Microchemical Journal 129 (2016) 16–22

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

A two-dimensional sensor based on dielectric barrier discharge molecular optical emission and chemiluminescence for discrimination analysis of volatile halohydrocarbons

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ARTICLE INFO

Article history:
Received 12 May 2016
Accepted 24 May 2016
Available online 26 May 2016

Keywords:
Dielectric barrier discharge
Microplasma
Molecular emission spectrometry
Chemiluminescence
Volatile halohydrocarbons
Air pollution

ABSTRACT

In this work, a two-dimensional sensor based on dielectric barrier discharge (DBD) molecular optical emission and liquid phase chemiluminescence (CL) was constructed for the discrimination analysis of hazard volatile halohydrocarbons (VHCs) including dichloromethane, chloroform, tetrachloromethane, 1,1,2,2,-tetrachloroethane, 1,4-dichloropropane, 1,2-dichloroethane, bromoform and iodomethane without any separation. Atmospheric pressure DBD induced not only multi-channel molecular optical emission spectroscopy (MES), but also chemiluminescence through the reaction of the DBD-split VHCs with luminol in aqueous solution. The DBD-MES and CL pattern of each analyte were unique, and the linear discriminant analysis (LDA) demonstrated the robustness of this optical sensor. Principal component analysis (PCA) revealed that MES and CL channels contributed at varied concentrations to the good discrimination capability due to the two distinct sensing mechanisms. The miniaturized optical sensor possessed the advantages of simple construction, low power consumption, and high sensitivity to VHCs, especially chlorinated hydrocarbons. It demonstrated for highly discriminative and precise identification of VHCs in air samples.

1. Introduction

Volatile halohydrocarbons (VHCs), such as chlorohydrocarbon, bromoalkane, iodohydrocarbon, are widely used as chemical intermediates and industrial solvents. For their toxicity and health hazard to the environment and human beings, analysis for VHCs is an important issue in ambient air monitoring [1–4]. Generally, VHCs were determined by gas chromatography-thermal conductivity detector (GC-TCD), GC-flame ionization detector (GC-FID), GC-electron capture detector (GC-ECD), GC-photoionization detector (GC-PID), or GC-mass spectrometry (GC-MS) [5–8]. However, these analytical instruments still exist more or less problems like large size (limited for in-lab use), or insufficient sensitivity, or high cost for instrumentation and maintenance. Therefore, it is still necessary to develop miniaturized/portable optical sensors for highly sensitive on site/real time environmental analysis/monitoring for VHCs in air samples [9,10].

Non-thermal plasma has attracted much attention in analytical chemistry for developing miniaturized analytical devices recent years [11–17]. Dielectric barrier discharge (DBD) [18] is a typical non-equilibrium non-thermal atmospheric-pressure AC discharge technology which can produce highly energetic electrons (1–10 eV), and various active radicals and ions generated by electrons collision with gas molecules (and sample molecules when used for analysis). DBD has been widely used in analytical spectrochemistry, such as atomic absorption spectrometry (AAS), optical emission spectrometry (OES), mass spectrometry (MS) and so on, because of its unique advantages including excellent dissociation capability, low gas temperature and low cost for instrumentation as well as atmospheric-pressure operation [19–24]. DBD can also induce molecular/radical emission spectra (MES), and we used DBD as a miniaturized excitation source to induce MES of amines and a fish sample for analysis for trimethyl amine (TMA) [25].

Chemiluminescence enjoys widespread applications in analytical chemistry, mainly because of its unique advantages of low or even almost no background nature, simplicity and high sensitivity [26,27]. Liquid-phase CL systems are usually based on the enhancement or depression of CL signal from a CL reagent such as luminol or lucigenin, but with limited applications. In fact, DBD-dissociated low molecular weight volatile organic compounds may contain radicals, excited species and the like, which can also react with luminol for the generation of CL emission, thus broadening the detectable analyte ranges of the CL-based methodology [28,29].

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http://dx.doi.org/10.1016/j.microc.2016.05.018
0026-265X/

In this work, therefore, a two-dimensional optical sensor based on multichannel DBD-MES and CL was constructed for rapid and sensitive discrimination and identification of VHCs. The two-dimensional sensor possesses the advantages of multichannel capability, simultaneous detection, low power consumption, compact instrumentation, simple fabrication and cost-effectiveness. Much information about the molecular structures of VHCs in air samples can be captured in the multichannel sensing.

2. Experimental

2.1. Chemicals

All chemicals used in this work were of at least analytical grade. Deionized water (DIW, 18 MΩ·cm) produced from a water purification system (Chengdu Ultrapure Technology Co., China) which was used throughout this work. A 25×10^{-3} mol/L luminol (Sigma Chemical Co., USA) stock solution in 0.1 mol/L NaOH (Kelong Reagent Co., Chengdu, China) was prepared and diluted to the desired concentrations with DIW prior to use. $NaHCO_3$–NaOH (Kelong Reagent Co., Chengdu, China) buffer was used to adjust the pH of the luminol solution.

Liquid dichloromethane, chloroform, tetrachloromethane, bromoform, 1,1,2,2,-tetrachloroethane, 1,4-dichloropropane, 1,2-dichloroethane and iodomethane (Kelong Reagent Co., Chengdu, China) were used for preparing the standard gas or sample gas through injecting them into a dilution bottle fully filled with ultrapure argon (99.999%, Qiaoyuan Gas Co. Ltd., Chengdu, China).

2.2. The two-dimensional sensor

The miniaturized two-dimensional sensor consists of a DBD device and a CL instrument, as shown in Fig. 1. The cylindrical DBD was made of a glass tube (2.0 mm i.d. × 3.0 mm o.d. × 50 mm in length), a copper rod (0.45 mm o.d. × 30 mm in length) aligned along the tube's centerline as the inner electrode, and a copper wire (0.45 mm o.d. × 50 mm in length) wrapped around the tube's outside as the outer electrode. The MES signal was recorded via optic fiber with a CCD spectrometer (Maya2000 pro; 200 nm to 600 nm; Ocean Optics Inc., Dunedin, FL, USA). The practical resolution of this CCD spectrometer was about 0.4 nm. The integration time was 100 ms with an average of three scans.

A computerized BPCL ultra-weak luminescence analyzer (BPII, Institute of Biophysics, Academia Sinica, Beijing, China) was connected with the DBD. Argon (99.999%, Qiaoyuan Gas Co. Ltd., Chengdu, China) played the roles of both carrier gas and discharge gas in this work. The DBD device was placed outside of the CL reaction chamber of the BPCL analyzer in order to eliminate its emission influencing on the CL detection. The outlet products from the DBD reaction cell were immediately mixed with the luminol solution which was pumped through the chamber by a peristaltic pump (HL-2D, Shanghai Qingpu Huxi Instrument Factory, Shanghai, China), and the CL signal was detected by the BPCL analyzer, simultaneously.

2.3. Sample preparation

Air samples were collected from outdoor, laboratory and fume cupboard, respectively, according to the standard method of "Methods for determination of halogenated alkanes in the air of workplace" (GBZ/T 160.45–2007, China). These real samples were analyzed with the miniaturized two-dimensional sensor, with the analytical results compared with those obtained by GC-ECD to validate the accuracy of the proposed method. In brief, air samples prepared with active carbon by using an air sampler with a flow rate of 300 mL/min. After 15 min air collection, the adsorbed sample was desorpted to 1.0 mL CS_2 and stored in a refrigerator at 4 °C. The sample blanks were processed along with the samples.

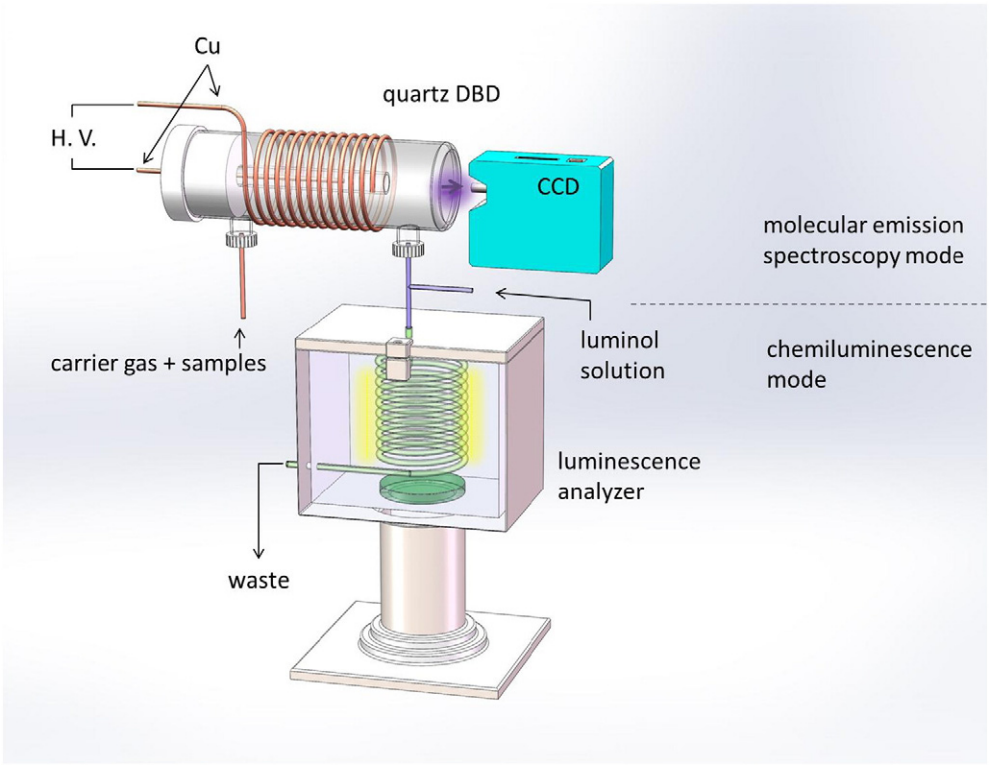

Fig. 1. Schematic diagram of the two-dimensional sensor.