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RESEARCH PAPER

Miniaturized Corona Discharge-Atomic Emission Spectrometer for Determination of Trace Mercury

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Abstract: A miniaturized atomic emission spectrometer composed of a corona discharge source and a handheld charge-coupled device detector was assembled for the sensitive determination of trace mercury, with photochemical vapor generation for sample introduction. By using formic acid, mercury vapor was generated under the irradiation of UV light, and then the vapor was introduced into the corona discharge area with the carrier gas flow of argon. The optical signals were captured and analyzed by the charge-coupled device detector at 253.7 nm. Under the optimized conditions of 4% formic acid, discharge voltage of 90 V, and at carrier gas flow rate of 200 mL min^{-1}, the stable detection signals were obtained (RSD = 2.5%). The calibration curve was plotted with the concentration of mercury ranging from 0.5 ng mL^{-1} to 1000 ng mL^{-1}, with a correlation coefficient > 0.99 and the limit of detection of 0.03 ng mL^{-1}. Two certified reference materials were analyzed, and a *t*-test demonstrated that the determined results by the proposed method had no significant difference with the certified values at the confidence level of 95%. Water samples collected from both Funan River in Chengdu and Lotus Pond on campus of Sichuan University were analyzed as well, with the recoveries of standard addition between 93.8% and 103%. The miniaturized instrumentation demonstrated several advantages such as easy construction, low power consumption, high sensitivity, and portability for field analysis.

Key Words: Corona discharge; Mercury; Photochemical vapor generation; Atomic emission spectrometry

1 Introduction

Mercury is regarded as one of the most toxic elements, which is usually released into the environment from both anthropogenic and natural sources. The released mercury species could be further accumulated and transformed into more toxic species through food chain, which would be very harmful to ecosystem and human health[1]. At present, mercury pollution has become a worldwide environmental problem. The determination of mercury species always attracts attentions for analytical purposes, with new and effective methods as favorite.

A number of analytical methods were employed for the determination of trace mercury, and cold vapor generation coupled with atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS) was the most commonly used method for the analysis of different kinds of samples in terms of mercury determination[1–4]. However, AAS or AFS could not meet the requirement of supervisory monitoring, emergency monitoring and in-field analysis due to their relatively bulky instrumentation, while compact instrumentation with portable scale, low cost, less power consumption and easy operation has become more popular for those analytical purposes. Recently, lots of research work has focused on the development of miniaturization of atomic spectrometric systems. For instance, innovated discharge technique producing and sustaining low temperature plasma such as dielectric barrier discharge[5–7], glow discharge[8,9],

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capacitively coupled plasma[10,11] and microplasma device[12] were the favorite options. Corona discharge (CD) was a common phenomenon of gas discharge, which was generated in electric field associated with small-diameter wires, needles, or sharp edges as possible electrodes. The applications employing CD could be dated back to the first electrostatic precipitator of Lodge years ago[13]. CD was used for analysis of complex mixtures of biological molecules[14] and purification of gas and water for many years[15,16]. It was used as an ionization source for mass spectrometry[17] and ion mobility spectrometry as well[18,19]. Moreover, with low-power electrical discharges under atmospheric pressure, it could be used for atomization of volatile species and even further excitation to obtain atomic emission spectra.

With traditional manner, cold vapor of mercury was usually generated through chemical reduction using $SnCl_2$ or $NaBH_4$ as a reducing reagent. However, the interference of extra generated gas (e.g. hydrogen), or low vapor generation efficiency ($SnCl_2$) restricted further widespread applications of these reducing systems[20]. Some regent-free methods were also used such as electrochemical vapor generation[21], ultrasound-promoted chemical vapor generation (CVG)[22,23] or photo-CVG[24–26]. Of all, photo CVG using no toxic reducing reagents is an attractive and green sample-introducing technique incorporating free radicals generated based on photo redox reactions, through which mercury species can be converted into mercury vapor with aid of free radicals generated from decomposition of organic acids via photo irradiation.

In this context, a miniaturized atomic emission spectrometer incorporating CD optical source, photo CVG sampling method and charge-coupled device (CCD) detector was developed for the determination of mercury, and demonstrated advantages of compact instrumentation, low cost, easy operation, and high sensitivity. Compared with traditional cold atomic fluorescence spectrometers for mercury determination, this device used CD as excitation source with stable discharging and strong excitation. Chemical vapor generation for sample introduction with the aid of formic acid and UV light irradiation demonstrated high efficiency and low consumption of chemical reagents, which also made the developed method efficient and green.

2 Experimental

2.1 Instrumentation

As shown in Fig.1, the miniaturized detection system was composed of four parts including a six-way valve, a laboratory-built CD device, a ultraviolet (UV) lamp and a USB2000 charge coupled device (Ocean Optics, USA). The six-way valve consisted of a quantitative ring (3 mL) for sampling. When the handle of six-way valve was set “Load”, the sample was firstly filled all through the quantitative loop. When the handle of six-way valve was set “Flow”, the sample was subsequently swept into the reaction tube by carrier liquid of 1% formic acid solution, where mercury vapor was generated under the irradiation of UV light, which was then introduced into the CD area by an argon flow. As the discharging gas, argon was ionized and excited, with CD then generated near the tip electrode with small radius of curvature because the local electric field intensity was greater than the ionization field intensity of argon. During the discharge process, argon flow rate and the pressure of the discharge tube was kept constant to make CD uniform and stable. The discharge energy could make mercury atoms excited with corresponding atomic emission spectra which were collected and analyzed by a CCD detector, using peak area of signals for quantification. The laboratory-built CD device consisted of a quartz cross tube (50 mm long, 5.0 mm i.d., 7.0 mm o.d.) and two pieces of platinum-iridium filament (0.5 mm in diameter) aligned along the tube’s centerline as electrodes. An inter-electrode distance of 1.5 mm could ensure the generation of most stable micro-plasma. An ozone generation device (YG. BP101P, Electronic Equipment Factory of Guangzhou Salvage, Guangzhou, China) and a transformer (TDGC2-1, Zhejiang Chint Electric Co. Ltd., Zhejiang, China) were used for power supply.

2.2 Reagents and materials

Argon (99.99%, QiaoYuan Gas Co. Ltd., Chengdu, China) was used as both discharge gas and carrier gas. Standard solutions, in the medium of 4% formic acid, were prepared via further dilutions of stock mercury standard solutions. All other chemicals were of analytical grade and purchased from Kelong Chemical Reagents Factory (Chengdu, China). Ultra-pure de-ionized water used for all experiments was obtained from a water purification system (Chengdu Ultrapure Technology Co. Ltd., China).

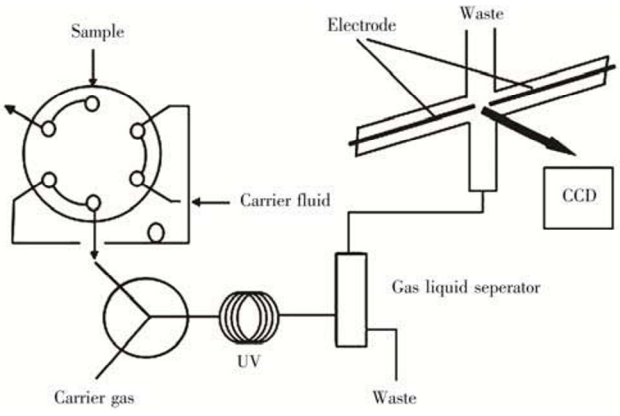

Fig.1 Schematic diagram of corona discharge-atomic emission spectrometer using charge-coupled device as spectral detector