Detection of trace heavy metals using atmospheric pressure glow discharge by optical emission spectra

Xiao Li¹, De-Zheng Yang¹,² ©, Hao Yuan¹, Jian-Ping Liang¹, Tao Xu¹, Zì-Lu Zhao¹, Xiong-Feng Zhou¹, Li Zhang¹,³, Wen-Chun Wang¹

¹Key Laboratory of Materials Modification, Dalian University of Technology, Ministry of Education, Dalian 116024, People’s Republic of China
²School of Science, Shihezi University, Shihezi 832003, People’s Republic of China
³Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610 Wilrijk-Antwerp, Belgium
© E-mail: yangdz@dlut.edu.cn

Abstract: In this Letter, atmospheric pressure glow discharge based on a small discharge gap is excited by sine AC voltage in air on purpose of detecting trace heavy metal elements in solid samples, which makes the detection limits of trace heavy metal elements reach tens μg/kg. The waveforms of voltage and discharge current, discharge images, plasma gas temperature, and optical emission spectra are obtained to discuss the feasibility of atmospheric pressure glow discharge on detection of trace heavy metals. The formation mechanism of optical emission spectra and the strong emission intensity of heavy metal elements show that energetic electrons and excited metal atoms are easily generated by atmospheric pressure glow discharge. The effects of applied voltage and discharge gap on atmospheric pressure glow discharge are discussed to acquire the optimal experimental conditions. And a smaller discharge gap and applied voltage can restrain the transition from glow discharge to arc discharge. Besides, the limits of detections of Cu and Cd are about 0.0241 and 0.0318 μg/g, respectively, by using atmospheric pressure glow discharge with an applied voltage of 3.8 kV, discharge gap of 3.5 mm, and driving frequency of 10 kHz.

1 Introduction

With the development of modern society and the further promotion of industrialisation and urbanisation, environmental pollution problem is becoming more and more serious [1–3]. Among all types of pollutants reported, heavy metals are considered to be the biggest threat to the environment and the human body [4–6]. Heavy metals with invisibility, persistence and irreversibility [7], are very difficult to be biodegraded. Moreover, heavy metals can interact strongly with proteins and enzymes in the human body, causing them to lose activity and accumulate in some organs of the human body thereby posing a threat to the health of human beings [8, 9]. Therefore, that is of great significance and application value to detect and treat heavy metal pollutants. The common methods for detecting heavy metals include inductively high-performance liquid chromatography (HPLC) [10], laser-induced breakdown spectroscopy (LIBS) [11], capillary electrophoresis (CE) [12] and so on. In recent years, because of low cost and no requirement for the vacuum system, atmospheric pressure plasma has been widely used in the diagnosis of various plasma parameters, particle types and reaction processes [13–15]. And it has been an ideal method for detecting trace heavy metal elements.

Kim et al. [16] found that the limits of detections (LODs) of Cr, Cu, Fe, Mn, Ni, Pb, and Zn are calculated to be in the ranges from 0.01 to 0.6 mg/l by open-air type electrolyte cathode atomic glow discharge (ELCAD). Yu et al. [17] determined copper and lead in ores samples by a novel liquid cathode glow discharge (LCGD) based on the principle of ELCAD. It is found that the LCGD has higher excitation efficiency, lower energy consumption and better discharge stability. Also, Webb et al. [18] studied the effects of discharge gap size, the pH and conductivity of the solution on the emission intensity of heavy metal elements. However, the properties and detection limits of trace heavy metal elements are usually determined by atmospheric pressure plasma in liquids but seldom in solid samples, because heavy metals in solids require higher energy to be excited, so it is a challenge to detect heavy metal elements in solids.

In this Letter, glow discharge based on a small discharge gap is generated by using AC voltage as the excitation voltage and applied for detecting heavy metal elements in solid samples. The waveforms of voltage and discharge current, the optical emission spectra (OES), plasma gas temperature are obtained to discuss the mechanism of atmospheric pressure glow discharge (APGD) on heavy metal element analysis. Comparing the OES and plasma gas temperature under different applied voltages and different discharge gaps, the optimum applied voltage and discharge gap are obtained in this study. Besides, the analytical performances of APGD and the limits of detections of heavy metal elements Cu and Cd are investigated.

2 Experimental

2.1 Experimental setup

The experimental setup for the analysis of heavy metal elements is schematically illustrated in Fig. 1, which is composed of a discharge reactor, a sine AC power supply, an electrical measurement system, and an optical detection system. A sine AC power supply (CTP-2000K, 5–15 kHz) is used to generate the plasma for detection of trace heavy metal elements, and the driving frequency chosen in the experiment is 10 kHz. The applied voltage can be adjusted between 0 and 5.0 kV. For discharge reactor, the anode is made of tungsten with the diameter of 4 mm and the curvature radius of the bottom is 0.4 mm, and the cathode is made of a graphite rod with 4 mm diameter. To fix Al₂O₃ pellets containing trace heavy metal elements, there is a groove with a diameter of 2 mm and the depth of 1 mm on the top of the graphite rod. The plasma is generated in the gap between the anode and the cathode, which can be adjusted between 3.5 and 5.5 mm. A 300 pF capacitance is connected between the plasma power supply and the anode. The sine AC power supply and the reactor are connected to the ground separately. For electrical measurement system, two high-voltage probes (Tektronix P6015A 1000 × 3.0 pF 0.001 MΩ and HV-P60 2000 × 5 P 1000 MΩ) connect both sides of the capacitor respectively, the data collected by probe 1 can be regarded as applied voltage, while the data collected by probe 2 can be approximated to gas voltage. The discharge currents are measured with a current probe (Tektronix TCP312 Bandwidth 100 MHz).
The calculated actual concentrations of Cu in Al$_2$O$_3$ pellets are 3.99, 1.90, 0.38, 0.19 and 0.040 µg/g, and the actual concentrations of Cd are 3.74, 1.75, 0.37, 0.18 and 0.036 µg/g. The difference in the actual concentration of Cu and Cd is due to the different adsorption capacity of Al$_2$O$_3$ pellets to the two salt solutions.

3 Results and discussion

3.1 Visualisation and electrical characters of APGD

When the high voltage applied on the upper electrode exceeds the breakdown voltage, plasma can be generated in the discharge gap. As shown in Fig. 2, the discharge images are captured by Cannon 70D digital camera with an exposure time of 100 ms, as the discharge gap and driving frequency are kept at 3.5 mm and 10 kHz, respectively. And three subpictures in the same line show the discharge images taken in different time at the same location, which are captured at the same discharge condition. It can be seen that the discharge shows a bright channel through the discharge area, and the most intense discharge takes place in the vicinity of the needle electrode. From Figs. 2a and b, it can be found that the light emission intensity and volume of the discharge increase with the increase of applied voltage. When the applied voltage is kept at 2.0 kV, the discharge region is only between the needle electrode and the top of Al$_2$O$_3$ pellet. It is clearly seen that the discharge region has been extended to the outside of the whole pellet when the applied voltage is kept at 3.8 kV. This is mainly due to the increase of electric field intensity with the increase of applied voltage, and there are more excited ions and molecules generated in a larger discharge region [19]. Therefore, the discharge volume and the discharge intensity increase. However, the discharge becomes very unstable and there is a bright arc in the discharge gap when the applied voltage is 5.0 kV from Fig. 2c. And the change of light emission intensity is obvious and the arc drifts around the graphite electrode under this condition.

The information about the voltage and the discharge current is important for revealing the mechanisms of the ignition and extinction of APGD, and the waveforms of voltage and discharge current are shown in Fig. 3 under the conditions of 3.5 mm discharge gap and 10 kHz driving frequency. As shown in Fig. 3a, the discharge belongs to a typical glow discharge mode [20–22]. In this case, it can be noted that the current variation is slower and of longer duration (∼35 µs), and the current peak is about 21 mA. When the applied voltage is 3.8 kV, the waveform of voltage and discharge current is almost consistent with that of 2.0 kV from Fig. 3b. And the discharge current increases and the gap voltage decreases. However, the discharge becomes instable and the conversion from glow discharge to arc discharge cannot be suppressed when the applied voltage is 5.0 kV, as shown in Fig. 3c. The gap voltage increases firstly and then decreases to zero when discharge occurs between two electrodes. After that, the gap voltage keeps almost constant and the current presents sinusoidal waveform, which is a typical characteristic of arc discharge.

3.2 Plasma temperature

Plasma temperature is a basic indicator which directly influences the reaction processes between active species generated by APGD and heavy metal ions and further affects the detection limits of heavy metal elements. Because of the small energy gap between the rotational levels of the molecules, the equilibrium between translational motion and rotational motion is readily achieved by frequent collisions between the heavy particles at atmospheric pressure, therefore, it can be considered that the rotational temperature is approximately equal to plasma gas temperature [23, 24]. The rotational temperature of N$_2$ (C$^3Π_u$→B$^3Π_g$, Δʋ = −2) can be acquired by Specair code developed by Laux et al. [25], owing
to the assumption that the rotational states are in equilibrium and characterised by a Boltzmann distribution with an intensity given in the following equation:

\[
I_M = a(2J + 1)A_JJ \nu_JJ \exp\left(-\frac{E_J}{kT_{rot}}\right),
\]

where \(a\), \(A_JJ\), \(\nu_JJ\) and \(E_J\) are a constant, the rotational transition probability, the transition frequency, and the rotational energy, respectively. The rotation temperature and the vibrational temperature of \(N_2 (C^3Π_u \rightarrow B^3Π_g, \Delta \nu = -2)\) can be obtained by comparing the best-fitted spectra simulated by Specair and the experimental spectra [25, 26]. To obtain an adequate rotational temperature, each group of data is recorded three times under the same condition. As shown in Fig. 4, it can be clearly seen that simulated \(N_2 (C^3Π_u \rightarrow B^3Π_g, \Delta \nu = -2)\) has good agreements with experimental spectra when applied voltage, discharge gap, and driving frequency are kept 3.8 kV, 3.5 mm and 10 kHz, respectively. Under these experimental conditions, the rotational temperature is about 2135 K, and the vibrational temperature is about 3505 K. This is, the plasma gas temperature is about 2135 K. This indicates that the discharge is in a non-thermal equilibrium state, which also confirms that the discharge generated by the device is atmospheric pressure glow discharge.

### 3.3 Optimisation of experimental conditions

In APGD, electrons and charged particles are accelerated by the electric field, and plenty of high energy particles are produced by collision, excitation and ionisation. These high energy particles collide with the surface of \(Al_2O_3\) pellet to form ground-state metal atoms. Then these ground-state atoms are further excited to the excited state through the electron impact excitation and thermal excitation, excited atoms transit back to the ground state and emit light, which is recorded by a grating monochromator and displayed as OES. The wavelengths of heavy metal elements are chosen as 324.8 nm (Cu I) and 228.8 nm (Cd I) in this experiment. Simplified reaction processes of active species during discharge and OES of Cu I and Cd I are depicted in Fig. 5.

Applied voltage and discharge gap are two main factors that directly affect active species reaction processes, OES of trace heavy metal elements and plasma gas temperature in APGD. Under the conditions of 10 kHz driving frequency and 3.5 mm discharge gap at atmospheric pressure, the effect of applied voltage on the emission intensity of Cu I is shown in Fig. 6. It can be clearly seen that with the increasing of applied voltage, the emission intensity of Cu I increases from about 792 a.u. at 2 kV applied voltage to 2997 a.u. at 3.8 kV and then decreases to 2054 a.u. at 5.0 kV applied voltage. When the applied voltage is >3.8 kV, the increase of applied voltage leads to the increase of energy injected into discharge gap, which increases the density of energetic electrons, increasing the collision frequency between electrons and active particles, so the emission intensity of Cu I increases. However, when the applied voltage is >3.8 kV, the emission intensity of Cu I decreases with the increasing of the applied voltage. Under the experimental conditions, the arc drifts around the graphite electrode, and the discharge becomes extremely instable, which can also be seen from the variation trend of plasma gas temperature with discharge duration time in Fig. 7. It can be found that plasma gas temperature keeps almost constant in a long operating time when applied voltage are 2.0 and 3.8 kV, which indicates that the APGD has an excellent thermal stability under the experimental conditions. Besides, as the increase of applied voltage, plasma gas temperature increases. However, the plasma gas temperature is very instable when the applied voltage increases to 5.0 kV. Based on the above discussion, 3.8 kV is selected as the optimal applied voltage.

Discharge gap is also one of the most important factors affecting APGD in air. As a result of the high breakdown threshold of air at atmosphere (32.0 kV/cm), a small discharge gap is necessary for the plasma generators to reduce the applied ignition voltages, the discharge gap in this study is adjustable from 3.5 to...
5.5 mm. Fig. 8 shows the effect of the discharge gap on the emission intensity of Cu I under the condition of 3.8 kV applied voltage and 10 kHz driving frequency. The discharge mode is glow discharge when the discharge gap is <5 mm. The plasma generated by atmospheric pressure AC discharge in the air has a higher gas temperature, which is conducive to a large number of heavy metal ions escaping from the Al$_2$O$_3$ pellet and then generating lots of heavy metal atoms. When the discharge gap is <4 mm. It can be seen from Fig. 9 that the plasma gas temperature decreases, which indicates that the amount of Cu$^{2+}$ escaping from Al$_2$O$_3$ pellet, so the emission intensity of Cu I decreases. When the discharge gap gradually increases to 5 mm, the plasma volume becomes larger and more light enters the optical fibre, which increases the emission intensity of Cu I. However, the discharge becomes unstable and conversion from glow discharge to arc discharge cannot be suppressed when the discharge gap is >5 mm, and the discharge channel that directly passes over the Al$_2$O$_3$ pellet, drifts around the graphite electrode. As shown in Fig. 9, the plasma gas temperature change irregularly when the discharge gap is 5.5 mm, which is the main reason for the decrease of emission intensity of Cu I at this time. However, the plasma gas temperature remains almost constant in 10 min operating time when the discharge gap is 3.5 and 4.5 mm. In conclusion, the optimal discharge gap is 3.5 mm.

### 3.4 Analytical performance.

The analytical performance of APGD is discussed under the experimental conditions of 3.5 mm discharge gap, 3.8 kV discharge voltage, and 10 kHz driving frequency. The Al$_2$O$_3$ pellets with a series of concentration of Cu$^{2+}$ and Cd$^{2+}$ and the blank Al$_2$O$_3$ pellets are used to determine the working curves and LODs of Cu and Cd analysis. The working curves of Cu and Cd with 3.8 kV applied voltage, 3.5 mm discharge gap and 10 kHz driving frequency are shown in Fig. 10. It is apparent that the emission intensities of Cu I and Cd I increase with the increase of calibration curves and
The OES of Cu I and plasma gas temperature studied under the varied discharge gap and applied voltage indicate that smaller discharge gap and applied voltage can effectively restrain the conversion from glow discharge to arc discharge, and glow discharge is a stable discharge which is beneficial to the detection of heavy metal elements in solids. The optimal experimental parameters of APGD for trace heavy metal elements analysis with 10 kHz driving frequency are 3.5 mm discharge gap, and 3.8 kV applied voltage. Under the optimal experimental conditions, the rotational and vibrational temperature of $N_2 (C^1H_2 + B^1H_2, \Delta v = -2)$ keeps about 2135 and 3505 K, respectively. Besides, the LODs of Cu and Cd are about 0.0241 and 0.0318 µg/g. Considering the low-cost and simple discharge device, APGD by OES could be a great alternative to detect trace heavy metal elements in solid samples.

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6 References
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Fig. 10 Working curves for Cu and Cd with 3.8 kV applied voltage and 3.5 mm discharge gap

Table 1 Analytical performance of APGD

| Elements | Working curves | $R^2$ | LOD, µg/g |
|----------|----------------|-------|-----------|
| Cu       | y = 335.52 + 753.97x | 0.9995 | 0.0241    |
| Cd       | y = 155.86 + 157.16x | 0.9905 | 0.0318    |

Table 2 Comparison of LODs obtained by APGD with other techniques for detecting trace heavy metals

| Metal elements | APGD, OES, µg/g | ETAAS, µg/g | LIBS, µg/g | MAE/GFAAS, µg/g |
|----------------|-----------------|-------------|------------|-----------------|
| Cu            | 0.0241          | 1.3         | 3.21       | 0.020           |
| Cd            | 0.0318          | 1.1         | 4.58       | 0.025           |

correlation coefficients ($R^2$) are obtained for Cu and Cd, and $R^2$ for Cu and Cd are 0.9995 and 0.9905, respectively. More than, the slope of Cu is more than Cd, which means the sensitivity of APGD is higher on Cu detection than Cd.

The LOD is a very important parameter for any analytical spectroscopic technique. LOD means the lowest analyst concentration that can be detected with this technique. The LODs of Cu and Cd using APGD are calculated by the following equation [27]:

$$\text{LOD} = \frac{3s}{k}$$

where $s$ is the standard deviation of ten measurements of blank Al$_2$O$_3$ pellets, and $k$ is the slope of the working curve. The coefficient 3 is used to give > 99% confidence that the signal detected is due to the analyte and not random error. The results of the calculation are given in Table 1, the LODs of Cu and Cd are about 0.0241 and 0.0318 µg/g, respectively. A comparison of the LODs obtained by APGD with electrothermal atomic absorption spectrometry (ETAAS) [28], laser-induced breakdown spectroscopy (LIBS) [29], and microwave assisted micellar extraction and graphite furnace atomic absorption spectrometry (MAME/GFAAS) [29] is shown in Table 2, it is found that LODs of Cu and Cd obtained by APGD are lower than or similar to those obtained in other studies. The lower LODs indicate that APGD has a good application value for direct detection of trace heavy metal elements in solid samples.

4 Conclusion
In conclusion, the capability of APGD by OES for direct detecting trace heavy metal elements in solid samplings has been demonstrated in atmospheric air. Discharge images and waveforms of voltage and discharge current show that the APGD maintains stable for a long operating time when the applied voltage is <3.8 kV, while the discharge stability is poor when the applied voltage is >3.8 kV. The OES of Cu I and plasma gas temperature studied...
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