. Ltd., China). An adjustable voltage is supplied to the electrodes by a neon power supply (ENT-106B, Guangzhou Xinxing Neon Light Supply, China) in conjunction with a voltage controller (DY-T20, Wuhan Da Yuan, China). Only one neon power supply is used for MPJA generation. The power consumption of the MPJA is 0.052W, which is calculated by measuring the resistance between the two electrodes during discharge and the output voltage of the power supply.

Below the MPJA, there is the sample injection unit of the system. The sample is pumped by flow injection pump (WK–101P, Nanjing Anerke Electronic Technology Co., Ltd., China) from the inlet to the passage for MPJA treatment. The passage is 10 mm long and 3 mm wide, and it is leaning at a 3° angle to the horizon. With a flow rate of 85 μ L s⁻¹, it takes 12 s for a sample of 1 mL to flow through the passage. The solution in the passage can adequately contact the MPJA due to the multiple arrangement of the array. After MPJA treatment, the sample flows to the detection cell with a view window. The cell contains about 800 μ L sample. The dimensions of the detection cell are marked in Fig. 1. The sample contains 5 mM TMB, 10 mM 8-HQ and a certain concentration of Cr (VI). The pH value of the sample is 3.8, which is maintained by acetic acid-sodium acetate buffer solution. After completing each sample analysis, the waste is drained from the outlet and the injection unit is washed by the ultrapure water.

On the opposite side of the view window, a halogen lamp (HL-2000, Ocean optics, USA) is set as light source for colorimetric system. An optical fiber with a diameter of 600 μ m (Shanghai Fibo Photoelectric Technology Co., Ltd, China) is inserted into the view window, with its other end connected to a spectrometer (PRO2000, Ocean Optics, USA). The spectrometer captures the absorption spectra, which are then processed on a laptop. In the basis of Lambert-Beer's law, the concentration



Fig. 1. Schematic diagram of the present detection system.

of Cr (VI) can be calculated.

3. Results and discussion

3.1. The mechanism of the colorimetric system

It is well known that with specific oxidants, such as the reagent of hydrogen peroxide, the blue-colored oxTMB is produced from TMB [25, 26]. This is ascribed to the blue charge-transfer complexes derived from the one-electron oxidation of TMB. In fact, the oxidation proceeds quite slow [27]. The MPJA is utilized instead of the oxidants for the rapid oxidation of TMB. The absorbance spectrum obtained after MPJA treatment is shown in Fig. 2. There is an obvious peak at 652 nm. To investigate the significant role of MPJA, hydrogen peroxide is also used as a reagent for comparison. A sample contains 100 µL of 30 % hydrogen peroxide is introduced to the system, there is no obvious absorption at 652 nm, indicating that barely oxTMB is produced during the analytical process. After 10 min, the absorption peak appears. However, the intensity of the absorption peak is not as strong as that obtained by MPJA treatment. The inset of Fig. 2 shows TMB solutions with MPJA treatment and H₂O₂ reagent addition for different time, respectively. The results demonstrate that MPJA can efficiently oxidize TMB. This is attributed to the abundant active radicals present in the microplasma, including ·OH, H_2O_2 , and others. The O_2^- radicals possess oxidation ability and can be obtained through the following process (1) [28],

$$\cdot \mathbf{OH} + \mathbf{H}_2 \mathbf{O}_2 \rightarrow \mathbf{O}_2^- + \mathbf{H}_3 \mathbf{O}^+ \tag{1}$$

Fig. S1 illustrates the EPR of the MPJA. With the spin trapping agent (5,5-dimethyl-1-pyrroline N-oxide, DMPO), the short-lived free radicals form to the stable spin adducts. Fig. S1A shows the typical 1:2:2:1 DMPO-·OH signal peak, indicating the existence of hydroxyl radicals. In Fig. S1B, it can be clearly observed 1:1:1:1 peak of DMPO-·OOH. EPR of the MPJA demonstrates the existence of hydroxyl radicals and super-oxide radicals. The presence of O_2^- radicals in MPJA, enables the production of oxTMB. There is no additional catalyst and oxidant reagent used.

On the basis of Lambert-Beer's Law, the colorimetric method is developed. In the system, the blue color of the solution becomes colorless upon the addition of 8-HQ due to the acquisition of electrons by oxTMB. When Cr (VI) is present in the solution, it acts as a chelating agent and reacts with 8-HQ. The process of the reaction is presented as.



Fig. 2. The absorption spectra of TMB oxidation by MPJA and hydrogen peroxide, respectively.



The oxidation process of TMB is strongly influenced by the pH value of the solution [29]. Fig. 3A shows that when pH value is adjusted to 2.0, the absorption peak at 652 nm and 370 nm disappears. The result exhibits there is only a small quantity of oxTMB is produced. It can be observed that an absorption peak appears at 450 nm, indicating the presence of another substance. The solution undergoes a color transition, which is manifested as yellow. This yellow substance is formed when TMB loses two electrons under low pH conditions, resulting in the formation of a stable quinone conjugated monomer structure [30]. As the pH value increases from 2.0 to 3.8, the solution gradually turns blue from yellow. The blue oxTMB becomes the dominant component. When the pH value exceeds 3.8, the solution color becomes lighter. This is due to the increased difficulty of oxidizing TMB under neutral pH conditions, which results in only a small fraction of TMB being converted into oxTMB.

The dependence of the value of $\triangle A$ (A–A₀, where A and A₀ represent the absorbance peak at 652 nm before and after Cr (VI) addition, respectively) on the pH value of the solution is investigated. With the pH values ranging from 3.4 to 4.2, the products are different, resulting in the transmutation of the color. Although the pH range is narrow (only 0.8), $\triangle A$ value changes greatly. At pH 3.8, $\triangle A$ reaches maximum value, which is indicated that there is the most oxTMB production. Therefore, weak-acid condition is in favor of the TMB oxidation.

The concentration of TMB and 8-HQ should be sufficient for the colorimetric reaction. The dependences of $\triangle A$ on the TMB and 8-HQ concentrations are depicted in Fig. S2A and Fig. S2B in Supplementary Materials.

3.2. The capacity of the MPJA

The MPJA and MPJ are used in the system to demonstrate the oxidation capability, respectively. The outer diameter and inner diameter of the ceramic tube for MPJ generation are 3 mm and 2 mm, respectively. After MPJA and MPJ treatment, the absorbance of the solution is shown in Fig. 4. The MPJA presents high capacity for TMB oxidation. The photographs of the MPJA and MPJ are illustrated as inset in Fig. 4. It is shown that the MPJA has greater luminosity. With four identical microplasma plumes, the MPJA can cover a larger area when treating the solution compared to the MPJ.

One possible reason for this phenomenon is the difference in electron excitation temperature between the MPJA and MPJ. The electron excitation temperature reflects the average energy of electrons and is typically calculated using the Boltzmann plot method, which is based on emission spectral line intensities and relevant parameters [31]. The optical emission spectra of MPJA and MPJ are recorded by a spectrometer (Avs-Desktop-Evo-Usb3, Avantes, Netherlands). The spectra are shown in Fig. S3A and Fig. S3B. A linear plot is obtained with ln $(I_{ki}\lambda_{ki}/A_{ki}g_k)$ on the y-axis, where I_{ki} represents the emission intensity, λ_{ki} denotes the corresponding wavelength, A_{ki} stands for the transition probability, and g_k represents the statistical weight. The excitation energy (E_k) is plotted on the x-axis, as shown in Fig. S4. The electron excitation temperature of the MPJA is calculated to be 3365 \pm 46 K, and that of the MPJ is 2817 \pm 34 K, based on the slope of the linear plot, respectively. The electron excitation temperature of the MPJA is significantly higher compared to that of MPJ. On the other hand, the gas temperatures of MPJ and MPJA are also measured using a thermometer (85-2A, Changzhou Yuexin Instrument Manufacturing Co., Ltd., China). The gas temperatures of MPJA and MPJ are approximately 338 K and 330 K, respectively. This demonstrates that the non-thermal MPJA show



Fig. 3. The absorption spectra of TMB oxidized in the solution with different pH values (A); the dependence of \triangle A on pH (B).



Fig. 4. The absorption spectra of TMB solution treated by MPJA and MPJ, respectively.

superior performance in the proposed system. The oxidation efficiency is tested in the experiment. Excess reagent of hydrogen peroxide is employed as oxidizing agent. The detection is conducted 5 h after hydrogen peroxide addition. The oxidation is presumed completed at this time. The efficiency is 28 %.

3.3. The generation of the MPJA

The active radicals produced from the MPJA oxidized TMB to oxTMB. The discharge voltage and argon flow rate are critical for producing radicals. An optimal discharge voltage is required to generate the MPJA. With an alternating voltage of 40 kHz, microplasma generates between the two electrodes, and the plume forms at the nozzle of the ceramic tube. The MPJA flows through the channel of the argon stream. As shown in Fig. 5A, \triangle A value decreases as the discharge voltage increases from 2.27 kV to 3.46 kV. Although a high electric field favors the formation of longer microplasma plumes and more active plasma chemistry, it also induces unstable discharge. In addition, from the photographs of the discharge with different voltages, it can be found that the jets from different channel is almost identical.

Argon, air and helium are employed as work gas in the detection system. However, it is hard for air to generate microplasma due to the high breakdown voltage. With helium as work gas, the oxidation efficiency is only 1.2 %, which is much lower than that with argon. Therefore, Argon stream is used to maintain the MPJA. A stable MPJA



Fig. 5. The dependence of $\triangle A$ on the discharge voltage (A) and argon flow rate (B), along with the photographs of MPJA with different conditions.

forms at the nozzle of the ceramic tube when the flow rate reaches 400 mL min⁻¹. The dependence of $\triangle A$ on the flow rate of argon stream is illustrated in Fig. 5B. With the higher flow rate, the value of $\triangle A$ decreases. A higher argon flow rate results in longer jet lengths and an increased contact area with the solution, leading to a greater production of reactive radicals in the solution. However, the excess free radicals continue to oxidize TMB when the 8-HQ and Cr (VI) exist in the solution [32]. The variation of absorbance induced by Cr (VI) is affected as a consequence. Besides, the low flow rate of argon stream is benefit to the low consumption and portable detection.

3.4. The rapid and sensitive detection of Cr (VI)

The proposed system is developed for rapid detection. With the 4channel MPJA placed above the sample passage, the TMB in the aqueous solution oxidizes to oxTMB as the sample flows through the passage. Controlling the sample flow rate is key to achieving sufficient and rapid oxidation. Fig. S5 illustrates that $\triangle A$ reaches its maximum value at a flow rate of 85 µL s⁻¹. With a sample flow rate higher than 85 µL s⁻¹, the MPJA treatment time is too short to complete oxidation. When the sample flow rate is below 85 µL s⁻¹, the excess of radicals is produced in the solution. This does not benefit the variation in absorbance induced by Cr (VI). When a 1 mL sample is injected into the system at a flow rate of 85 µL s⁻¹, the MPJA treatment can be accomplished in just over 10 s.

With the optimal working conditions (summarized in Table S1), a series of solutions with different concentrations of Cr (VI) are injected into the system. The $\triangle A$ values obtained are shown in Fig. 6. It is illustrated that values of $\triangle A$ increase with the concentration of Cr (VI). Within the range of 0.3–1.2 μ mol L⁻¹, there is a strong linear relationship between A values and Cr (VI) concentration. The most important reason for the narrow detection range is probably the incomplete oxidation of TMB. Although the oxidation capacity of the proposed MPJA is superior to the MPJ and hydrogen peroxide, the oxidation efficiency is still not high in a short time. The proposed system has a detection limit (LOD) of 0.11 μ mol L⁻¹ for Cr (VI) detection, which is significantly lower than the permissible level of Cr (VI) in daily drinking water (10 μ mol L⁻¹). The LOD of the proposed method is satisfactory. The LODs of this method, along with those of other reported methods, are presented in Table 1. Besides, the present system is both portable and free of oxidants. With the usage of mobile power supply, the emergency analysis can be accomplished.



Fig. 6. The calibration curve of $\triangle A$ caused by different concentration of Cr (VI).

Table 1

Comparison of analytical performance for Cr (VI) obtained by different methods.

Methods	Detection range (μ mol L ⁻¹)	LOD (µmol L ⁻¹)	Ref.
Eu ³⁺ complex-based	1–60	0.44	[33]
Electrocatalytic reduction	10–130	2.97	[34]
A "turn off-on" fluorescent	0.5–400	0.36	[35]
Electrochemical detection	1–2000	0.138	[36]
Inner-filter effect induced carbon	0.5–400	0.10	[37]
Carbon dots derived from kanamycin sulfate	10–30	2.4	[38]
Colorimetric system assisted by MPJA	0.3–1.2	0.11	This work

3.5. The real-word samples determination

The interference caused by the sample matrix is investigated. Some compounds are added to the solution, which contains 0.50 μ mol L⁻¹ of Cr (VI). It is turned out that the addition of 200-folds Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, CO₃²⁻, S²⁻, SO₄²⁻, ethylenediamine and alcohol, 50-folds Zn²⁺, Ag⁺, Co²⁺, Al³⁺, Cd²⁺, Fe³⁺, Li⁺, Mn²⁺, Ni²⁺, Cu²⁺ and Pb²⁺ does not have any obvious interference with Cr (VI) detection, respectively.

The system is applied for determination of real-word samples. Several water samples, including rainwater and welted snow water (collected in Qinhuangdao, China), as well as a certified water sample (purchased from the National Reference Material Center), are determined by the present system. The results are shown in Table 2. For the certified water sample, the detection value is closed to the certified value. No analyte has been detected in the rainwater. Spiked with 0.40 μ mol L⁻¹ of Cr (VI) in the samples, the recovery of certified water sample, rainwater and melted snow water are 102 %, 104 % and 106 %, respectively. The practicability and reliability are demonstrated.

4. Conclusions

A 4-channel MPJA is developed for the TMB colorimetric system in this study. The MPJA, as an integral part of the system, can rapidly oxidize TMB within a short period of time without requiring additional oxidants or catalysts. Under optimal operating condition, the system exhibits a linear relationship in the range of 0.3–1.2 $\mu mol \ L^{-1}$ for Cr (VI) detection, with a detection limit (LOD) of 0.11 μ mol L⁻¹. The detection is rapid. This miniature system exhibits excellent analytical performance, and the reliability and practicality are also demonstrated. The mechanism of the colorimetric system, the generation and the capacity of the MPJA are discussed in the study. With the higher electron excitation temperature, MPJA plays a significant role in the system for rapid and sensitive detection of Cr (VI). The proposed MPJA provides a new way for hazard detection in emergency. Predictably, the MPJA has great potential to become a powerful tool in the field of detection as novel excitation source for optical emission spectrometry, the ionization source for mass spectrometry, etc. And also, it can be employed for surface treatment. Further investigation should be conducted on the structures and mechanism to improve the performance of the MPJA.

Table 2
Determination of Cr (VI) in practical samples using the present system.

Sample	Certified (µmol L ⁻¹)	Found (µmol L ⁻¹)	Spiked (µmol L ⁻¹)	Recovery (%)
GSB 07–3174–2014	$\textbf{0.68} \pm \textbf{0.04}$	$\textbf{0.68} \pm \textbf{0.09}$	0.40	102
Rainwater	-	Not found	0.40	104
Melt snow water	-	$\textbf{0.40} \pm \textbf{0.04}$	0.40	106

CRediT authorship contribution statement

Cheng Yao: Writing – original draft, Investigation. **Yi Cai:** Writing – review & editing, Methodology. **Yali Gong:** Validation. **Yong Zhao:** Supervision. **Qing Chen:** Methodology, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2024.127286.

Data availability

No data was used for the research described in the article.

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