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Dielectric barrier discharge molecular emission spectrometer as gas chromatographic detector for amines

Chenghui Li [a], Xue Jiang [a], Xiandeng Hou [a,b,*]

[a] College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China
[b] Analytical & Testing Center, Sichuan University, Chengdu, Sichuan, 610064, China

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ABSTRACT

Nano-SiO_2 was immobilized on the inner wall of a dielectric barrier discharge (DBD) tube, and it was coupled to a conventional gas chromatographer to investigate its performance as a molecular emission spectrometric detector for the determination of five volatile aliphatic amines. A charge-coupled device (CCD) was applied to observe the nano-SiO_2-enhanced molecular emission spectra. The characteristic molecular emission bands of volatile aliphatic amines at 326.5 nm, 336.0 nm and 388.3 nm can be clearly resolved from the background emission spectra of carrier gas argon. The emission band of CN at 388.3 nm was used for quantitative detection of volatile aliphatic amines due to its high sensitivity. Nanomaterial catalysts including TiO_2, MnO_2, SiO_2 and ZnO were tested to enhance the emission signal of amines, and SiO_2 shows the best performance. The factors that influence the emission signal, such as discharge voltage, inner electrode length and carrier gas flow rate, were investigated in detail. The analytical performance of this method was evaluated by separation and detection of the mixture of five volatile aliphatic amines. Under the optimal experimental conditions, the limits of detection were found to be 4.4, 2.5, 2.2, 1.8 and 2.4 μg for dimethylamine, trimethylamine, n-butylamine, cyclohexylamine and ethylenediamine, respectively. This GC detector is not only sensitive but also fast in response to volatile aliphatic amines with good stability. Trimethylamine in a carp fish sample was monitored with storage time by the proposed method.

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1. Introduction

Volatile aliphatic amines like dimethylamine (DMA), trimethylamine (TMA), n-butylamine (BA), ethylenediamine and cyclohexylamine are important industrial chemicals with a wide range of applications as raw materials or intermediate products in the manufacturing of other chemicals, pharmaceuticals, polymers, pesticides, rubber, dyes, adhesives, solvents and corrosion inhibitors [1,2]. Volatile aliphatic amines are also well known as air pollutants, which are emitted to the atmosphere through a variety of channels, such as waste incineration, sewage treatment, vehicle exhaust gases, cigarette smoke and so on [3]. In addition, some volatile aliphatic amines are generated in the process of biodegradation of animal tissue like fish and meat. Trimethylamine (TMA) is infamous for its pungent and fishy smell, which is generated during the bacterial or enzymatic deterioration of trimethylamine oxide in dead fish [4,5]. An increase in concentration of TMA could be used as an indicator of the degree of spoilage of fish. Due to their pungent odorous and toxic characteristics, most of volatile aliphatic amines are sensitizers and irritants to the skin, the eyes and the respiratory and central nervous systems. Some amines can react with nitrite, forming the N-nitroso compounds that are potentially carcinogenic [6]. Therefore, it is necessary to monitor the levels of volatile aliphatic amines to protect human health, environment and infer food quality. There have been various research works carried out for the development of analytical methods for determining amines by using gas chromatography (GC) [7–9], high performance liquid chromatography (HPLC) [10,11], ion chromatography (IC) [12], capillary electrophoresis (CE) [13], sensors [14], spectrophotometry [15] or other methods. However, most of these methods need complicated pretreatments such as derivatization [16].

As an old but recently renewed plasma technology, dielectric barrier discharge (DBD) is a typical non-equilibrium atmospheric pressure ac gas discharge technology that was first reported by Siemens in 1857 [17]. It has at least one dielectric material (e.g., glass, quartz, ceramic or polymer layers) to block discharge channel, with a gap distance in the range of 0.1–10 mm between the two electrodes. When the electrode is powered by an alternating current voltage with a frequency ranging from a few Hz to MHz, the DBD could generate discharge for high energy electron of 1–10 eV [18,19]. These electrons will dissociate the surrounding gas molecular and produce plasma that contains free radicals, ions, atoms, molecules and so on. The unique features and characteristics of DBDs, such as simple configuration, low energy consumption, long lifetime, easy operation under ambient temperature and

* Corresponding author at: College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China.
E-mail address: houxd@scu.edu.cn (X. Hou).

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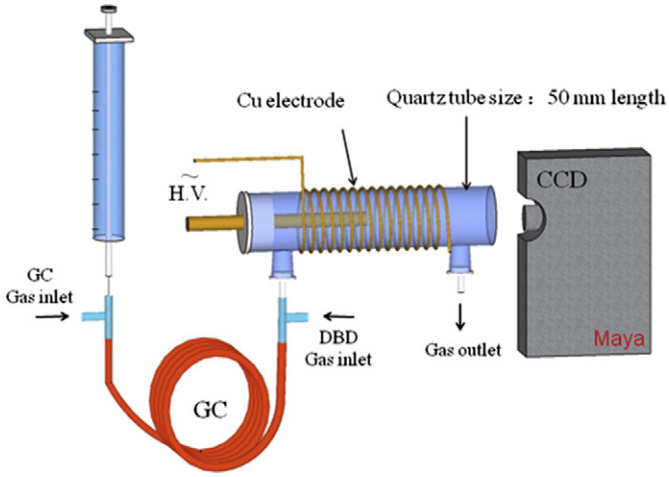

Fig. 1. Schematic diagram of the experimental arrangement.

pressure, offer a wide range of analytical applications. Up to now, DBDs have been introduced into analytical chemistry as detectors for gas chromatography (GC) [20–22], as ionization sources for ion mobility spectrometry (IMS) [23] and mass spectrometry (MS) [24], as atomizers for atomic absorption spectrometry (AAS) [25] and atomic fluorescence spectrometry (AFS) [26], as excitation sources for atomic emission spectrometry (AES) [27] and molecular emission spectrometry [20]. In order to expand the application scope of DBD, extensive research has been conducted on the combination of a DBD and a catalyst to enhance its excitation capability. DBD-catalysis technique has the advantages of high selectivity from catalysis and fast response from DBD technique. The combination of a DBD and a catalyst creates a synergistic effect because both plasma and catalysis take place simultaneously and interact with each other [28]. The DBD-catalysis technique is mostly applied for environmental protection such as pollutants abatement, but much less for spectrochemical analysis.

Micro-plasma-based optical emission spectrometry (OES) has proven to be an effective detection method for chemical analysis [29,30]. This technique was first used as a GC detector by McCormack et al. [31]. The molecule was fragmented and excited by argon microwave-induced plasma (MIP) and observed through molecular emission bands (e.g., C_2, CH and CN). Since then, the combination of micro-plasma OES with gas chromatograph, by the analysis of high-resolution rotational bands in the emission spectra of suitable electronically excited molecular species present in the discharge, for example, C_2, CN, CH, NH, OH, F, Cl, Br [32], has attracted growing interest in the past decades due to its good linearity and sensitivity [33–35]. DBDs have recently received much attention for GC-MES due to their beneficial analytical properties [20], such as a low gas temperature for weak background radiation and high electron temperatures for excitation of molecular/radical emission. Our group has also established DBD molecular/radical emission spectrometric (MES) detectors using characteristic emission bands of analytes [21,22,36]. Li et al. [20] reported a multi-channel GC detector for the detection of VOCs, by use of DBD MES with a linear CCD. Compared to the traditional elemental detectors such as MS or ICP-AES/MS, a DBD-based spectrometric detector possesses some attractive characteristics such as multi-channel, fast respond, high sensitivity, compactness and simplicity and low-cost in construction and maintenance.

In the present work, we propose nano-SiO_2-assisted DBD-MES as a GC detector to determinate five volatile aliphatic amines by use of CN radical emission at 388.3 nm. Compared with other nanomaterials like TiO_2, MnO_2 and ZnO, SiO_2 can significantly enhance the intensity of the molecular emission. The approach is successfully applied to monitor the biodegradation of a spoiled fish sample. The results show that GC detector is not only sensitive but also fast in response to volatile aliphatic amines with high stability.

2. Experimental section

2.1. Reagents

All chemicals used in this experiment were of analytical reagent grade. As analytes, dimethylamine and trimethylamine were purchased from Aladdin Reagent Company (Shanghai, China), while n-butylamine, ethylenediamine and cyclohexylamine were purchased from Kelong Reagent Company (Chengdu, China). High purity argon (Ar, 99.999%) (Qiaoyuan Gas Co. Ltd., Chengdu, China) was used as the discharge and carrier gas. The carp was obtained from a local market. The chemicals used for synthetic nanomaterials (MnO_2, TiO_2, Al_2O_3, SiO_2 and ZnO) received from the supplier (Kelong Reagent Company, Chengdu, China) expect Triton X-114, which was purchased from

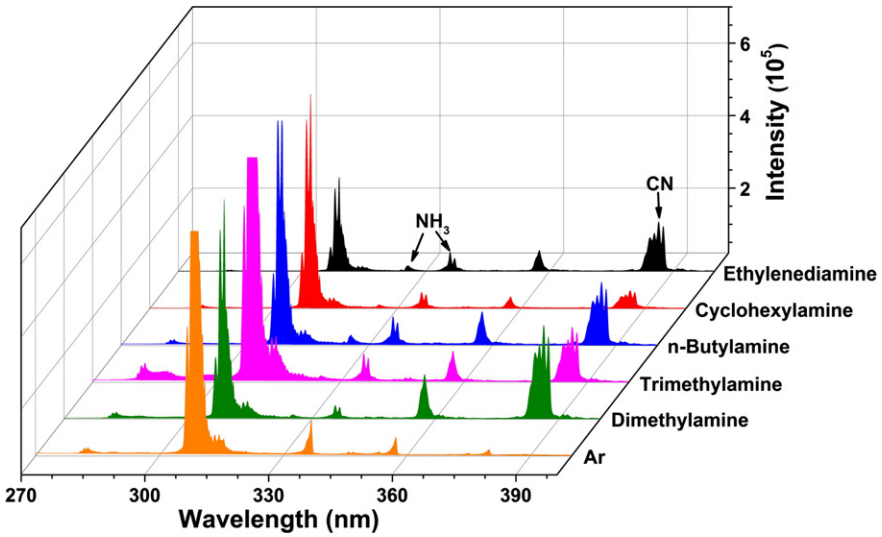

Fig. 2. Molecular/radical emission of amines. Experimental conditions: input voltage, 195 V; argon discharge gas flow rate, 600 mL min^{-1}; and integration time, 100 ms.

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