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A highly sensitive and selective dimethyl ether sensor based on cataluminescence

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ABSTRACT

A sensor for detecting dimethyl ether was designed based on the cataluminescence phenomenon when dimethyl ether vapors were passing through the surface of the ceramic heater. The proposed sensor showed high sensitivity and selectivity to dimethyl ether at an optimal temperature of 279 °C. Quantitative analysis were performed at a wavelength of 425 nm, the flow rate of carrier air is around 300 mL/min. The linear range of the cataluminescence intensity versus concentration of dimethyl ether is 100–6.0×10^3 ppm with a detection limit of 80 ppm. The sensor response time is 2.5 s. Under the optimized conditions, none or only very low levels of interference were observed while the foreign substances such as benzene, formaldehyde, ammonia, methanol, ethanol, acetaldehyde, acetic acid, acrolein, isopropyl ether, ethyl acetate, glycol ether and 2-methoxyethanol were passing through the sensor. Since the sensor does not need to prepare and fix up the granular catalyst, the simple technology reduces cost, improves stability and extends life span. The method can be applied to facilitate detection of dimethyl ether in the air. The possible mechanism of cataluminescence from the oxidation of dimethyl ether on the surface of ceramic heater was discussed based on the reaction products.

1. Introduction

Dimethyl ether (DME) is a colorless gas in ambient conditions and easily liquefied under light pressure. Since its physical and chemical characteristics are very similar to those of LP gas, it is an easy substitute for LP gas and also a very clean substitute for diesel fuel because a DME fueled diesel car emits neither soot nor particle matters [1]. DME is the simplest aliphatic ether without carbon–carbon bonds. It has a high oxygen fraction, high cetane number, low combustion noise, and smoke-free combustion [2,3]. It is widely used in environment-friendly refrigerant, gasoline, diesel and gas additives and chemical raw materials [4,5]. DME is a kind of weak anesthetic, smelling DME would cause inhalation anesthesia and the sense of suffocation. DME is a kind of fire goods that would produce an explosive mixture when mixed with air and also could burn and blast when it meets open flame. Therefore, it is a very important task to monitor its concentration in many cases.

The primary analytical method for the determination of DME in air is gas chromatography (GC). This technique is powerful for DME determination with high performance and sensitivity, which, however, has its inherent disadvantages of not being able to monitor the contamination in real time. In contrast, gas sensors which can perform in real time and on-line monitoring, have the features of simple operation, high analysis speed, low cost and small size. Although electrochemical sensor for detecting DME was reported [6], the selectivity needs to be improved. Therefore, there is still a demand for a simple, rapid, sensitive and potentially portable method for the determination of trace DME.

Cataluminescence (CTL)-based sensors have been developed since the 1990s. CTL is a kind of chemiluminescence (CL) emitted during catalytic oxidation of gaseous species and was first observed by Breysse et al. [7] during the catalytic oxidation of carbon monoxide on the surface of thoria. CTL can be defined as the emission of electromagnetic radiation (usually in the visible or near-infrared region) produced by a catalytic oxidation reaction of organic molecules on the surface of catalytic solid materials that generally yields excited intermediates of the organic molecules in the electronic excited state, producing photoemission returning to the ground state. CTL phenomenon has attracted much attention of analytical chemists, Nakagawa et al. [8–11] and Zhang et al. [12–17] have made great efforts to explore a series of CTL gas sensors. Especially, the application of nanomaterials to design chemical sensors is one of the most active research fields nowadays, mainly owing to their high activity, good selectivity, tremendous specific surface area and small size [18]. Many nanomaterials, such as ZnO, La_2O_3, CeO_2, $ZnWO_3$ and WO_3, were applied to determine volatile organic compounds (VOCs), including ethanol [19], acetone [20], carbon disulfide [21] and ethyl ether [22]. The future development of CTL sensor is the array of sensors, which can discriminate several gases [23].

Although the CTL sensors do not require light source and are easy to miniaturization, preparing and fixing up the catalytic materials

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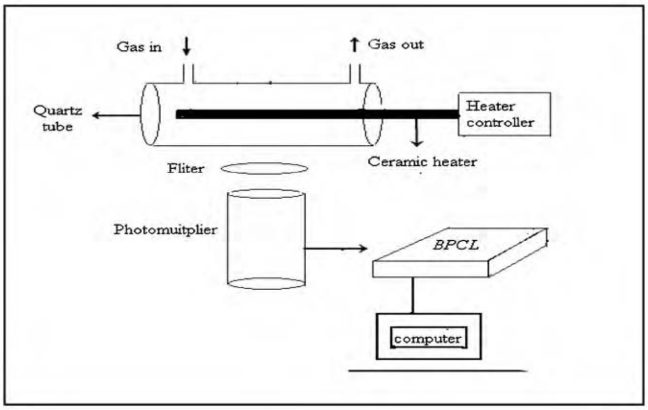

Fig. 1. Schematic diagram of the CTL sensing system.

are still relatively cumbersome, and sometimes the reproducibility will be affected by subtle change in experimental conditions. In the present work, CTL emission was observed when DME vapor passed through the surface of ceramic heater without any adscititious catalysts, a gaseous sensor for detecting DME was developed based on this phenomenon. Since this sensor does not need to prepare and fix up the granular material, the simple manufactory technology reduces cost, improves stability and extends life span, and it has the advantage of high selectivity.

2. Experiment

2.1. Apparatus and reagents

The schematic diagram of the CTL detection system is shown in Fig. 1, the 5 mm diameter ceramic heater is placed inside a 10 mm inner-diameter quartz tube. The temperature of ceramic heater could be adjusted by controlling the voltage. When the DME vapor mixed with the carrier air flowed through the ceramic heater surface, a catalytic reaction occurred on the surface of ceramic heater. The CTL intensity was measured by a BPCL Ultra Weak Chemiluminescence Analyzer. The wavelengths could be selected over the range of 400–640 nm by changing the optical filters.

BPCL Ultra Weak Chemiluminescence Analyzer was made by the Biophysics Institute of Chinese Academy of Science in China. The energy dispersive X-ray spectrometer (EDS) was manufactured by Oxford (England). The GC instrument (Model: SP6800A) with a thermal conductivity detector (TCD) was purchased from LuNan, RuiHong Chemical industry Co. Ltd. (Shandong, China). The ceramic heater (Model: ZF-35) was fabricated by Ningbo electric iron factory (China). Standard DME (purity > 99.5%) was purchased from Keming air equipment Co. Ltd. (Guangdong, China).

2.2. Mechanism investigation

In order to clarify the mechanism of the CTL emission, GC instrument was used to identify the products of the catalytic reaction of DME on ceramic heater surface. The GC instrument was directly coupled to the CTL detection system for the rapid determination of reaction products from the tail gas. Products were identified by comparison of their retention time. The conditions for GC experiments were as follows: gasification temperature operated at 120 °C, column temperature operated at 80 °C, detector temperature operated at 100 °C and the pressure of carrier gas of (H_2) kept at 50 mL/min.

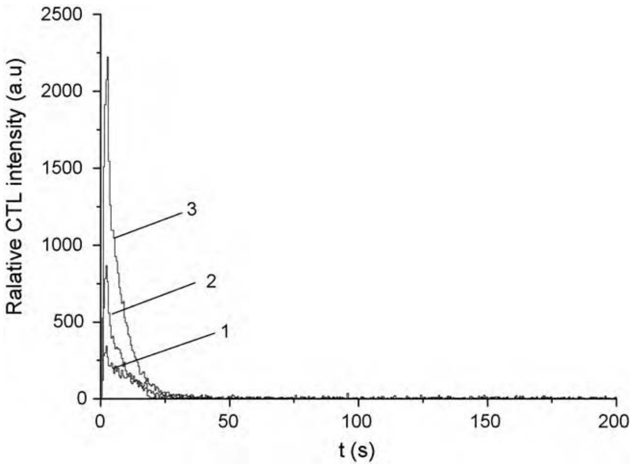

Fig. 2. CTL response profiles of different concentrations of DME (conditions: concentrations, 1–3.0×10^3, 2–7.8×10^3 and 3–1.5×10^4 ppm; temperature, 279 °C; flow rate, 300 mL/min; wavelength, 425 nm).

3. Results and discussion

3.1. Materials evaluation for CTL

To study the feasibility of the sensing mode, ceramic, nano-Y_2O_3, nano-In_2O_3, and nano-MgO were estimated. The CTL on the surface of these materials were detected when DME or other vapors, which may coexist with DME in contaminated air, were passing through at a wavelength of 425 nm. The concentration of each vapor was 1.0×10^3 ppm. The different temperatures and flow rates were tested to obtain the highest CTL intensities for each material. The results were shown in Table 1, taking sensitivity and selectivity factors into consideration, ceramic were the best sensor elements selected for the subsequent study in the present work.

The CTL response profile of DME on ceramic surface was studied by injection different concentrations of DME into the carrier with a flow rate of 300 mL/min. The working temperature was controlled at 279 °C with the wavelength of 425 nm. The results were shown in Fig. 2. Curves 1, 2 and 3 denote the results for DME concentrations of 3.0×10^3, 7.8×10^3 and 1.5×10^4 ppm, respectively. From Fig. 2, we could observe that the CTL signals were increased along the concentration of DME, but the similar profiles were obtained by injection of different concentrations of DME. For all the three concentrations of DME in Fig. 2, the maximum signals were achieved at around 2.5 s after sample injection, indicating a rapid response of this sensing mode to different concentrations of DME.

Table 1
Effect of some materials on the CTL intensity and selectivity.

Materials	Relative CTL intensity					Selected conditions
	DME	Acetic acid	Ethanol	Formaldehyde	2-Methoxyethanol	
Ceramic	140.8	Not detectable	24.5	Not detectable	26.8	279 °C, 300 mL/min
MgO	235.4	43	125	13.7	158.4	279 °C, 300 mL/min
In_2O_3	Not detectable	Not detectable	Not detectable	Not detectable	9.3	293 °C, 245 mL/min
Y_2O_3	23.7	Not detectable	142.7	13	21.1	279 °C, 300 mL/min

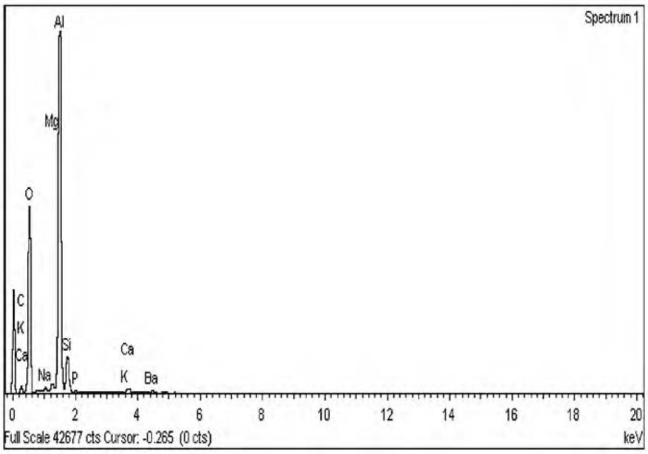

Fig. 3. EDS result of ceramic heater.

3.2. *Characterize the ceramic heater*

EDS was used to detect the ingredients of the ceramic heater under 20 keV condition. Primary chemical elements of ceramic heater including Mg, Al, Si, Na, Ba, O and other elements were detected as shown in Fig. 3. From Table 2 we can obtain the weight ratios and the atomic weight ratios of these elements and what the ceramic heater contains most are C, O, Al, Mg, Si, the atomic weight ratio of these elements are 15.72%, 60.02%, 20.29%, 0.35%, 2.78%, respectively. We can speculate that those elements were in the form of oxide or carbonate, since Al_2O_3, SiO_2, MgO were used as catalysts frequently [24–26], and some carbonates can also be used as catalysts in the field of cataluminescence [27,28] Therefore, it's possible that the oxidation of DME on ceramic heaters surface was due to the integrated effects of these oxides and carbonates.

3.3. *Optimization of working temperature*

Temperature plays an important role in the reaction rate of the catalytic oxidation reaction. To estimate the effect of temperature on the CTL intensity, a 1.0×10^3 ppm DME vapor sample was determined at varied temperatures. Fig. 4 presents the relationships between the relative CTL intensity versus the catalysis temperature at a carrier gas flow rate of 300 mL/min. The results showed that the CTL intensity increased when the temperature increased from 225 to 395 °C. However, the experiments indicated that when temperature increased, the background signals were also increased and even faster than the real CTL intensity increased. Furthermore, the signal to noise ratio (S/N) reached a maximum value on the ceramic heater surface at 279 °C. Below or above this temperature, the S/N decreased. Therefore, 279 °C was chosen for the following experiments.

Table 2
The ratios of the different chemical elements of ceramic heater.

Element	Weight%	Atomic%
C K	10.31	15.72
O K	52.44	60.02
Na K	0.33	0.26
Mg K	0.47	0.35
Al K	29.89	20.29
Si K	4.27	2.78
P K	0.11	0.06
K K	0.08	0.04
Ca K	0.61	0.28
Ba L	1.51	0.20
Total	100.00	

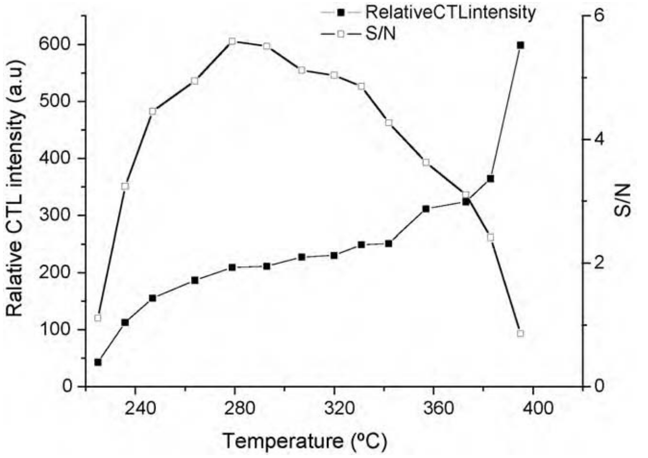

Fig. 4. Temperature dependence of CTL intensity of DME (conditions: concentration, 1.0×10^3 ppm; flow rate, 300 mL/min; wavelength, 425 nm).

3.4. *Optimization of wavelength*

In order to investigate the effect of wavelength on the CTL intensity of DME, the following bandpass filters were introduced: 400, 425, 440, 460, 490, 535, and 555. Fig. 5 showed that the CTL intensity increased with the increase of wavelength, however a significant increase in noise was observed with the increase of wavelength. The maximum value of S/N was observed at 425 nm. Therefore, 425 nm was selected as the optimal wavelength for the quantitative detection of DME in the subsequent experiments.

3.5. *Optimization of flow rate of carrier gas*

The impact of carrier gas flow rate on the CTL intensity was examined in the range of 20–320 mL/min at 279 °C. As illustrated in Fig. 6, expectedly, a proper flow rate could bring a proper contact time between the DME vapor and the selected catalyst, resulting in a sufficient reaction. However, at higher flow rates (>300 mL/min), the reaction time between DME and catalyst would possibly not be sufficient so the CTL intensity decreased slightly. Therefore, 300 mL/min was chosen as the optimal flow rate for the subsequent studies.

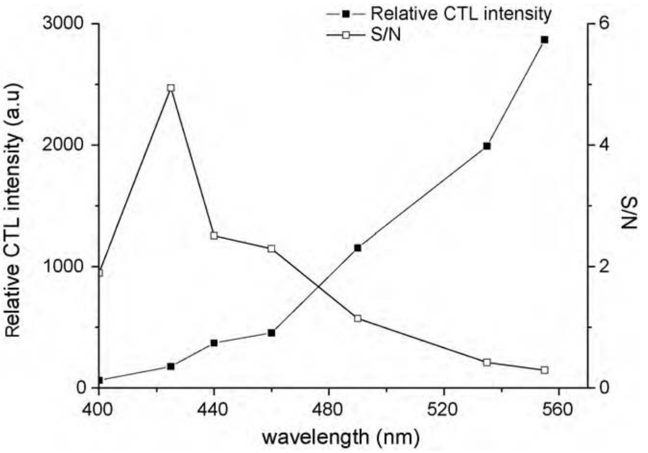

Fig. 5. Wavelength dependence of CTL intensity of DME (conditions: concentration, 1.0×10^3 ppm; temperature, 279 °C; flow rate, 300 mL/min).

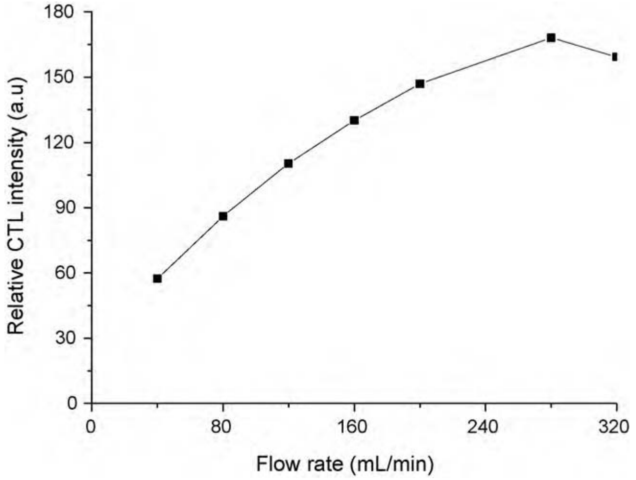

Fig. 6. Effect of flow rate on CTL intensity of DME (conditions: concentration, 1.0×10^3 ppm; temperature, 279 °C; wavelength, 425 nm).

3.6. Analytical characteristics

Under the optimal conditions as described above, the calibration curve of CTL intensity versus DME concentration was linear in the range of 100–6.0×10^3 ppm (192–1.2×10^4 mg/m^3) with a detection limit of 80 ppm (153 mg/m^3). The linear regression equation is described as $I = 0.1146C + 30.38$ ($R = 0.9994$). I is the CTL intensity, C is the concentration of DME and R is the regression coefficient, and each point is gathered from the average result of two replicated tests. Relative standard deviation (R.S.D.) was 2.0% for five times determination of 7.8×10^3 ppm DME vapor, as shown in Fig. 7.

According to the workplace exposure limits (EH40/2005, England), the permitted long-term exposure limit (8-h TWA reference period) and short-term exposure limit (15-min reference period) for DME in the workplace are 400 ppm (766 mg/m^3) and 500 ppm (958 mg/m^3), respectively [29]. Since the detection limit of DME is below the standard permitted concentrations, the proposed sensor could be used for safety control and air quality monitoring of the content of DME in the workplace. Moreover, the proposed sensor could be used for quality monitoring of the DME manufacturing process.

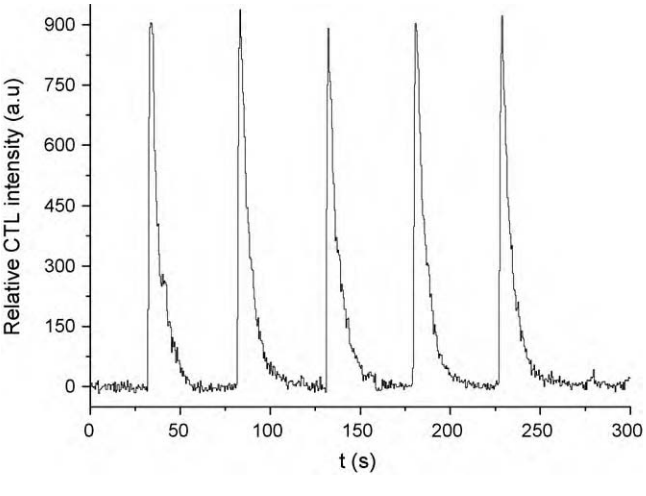

Fig. 7. Typical results obtained from five replicate injections of DME within 300 s (conditions: concentration, 7.8×10^3 ppm; temperature, 279 °C; flow rate, 300 mL/min; wavelength, 425 nm).

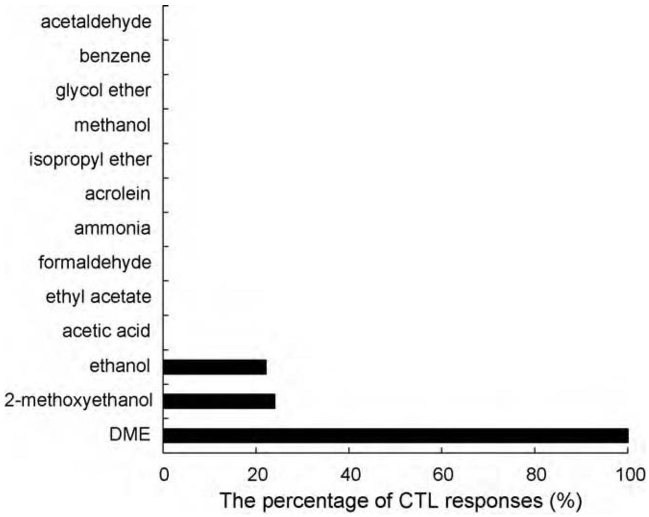

Fig. 8. The percentage of CTL responses of different compounds (conditions: concentration, 1.0×10^3 ppm; temperature, 279 °C; flow rate, 300 mL/min; wavelength, 425 nm).

3.7. Lifetime of the sensor

The experiments about stability and durability of the sensor were carried out by continually injecting a sample of 1.0×10^3 ppm DME into the sensor chamber under the optimal conditions. The CTL emission was recorded one time per 10 h for 100 h, and no significant decrease of CTL intensity was observed, The R.S.D. ($n = 11$) was about 2.3% in a successive experiment, which indicated good stability and durability of the sensor.

3.8. Specificity of the sensor

Specificity plays a key role in a sensor, as poor specificity would result in the ostentation of false positives. Unrelated compounds, including benzene, formaldehyde, ammonia, methanol, ethanol, acetaldehyde, acetic acid, acrolein, isopropyl ether, ethyl acetate, glycol ether and 2-methoxyethanol which can sometimes interfere with DME, were investigated by introducing each compound into the proposed sensor chamber at a concentration of 1.0×10^3 ppm. According to Fig. 8, no or very weak CTL emissions for most compounds were observed. Although CTL emissions were detected from 2-methoxyethanol and ethanol, The CTL intensity was much lower than that of DME. Strong CTL emission was observed when ethyl ether passed through this sensor [30]. However, it seldom coexists with DME, which will not interfere with the determination of DME in most substances.

3.9. Sample analysis

Three artificial air samples were analyzed to evaluate the analytical application of the sensor system. Since formaldehyde, ethanol and benzene are the common organic compounds in the air, a series of mixed samples containing known concentrations of compounds mentioned above with DME are prepared for the measurements. The artificial gas samples were prepared by the following procedures: a certain volume of the mixed sample was injected into an airtight bottle of 600 mL. The vapor samples were carried into the sensor chamber for measurement. Sample 1 was a mixture of DME and ethanol, sample 2 was a mixture of DME and benzene, and sample 3 was a mixture of DME, ammonia and formaldehyde. The results were shown in Table 3, the concentrations of DME in three samples were well quantified with satisfied recoveries.

Table 3
DME vapor analysis in artificial samples.

Sample no.	Composition	Standard values (ppm)	Measured values (ppm, $n=6$)	DME recovery (%)
1	DME	1000	995.2 ± 17.2	99.5%
	Ethanol	1000	–	
2	DME	1000	961.1 ± 10.2	96.1%
	Formaldehyde	1000	–	
	Ammonia	1000	–	
3	DME	1000	1014 ± 20.3	101.4%
	Benzene	1000	–	

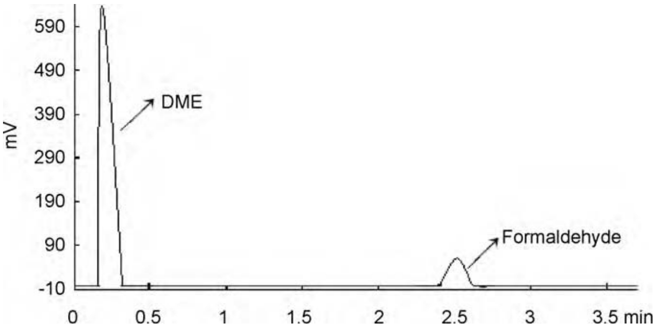

Fig. 9. Chromatogram map of the tail gas from the catalytic oxidation of DME.

3.10. Possible mechanism of the CTL reaction

To study the CTL mechanism of the DME sensor, GC experiments were carried out to detect the reaction products of the catalytic oxidation of DME, which was attributed to the oxidation processes. In chromatogram (Fig. 9), traces of DME and formaldehyde are detected, Therefore, possible mechanism of the DME CTL is: (1) when DME vapor passed through the surface of the ceramic heaters, it was oxidized by O_2 to produce formaldehyde molecules in the electronic excited state (CH_2O^*), and (2) formaldehyde molecules in the electronic excited state produced photoemission when returning to their ground states.

4. Conclusion

The results in the present work have demonstrated the feasibility to design a sensor based on cataluminescence for the determination of trace DME. The influence of sensor temperature, wavelength and carrier gas flow rate on the CTL intensity was investigated. Under the optimized conditions, it has a wide linear range, with a detection limit of 80 ppm. The proposed DME sensor has a better selectivity and stability in comparison with the electrochemical sensor mentioned before. It also has a longer life span since it does not need to prepare and fix up the granular material. The sensor shows potentials in industrial and environmental application.

Acknowledgements

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