



Needle electrode-based microplasma formed in a cavity chamber for optical emission spectrometric detection of volatile organic compounds through a filter paper sampling



Daibing Luo^{a,b,c,*}, Daichuan Ma^a, Yi He^a, Xinsheng Li^d, Sheng Wang^d, Yixiang Duan^{b,**}

^a Analytical & Testing Center, Sichuan University, No. 29 Wangjiang Road, Wuhou District, Chengdu, Sichuan 610064, PR China

^b Research Center of Analytical Instrumentation, Key Laboratory of Bio-resource and Eco-environment, Ministry of Education, College of Life Science, Sichuan University, No. 29 Wangjiang Road, Wuhou District, Chengdu, Sichuan 610064, PR China

^c Photocatalysis International Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

^d College of Computer Science, Sichuan University, No. 24 South Section 1, Yihuan Road, Wuhou District, Chengdu, Sichuan 610065, PR China

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ABSTRACT

A novel microplasma device, which generates discharge in a Poly (dimethylsiloxane) (PDMS) cavity chamber with two normal syringe needles, serving as both gas channels and electrodes, was prepared by an innovative casting technology. This microplasma device maintains a stable discharge even after working under large periods of time (4 h) and even if impurity deposition is produced on the needle electrode tips. The cavity discharge chamber of this device can also be used as a sampling compartment. 14 kinds of volatile organic compound (VOC) samples, with 6 series depending on carbon chain structures and boiling points (from 34.6 to 232.9 °C), can directly diffuse into the plasma by using a filter paper. The filter paper was placed right under the microplasma zone in the chamber. Most VOC samples could be well detected (<20 min for each) and discriminated in this microplasma system through a portable spectrometer. Combined with the peak ratio (300–900 nm spectrometric range available) analysis, discharge parameters, specific characteristics of each sample and comparison of each homologous group could be systematically made by this device. The present work proposes a new approach for fast screening of volatile organics in water bodies or other solvents. The utility of this device was demonstrated by that BTEX-containing aqueous samples, as an example, could be detected at 50 mg/L level with detection limits of 2.5 µg/L.

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1. Introduction

Since plasma has shown to have great promise in the fields of chemistry, biology, physics, biotechnological and medical sciences, research on plasma has attracted a great deal of attention due to its possible application in scientific and technical areas [1–3]. Plasmas are produced when energy supplied to a neutral gas converts the gas molecules into charged carriers such as electrons, ions, radicals and excited atoms [4]. These electrons and photons possess sufficient energy to produce ions and further electrons through collisions with neutral atoms and gas molecules. Numerous efforts have been made by the scientific and technological community to generate, sustain, and utilize microplasmas. Microplasmas are smaller in size and partially ionized discharges that represent a new and fascinating realm of plasma science [5–7]. The microplasma is highly concentrated with charged and chemical species

that can be used to lower the activation energy for chemical reactions. Electrodes in microplasma devices can be configured in a variety of ways and can be powered using DC (direct current), AC (alternating current), or pulsed potentials [4,6,8].

Microplasma devices can be effectively used in the detection of volatile organic compounds (VOCs). The emission of VOCs from various industrial processes represents a major source of air pollution, and therefore VOC detection and removal is an essential issue of environmental importance. The study of emission spectra of VOCs can be traced all the way back to the 1920s, and some similar work continues today [9, 10]. Unfortunately, attempts at using emission spectra for qualitative and quantitative analysis of chemical vapors by observing emissions from fragments larger than diatomic molecules are very difficult. This may be because plasma discharges and breaks molecules into similar little-mass fragments. Furthermore, the emission intensities of the larger fragments are always weak or obscured through diatomic molecule emission. However, when associated with the technique of gas chromatography, the use of emission spectra for the analysis of VOCs is feasible. Additionally, through years of research on microplasma emission spectrometry, our group found that certain VOCs, with similar

* Correspondence to: D. Luo, Analytical & Testing Center, Sichuan University, No. 29 Wangjiang Road, Wuhou District, Chengdu, Sichuan 610064, PR China.

** Corresponding author.

E-mail addresses: luodb@scu.edu.cn (D. Luo), yduan@scu.edu.cn (Y. Duan).

molecular structure, can be well distinguished by specially-designed microplasma devices, even without any GC equipment [11,12]. By precise analysis and comparing the Optical Emission Spectrometry (OES) details of the VOCs in stable microplasmas, accompanied with discharge parameters, characteristics of each sample can be found and classified.

Currently the main drawback of conventional microplasma devices for VOC detection is the limited life time caused by the cathode sputtering and the fluctuation of the discharge zone due to the disturbance from the substrates, the deposition on the configurations, and the parasitic capacitance [6,13]. Another problem in using a traditional microplasma detector is that they always suffer from overheating due to the direct contact between the microplasmas and the substrates [14]. The heat from the plasma region would increase the temperature of the probe or sample mount, with subsequent losses of volatile sample constituents.

Many attempts have been made to overcome such drawbacks or minimize the negative effects. In this paper, we report a needle electrode based microplasma in a Poly (dimethylsiloxane) (PDMS) cavity chamber (NMCPC: needle, microplasma, cavity, PDMS, chamber) as an energy source for molecular fragmentation and excitation. The needles are employed as both electrodes and gas channels. Interestingly, when the microplasma volume is sealed in a larger-sized transparent substrate, it possesses some special features and characteristics. This configuration has distinct features or advantages including: (1) the discharge zone is separated from the substrate and surrounded by argon atmosphere only so that the heating from the plasma can hardly damage the optical walls; thus, it is beneficial for maintaining the plasma in stable state for a longer time; (2) the chamber is separated into two compartments, where the upper compartment is used for the discharge and the lower compartment is used for sampling with a filter paper. This configuration facilitates the comparison of discharge properties and emission spectrometry of VOC samples; (3) the discharge chamber can be used as the sample evaporation room so that a fast detection upon direct sampling can be expected; (4) the needle electrode can be replaced easily if there is heavy sputtering that occurs on the electrode tips. A study has been performed for the purpose of spectral detection of a series of compounds with specific characteristics. Several kinds of VOC samples were detected by this microplasma, through the various evaporating chemicals that came from a piece of filter paper placed at the bottom of the chamber. This sampling mode is suitable for fast detection and direct analysis of VOCs with middle to low volatile property. Different from our previous works [6,11], this research affords a novel strategy for the discrimination of VOC samples with similar structures by microplasma OES chemistry, and is also focus on the development of a method for fast screening of volatile organics in liquid solutions using a special microplasma chamber and sampling mode.

2. Experimental

2.1. NMCPC preparation

The preparation of a typical NMCPC was described in detail by another published paper [15]. Briefly, A Sylgard 184 kit (Dow Corning Corporation) containing PDMS pre-polymer (Sylgard 184-A) and curing agent (Sylgard 184-B) was used. A mixture of the pre-polymer and the curing agent was baked in an oven at 120 °C for 15 min. A rectangular block iron template was used as a pattern template placed right in the center of the mixture. After solidification of the pre-polymer mixture, the template iron plate was pulled out, allowing a hollow chamber to form in the PDMS substrate. Then the PDMS substrate was cut into a cuboid shape with a square chamber. Another two PDMS cuboids, with the same dimensions of the iron template in length and width, were employed to serve as the seal plug of the cavity chamber. The outer dimension of the chamber is $10 \times 15 \times 26 \text{ mm}^3$. Two penetration

slots in rectangular size ($2 \times 5 \text{ mm}^2$) were made in the side walls of the chamber in the middle points. A rectangular bar ($2 \times 5 \times 25 \text{ mm}^3$) made by PMMA (Polymethyl methacrylate), according to the size of the opening slot, was used as a sealing switch. This switch, with an open hole at one side, was inserted in the penetration slot, which separated the chamber into two compartments. The upper compartment was used as the microplasma discharge chamber while the lower compartment was employed as the sampling chamber. Two needles (outer diameter 1.61 mm, inner diameter 1.25 mm) were inserted into the side walls of the discharge chamber as tip-to-tip configuration. A distance of 0.5 mm between the needle tips was selected. The needles served as the discharge electrodes as well as the gas channels. A detailed illustration of the NMCPC (with a total $5 \times 10 \times 10 \text{ mm}^3$ room when sealed) is shown in Fig. 1(I). A DC power was applied to the needle electrode with a ballast resistor connected in order to create a microplasma discharge inside the cavity chamber.

The open and close states between the compartments can be controlled by the PMMA switch. When switching to the open state, the upper and lower compartments were connected through the square hole in the switch. Fig. 1(I) shows an empty chamber with the close state between the upper and the lower compartments. The filter paper can be placed in the lower compartment and replaced by another one by opening and sealing the lower plug (Fig. 1(II)). In the open state, the microplasma could be ignited between the needle tips in the upper compartment (Fig. 1(III)). When switching to the open state, the vapor, in the lower compartment from the filter paper, could diffuse into the microplasma as shown in Fig. 1(IV), which could possibly affect the discharge properties.

We can collect the OES of VOC samples directly in the open state (Fig. 1(IV)), which can be used for measurements of the ignition voltage. In this process, the NMCPC is kept in the open state and after the filter paper is soaked with one VOC sample, it is placed in the lower compartment. DC power is supplied from a value of zero in order to ignite the discharge. This measurement is defined as the evaporation-diffusion-ignition process. We can also obtain the OES signals, residue time and discharge power through an integral process from I to IV (Fig. 1). In this process, the filter paper soaked with a VOC sample is placed in the lower compartment in the closed state. Soon enough, the lower compartment is filled with the vapor of the sample (II, Fig. 1). Then the microplasma discharge is ignited in the argon flow gas and then maintained (III, Fig. 1). After that, the NMCPC is changed into the open state by the switch, hence, the vapor of the sample in the lower compartment will immediately diffuse into the discharge and affect the microplasma state (IV, Fig. 1). This measurement is defined as the evaporation-saturation-diffusion process.

2.2. Measurements

The NMCPC was mounted on an optical platform for the VOC detection as indicated in Fig. 2(a). Fig. 2(b) is a photograph of the optical support and measurement system used by the NMCPC. As shown in Fig. 2, the NMCPC device was fixed on a three-dimensional stainless steel holder, which could be adjusted manually. The base holder was constructed with standard optical units. An optical fiber, aiming at the plasma zone, was fixed by screws next to the NMCPC.

The microplasma could be operated in a constant voltage mode from 200 to 2000 V, with the argon flow rate at 250 mL min^{-1} controlled by a mass flow controller. The inlet needle was connected to the cathode while the outlet needle to the anode, both of which were connected with copper wires due to the many emission peaks that are stronger in the cathode. The light emitted from the rectangular microplasma chamber was picked by the optical fiber and guided to an Ocean Optics S2000 spectrometer (grating, $600 \text{ lines mm}^{-1}$; slit width, $50 \mu\text{m}$). The light intensity for all optical emission spectra, in this work, was given in units of a.u. counts. A portable PC connecting to the optical fiber was employed for the emission spectral data collection.

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