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

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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 hours) 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 (less than 20 minutes for each) and discriminated in this microplasma system through a portable spectrometer. Combined with the peak ratio (300-900nm 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 50mg/L level with detection limits of 2.5 µg/L.

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 1920's, 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 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 (NMPC: 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. NMCPD preparation

Fig. 1. Schematic illustration of the sampling and measurement steps of the NMCPD, and its structure and components in detail. The microplasma interacts directly with the diffused samples from the filter paper.

The preparation of a typical NMCPD 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 minutes. 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

Fig. 2. Illustration of the NMCPC setup (a) schematic diagram and (b) photograph for spectrometric 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.

Liquids or solutions of the VOC samples were directly used as the analytical grade reagents. Before each measurement, the device was discharged in pure argon gas in the open state for 10 min to remove the possible residuals caused by previously measured samples. A little piece of filter paper (about $3 \times 5 \text{ mm}^2$) was dipped into the liquid samples for 5 seconds. After the filter paper was soaked with the sample liquid, tweezers were used to place it in the lower chamber right under the switch. With the argon gas flow, the applied voltage was adjusted until the microplasma was started, and then the signals were quickly captured by the spectrometer and software.

3. Results and discussion

3.1. Background emission

Fig. 3. Background emission of the argon microplasma in the NMCPD.

Firstly the NMCPD discharge was characterized by optical emission spectroscopy with argon as the working gas. There has been considerable discussion in different literature on the mechanism of plasma formation [4]. Argon plasmas that are exposed to ambient air are sources of reactive oxygen-based and nitrogen-based species, such as O, O₂^{*}, O₃, OH, NO, NO₂, etc. A stable discharge can be quickly obtained with a 0.5-mm electrode gap and a power supply at 800V. Fig. 3 shows an argon emission spectrum of the NMCPD over the spectral range of 200-1000 nm. The argon background spectrum indicates, apart from the Ar emission lines, N₂ bands, mainly since the microplasma was maintained in ambient air [16]. The N₂ bands are the wide spectral features found in the lower wavelength part of the spectrum, while the Ar lines are predominantly found in the longer wavelength range located between 690 and 850 nm corresponding to the Ar 4p → 4s transitions. Under an atmospheric discharge condition, the emission of N₂ bands is inevitable. A 306 nm band is notable, which is attributed to the OH group caused by the H₂O in the environmental atmosphere.

3.2. Discharge description

For comparison, 14 VOC samples divided into 6 groups were detected using the NMCPD device without GC systems. Each group has specific characteristics to estimate the performance of the NMCPD. These series of compounds include one nitrogen-containing compound (DMF), two hydrocarbons (volatile properties comparison), two aldehydes, two chlorinated compounds, three aromatic compounds, and three aliphatic alcohols as listed in Table 1.

The molecular structures of the VOCs affect the combustible properties in the microplasma. Various colors for each of the different samples were observed in the discharges. These colors are due to the presence of electronic transitions inside the visible spectrum in argon gas. The strong emission light also indicates that the PDMS walls have a fine transmittance of signal light. Upon direct observation on the discharge, we found the shape of the microplasma between the needle tips appeared like a rainbow and was

maintained in a stable constant state, which may partly benefit from the tip-to-tip configuration. By discharging between sharp-tip electrodes, the instability caused by the parasitic capacitance could be effectively decreased [13].

3.3. VOC Identification

First, as shown in Table 1, each sample was measured through the evaporation-diffusion-ignition process in order to obtain the ignition voltage. These VOC samples were detected through the evaporation-saturation-diffusion process as mentioned above in Fig. 1. Analysis of the OES with discharge parameters for 14 samples divided into 6 groups is presented in detail in Table 1. Measurements at a fixed voltage of 800V of the emission spectrum were repeated three times and the final data presented here comprise an average of these measurements. In this kind of measurement, the saturated vapor filled in the lower chamber diffused into the microplasma when the NMCPC was switched from the closed to the open state. Therefore, it was easy to calculate the residence time of each sample in the microplasma. As was expected, the samples with higher volatility displayed approximately shorter residence times. Generally, the volatility is associated with the boiling point. As can be seen in Table 1, the boiling points of these VOCs ranged between 34.6 and 232.9°C. Obviously, the addition of organic compounds into the microplasma decreases the molecular emission from N₂ and the atomic emission from Ar. For highly volatile VOCs such as acetone, ester, and trichloromethane, it is difficult to capture their emission signals in a relatively short period of time. These VOCs quickly evaporate and are carried out of the chamber by the argon gas. It should be noted that the residence time for most samples in the NMCPC is much longer (within minutes) than many conventional microplasma types, which facilitate a precise analysis of the samples through emission spectrometry. At the end of the response time, a decrease of the analyte response from the VOCs inside the chamber was observed and thus the OES returned to the argon spectrometry. Therefore, the residence time represents the burning period from switching to the open state to the appearance of the argon gas in the background. Generally, the residence time is directly proportional to the boiling point and inversely proportional to the discharge power. Using filter paper sampling on relatively low evaporating rates can obtain favorable kinetic charge / proton transfer from primary reagents to analyte ions.

Fig. 4. OES recording of 14 VOC samples dividing into 6 groups in the evaporation-saturation-diffusion process. OES from each sample was recorded in different discharge power because the discharge parameter for each is different (Relative discharge power ratio in mW: DMF: 4.7, diethyl ether: 4.1, *n*-decanol: 6.1, dichloromethane: 6.0, trichloromethane: 5.2, formaldehyde: 8.9, acetaldehyde: 6.5, *o*-xylene: 4.6, *m*-xylene: 4.5, *p*-xylene: 4.3, ethylbenzene: 6.2, butyl alcohol: 5.9, 2-butyl alcohol: 6.6, *tert*-butanol: 7.1).

Normally, a lower power is applied, and a lower response is observed, which is attributed to fewer active ions and radicals produced in the microplasma. The VOC samples displayed different ignition voltages and residence times in the NMCPD. The ignition voltage is the voltage required to ignite the mixture discharge. When directly measuring the VOC-mixed samples through the open state (Fig 1(IV)), a different ignition voltage was required since the VOC-mixed argon gas alters the operating power level to a certain extent. The operating power of the NMCPD detector depends upon the plasma gas composition. When the constant voltage is fixed to 800V in the evaporation-saturation-diffusion process, the discharge current affects the VOC sample that diffused from the lower chamber into the microplasma in the upper chamber. Therefore the discharge power (voltage $\times$ current) recording for each sample was different and some features are presented as the emission intensity per discharge power listed in Table 1.

The organic vapors could give at least several significant peaks in the spectral range from 300 to 1000 nm as shown in Fig. 4. The spectral peaks were identified and assigned using online data available from the National Institute of Standard and Technology (NIST) and from data previously reported in other studies [9, 17]. Among the different bands detected, apart from the Ar emission lines mainly at 700-900 nm and the OH band at 306 nm, the most important features correspond to the CH emission bands located at 314 and 431

nm. Another important feature that corresponds to the CH emission band is the Swan band system of C₂ between 467 and 564 nm, having the strongest emission from the band heading at 516 nm [16, 18]. CH is formed directly from the H subtraction of CH_x fragments, mostly due to electron impact dissociation. The emission at 387 nm is attributed to the CN band, which may be caused by the reaction between CH and N₂ (for molecules without N atoms, nitrogen being available as an impurity in the chamber under atmospheric discharge) [9, 19]. Additionally, we also observed the H_I line at 656.3 nm for certain samples [18].

Table 1

Comparison of the special features of the tested VOC samples in the NMCPD.

VOC samples				Special features		
Group	Compound (Boiling point (°C))	Residence time (min) and ignition voltage (V)	Peaks for study (nm)
1	N,N-Dimethylformamide (DMF) (153)	12, 950	387	Highest CN emission (387nm) per discharge power: 736.67 (a.u. mW ⁻¹)		
2	Diethyl ether (34.6)	0.2, 800	307	Shortest residence time (<1min) with only obvious OH emission band at 307nm		
	n-decanol (232.9)	20, 1200	516, 563	Highest C ₂ emission (467-564nm) per discharge power	516nm: 1128.97 (a.u. mW ⁻¹) 563nm: 325.59 (a.u. mW ⁻¹)	Longest residence time: 20min
3	Dichloromethane (39.6)	1, 1200	309.2, 413.2	Highest Cl _{II} emission (413.2nm) per discharge power: 273.1 (a.u. mW ⁻¹)		Shortest residence time (1min) with more CH and C ₂ emission bands
	Trichloromethane (61)	3, 1000	309.2, 589.2	Highest Cl _{II} emission (309.2nm) per discharge power: 528.17 (a.u. mW ⁻¹)	Highest C ₁ emission (589.2nm) per discharge power: 634.96 (a.u. mW ⁻¹)	A hump between 500 and 1000 nm Longer residence time (4min) with obvious 309.2 and 589.2nm emission
4	Formaldehyde (mixture)	1, 1850	387, 431	[CN (387nm) /C ₂ (516nm) ratio] per discharge power	0.0066 (mW ⁻¹)	Highest ignition voltage More CH and C ₂ emission bands A hump between 500 and 1000 nm

	Acetaldehyde (mixture)	1.8, 1300	387, 516		0.015 (mW ⁻¹)	Higher C ₂ band at 516nm
5	<i>o</i>-xylene (144.4)	7.5, 900	387, 516	[CN (387nm) /C ₂ (516nm) ratio] per discharge power	0.029 (mW ⁻¹)	Intensity of C ₁ band at 589.2nm and H ₁ band at 656.3nm are very low
	<i>m</i>-xylene (139)	7, 900	387, 516		0.031 (mW ⁻¹)	An average intensity of C ₁ band at 589.2nm
	<i>p</i>-xylene (138.5)	7, 880	387, 516, 589.2		0.034 (mW ⁻¹)	Much higher C ₁ band at 589.2nm
	Ethylbenzene (136.2)	10, 1250	387, 516, 656.3		0.014 (mW ⁻¹)	Higher H ₁ band at 656.3nm
6	Butyl alcohol (117.7)	5, 1150	387, 516	[CN (387nm) /C ₂ (516nm) ratio] per discharge power	0.0056 (mW ⁻¹)	Higher discharge power
	2-butyl alcohol (99.5)	5, 1300	387, 516		0.0097 (mW ⁻¹)	Higher discharge power
	Tert-butanol (82.84)	4, 1400	387, 516, 403.5, 520.7		0.0037 (mW ⁻¹)	More CH and C ₂ emission bands Highest discharge power

Note: The ignition voltage was recorded through the evaporation-diffusion-ignition process. The OES, discharge power and residence time were obtained from the evaporation-saturation-diffusion process.

Specific characteristics and discrimination are found when carefully comparing some details from the CH, C₂, and CN emission peaks for all the VOC samples when combined with the discharge parameters. The ratios of these peaks and the absolute peak intensities are varied for each sample. It is possible to compare the ratios of CN/C₂, CH/C₂, etc...between the compounds because these ratios of the compounds appear to be comparatively constant, regardless of hydrocarbon types [11, 12]. It was expected that the emission responses would depend upon the manner in which the organic compounds broke down in the plasma and ultimately upon the structure of the analyzed compounds. Thus, these compounds would be expected to exhibit different emission responses at certain wavelengths. In the case of stable and highly-sensitive plasma sources used in combination with the discharge power and residence time listed in Table 1, a number of comparisons and discriminations at certain wavelengths or intensity ratios could be made, thus giving the “fingerprint” for each measured VOC sample using the NMCPD device.

N,N-Dimethylformamide (DMF) was initially selected for study of the NMCPD response. It was selected because of its moderate volatility and the presence of a C-N group in its structure, thus permitting observation of dependence for emission intensity by the CN emission band. As the DMF molecules evaporate into the plasma, the CN band, at 387 nm, increases dramatically compared with other VOC samples. The CN band is thus permitted to be used for the determination of N-containing samples and as an indicator to assess the discharge performance of the NMCPD. The CN emission intensity increases in a fine

linear relation with increasing voltage as shown in Fig. 5.

Fig. 5. Relationship between the emission intensity and the supply voltage by monitoring the CN emission band at 387 nm.

For compounds without N atoms, in microplasma emission spectrometry, some carbon-containing species can yield an emission line at 387 nm if in the presence of nitrogen.²⁰

The following reactions are offered as possibilities:

In this case, the CN band could be used for monitoring the amount of CH produced from samples when broken in the NMCPD plasma as mentioned in reactions (1) and (2). On the other hand, the NMCPD discharge stability can be estimated by monitoring the changes of the CN emission upon the discharge power. From the linearity between the applied voltage and emission intensity in Fig. 6, we can draw a conclusion that the NMCPD microplasma was maintained in a stable condition and showed a good linear fit upon operating power.

Diethyl ether, with a very high volatility, and *n*-decanol, with a very low volatility, were chosen to test the response volatility of the NMCPD device. The volatile and discharge properties of the samples are referenced in Table 1. From the OES results, we found that it is very difficult to capture the emission from diethyl ether. On the contrary, we obtained a relatively high quality OES from *n*-decanol. As mentioned above, the diethyl ether molecules moved quickly because of a low boiling point; hence, the emission signals could rarely be captured by the portable spectrometer. With a high boiling point or low volatility, *n*-decanol displayed a very stable emission within a longer time period of 20min. Examination of the emission bands permitted the selection of a few listed peaks because they have the highest intensities. The most unique feature of *n*-decanol is that the molecule has the emission from C₂, between 467 and 564 nm, with the highest intensities per discharge power of all the tested samples [11, 17]. As the carbon and hydrogen number of a compound in a homologous series increases, the emission response per mole increases [9]. In addition, as a long-chain aliphatic compound, *n*-decanol was broken into more C₂ pieces in

the NMCPC microplasma than any other VOCs. The OES results indicate that this NMCPC device equipped with a portable spectrometer is not viable, to a certain degree, for sensing extremely high-volatile VOC samples.

The CH and C₂ bands are clearly observed from dichloromethane emission in the 250-650 nm range. It should be noted that as more CH and C₂ bands appear from dichloromethane, the emission noise also increases linearly to form a hump between 500 and 1000 nm. The discharge power of dichloromethane is higher than that of trichloromethane. Further increasing the power supply usually increases the emission background, which in turn influences the emission measurement. Except for the emission bands at 309.2 nm and 589.2 nm, the C₂ and CH emission bands for trichloromethane are hardly observed in the spectrum, which may be attributed to the relatively low power of the microplasma that can hardly break the CHCl₃ molecule [14]. In general, the CH emission increases with an increasing number of H atoms in the molecule. Previous reports also indicated that the CH emission is twice from CHCl₃ to CH₂Cl₂ [17]. The 309.2 nm peaks are very high for both dichloromethane and trichloromethane, which may be due to the Cl_{II} emission, and even possibly some OH emission. The 589.2 nm band should be caused by the C_I emission since both dichloromethane and trichloromethane have only one carbon atom.¹⁷ The strong 413.2 nm band observed for dichloromethane is mainly attributed to the Cl_{II} emission, which may include contributions from the CH emission at 431 nm, while the 602.8 nm band observed for dichloromethane is ascribed to the C_I emission. The 403.5 nm and 520.8 nm may be attributed to the O_{II} emission. In general, the strongest emission at 309.2 nm is more specific to chlorine-containing hydrocarbons than from other VOCs.

In the emission range of 300-650 nm, formaldehyde has more emission bands than that of acetaldehyde. The ratio of CN emission at 387 nm and the ratio CH emission at 431 nm for acetaldehyde are especially greater than that of formaldehyde [18]. The presence of an HO functional group appears to change the CN/C₂ ratio. The OH band at 306 nm also decreases significantly when the VOC samples are introduced, but increases slightly when added upon formaldehyde solution due to the presence of water in the formaldehyde solution. For formaldehyde with a symmetric molecular structure, the $n \rightarrow \pi^*$ transition involves excitation of an electron from a non-bonding orbital to an anti-bonding π orbital which weakens and lengthens the C-O bond. This produces a long progression in the C-O stretching vibration [21]. Comparisons of the OES molecules should be made as the energies and molecular structures of the (n , π^*) excited states are substantially different. By comparing the couples of dichloromethane and trichloromethane, formaldehyde and acetaldehyde, and the aliphatic alcohol series, we found that if the molecule with a higher symmetry gives less C₂, but has a stronger CH band, it peaks in the spectrometer. The Swan bands in the hydrocarbon flame spectra are a progression in the C-C stretching vibration of the dicarbon radical, C₂ for the $d^3\Pi_u \leftrightarrow a^3\Pi_g$ electronic transition. For polyatomic molecules, progressions are most often observed when the change in bond lengths upon electronic excitation coincides with the change due to a ‘totally symmetric’ vibration.

In reality, it is very difficult to distinguish *p*-xylene, *m*-xylene and *o*-xylene, even through mass spectrometry, without having a combination of chromatographic separation.^{22,23} For the aromatic series, we

noted that the emission lines at 589.2 and 656.3 nm are different for the three samples tested. The response data at the 589.2 nm line for *p*-xylene appears to be higher than other aryl-compounds while the 656.3 nm line of ethylbenzene is higher than the other three (measurements of ethylbenzene). The 589.2 nm band may be ascribed to the C₁ emission while the 656.3 nm band to the H₁ emission [17, 20]. Note that the CN/C₂ ratio for ethylbenzene is lower than that of dimethyl-benzene, indicating a decreasing molecular fragmentation of ethylbenzene that produces CH species with relatively more C₂ groups. Upon ionization, an alkyl substituted benzene will readily rearrange to produce the tropyllium cation through A4 cleavage. The spectrum reported, in other literature, verified the proposed structure due to the presence of cleaved benzene (C₆H₅⁺ at 77u) and the ethyl ion (C₂H₅⁺ at 29u) [22]. Hence more C₂ emissions from C₂H₅⁺ are observed for ethylbenzene. The CN/C₂ ratios per energy of *p*-xylene, *m*-xylene and *o*-xylene are located at almost the same levels. Ethylbenzene undergoes a simple charge exchange with reagent ions in order to produce molecular ions (with) xylenes, which have the highest proton affinity among the BTEX family; thus, yielding pseudomolecular ions by proton-transfer process with (H₂O)_nH⁺ ions [23].

The series of aliphatic alcohols were studied in a similar manner with the aromatic compounds. In the Ar/alcohol discharges, the C₂ Swan bands have the most intense peaks. It is worth noting that even the molecular emission of butyl alcohol and 2-butyl alcohol are almost the same, while the ratio of CN/C₂ per energy is different. The CN/C₂ band emission for 2-butyl alcohol is greater than that for butyl alcohol. The CN that appears in the emission reflects the CH amount produced in the plasma as mentioned above. These results indicate that more CH groups are produced for 2-butyl alcohol than for butyl alcohol. The 403.5 nm band and 520.7 nm band for the tert-butanol emission are very strong, which may be caused by the O_{II} emission [17]. This result may be explained by the (CH₃)₃ groups that are easily broken down from the structure; thus, producing lots of OH groups which produce an abundance of O_{II} emission.

A distinct difference is noted in comparing the CN/C₂ ratio of the aromatic compounds to those of the aliphatic alcohols. A decrease in the CN/C₂ ratio indicates a decrease of molecular fragmentation for CN diatomic species [9]. The CN formation is much greater for aromatic compounds in the NMCPC discharge, which means more CH groups are produced from the aromatic compounds than the aliphatic alcohols [9]. Additionally, when combining the ignition voltage, discharge power, residence time and the emission analysis together, we can identify each VOC sample in this research just based on these parameters, which could be used as a specific ‘fingerprint’ for each sample. Even with the relatively simple introduction and convenient operation, the definition for certain kinds of homologous VOCs of the NMCPC is desirable to a certain degree. Our results may correlate, but do not confirm, as shown as analysis in some other literature. This is not surprising, as the instruments and power for each of the measurements are different.

Stability of the discharges was characterized using current measurement versus time in argon under a fixed voltage (800V). Current-time characteristics of argon discharge only when the constant power has been recorded during the time duration of 4 hours. After working for a period, the electrode deposition with black coatings was found abundantly on the cathode tips. Interestingly enough, even some deposition was

found on the cathode. The discharge did not change much within 4 hours and the discharge current almost kept constant (within mA range), with no significant decreasing tendency.

According to previous literature on conventional microplasma [24,25], the space between the electrodes are almost completely filled with dust particles after igniting the gas discharge, and several minutes have passed, a dust-free zone develops in the central region between the two electrodes. It should be noted that, in the NMCPC configuration, the space between and around the needle electrodes is filled with gas not made from the substrate materials; hence a dust-free zone that will not form and grow, which also facilitates stabilizing the microplasma state. Additionally, it is easy to clean the inside of the discharge/sampling chamber using a microbrush and proper chemical solutions when deposition or other foreign materials are found. The needle electrode could conveniently be replaced by another one after being used for long periods of time. These distinct advantages can greatly prolong the lifetime of the microplasma device.

From the test on the direct sampling mode, we can expect that even without a GC system, discrimination of certain VOC samples by OES analysis, using an ideal microplasma source and sampling mode, could be available to some extent. However, it is difficult for this proposed microplasma to perform heavier-elemental analysis because the total power of the discharge is not sufficient to activate heavy atoms. Despite these limitations, it is still worth investigating the proposed microplasmas even further.

The cost-effective and portable features of the NMCPC device make this microplasma-based process a potential candidate for preliminary screening of VOCs in liquid phase. For real applications, we have tested experiments for the fast screening of *p*-xylene, *m*-xylene, *o*-xylene, and ethylbenzen (xylene isomers, BTEX) in groundwater at the suburb of Chengdu city by using this strategy. Some preliminary results are shown in the supporting information. The detected concentration level of the BTEX species could reach 50 mg/L with limits of detection (LOD) of 2.5 µg/L. This study proposes a new approach for the fast screening of volatile organics in aqueous or other liquid samples.

4. Conclusions

A novel microplasma (NMCPC) device was developed for quick sensing of VOC samples. Two needles inserted in the device are used as the electrodes and gas channels. The NMCPC displayed a continuous and stable work time due to the separation of the plasma zone from the substrate and the special tip-to-tip electrode arrangement. A moveable switch divides the NMCPC into two compartments. The upper NMCPC chamber serves as a protection cell for the discharge, while the lower chamber is used as sample introduction part. With special advantages and characteristics, it is ideal to use such microplasma as an energy source for VOCs detection. 14 VOC samples divided into 6 groups were quickly directly detected in the chamber using a filter paper sampling. The operating power of the NMCPC detector was found to be closely related to the plasma gas composition. Response data was obtained at CN, CH, C₁, C₂, O₂ and H₁ band wavelengths. The VOC samples with similar molecular structures were well discriminated by a combination of precise analysis of the emission pattern, the ratios of certain emission bands per discharge

powers, the ignition voltages and the residence time. A relatively longer residence time (minute range) of samples in the microplasma is also helpful for the spectrometric analysis. Comparisons were made in each group of samples and between the different groups by the measurements of discharge characteristics and OES analysis. Interestingly enough, we found that the NMCPC device was very stable, even after 4 hours of working time. This may be caused by the specific spatial factors of the microplasma discharge, which is fully surrounded by an ideal argon atmosphere and well protected by the PDMS walls. In addition, it is convenient to replace the needle electrode if heavy deposition were found on the tips. The discharge / sampling chamber can be easily cleaned when dirty materials are accumulated on its inner walls. Besides, this NMCPC device is simple for construction, running at low power, convenient for operation (since no vacuum and/or GC system is needed), and fast for detection, all of which can make it an ideal candidate for future on-line VOC detection. The potential application of this device was demonstrated by fast screening of BTEX-containing underground water samples at 50mg/L level with LODs of 2.5 µg/L

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