

Characteristic Dynamic Responses for Pesticide Residue Detecting on the Surface of the SnO₂ Gas Sensor

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Abstract: A new rapid detecting method (called dynamic measurements) to detect and distinguish the presence of two pesticide gases acephate and trichlorphen and their mixture in the ambient atmosphere is reported. The method only employed a single SnO₂-based gas sensor in a sinusoidal temperature mode to perform the qualitative analysis of pure pesticide gas and mixture of binary gases (acephate and trichlorphon) in air. The dynamic responses under different concentrations are also discussed. Experimental results show that high selectivity of the sensor presents in the range of temperatures 250 ~ 300°C and the modulating frequency 20 MHz. The quantitative analysis between the pure pesticide gases and their mixture was performed by Fast Fourier Transformation (FFT). The higher harmonic terms of the FFT characterized the nonlinear properties of the response at the sensor surface. The amplitudes of the high harmonic terms exhibited characteristic changes which depend on the concentration and the kinetic reaction of gas species on the sensor surface. Nonlinear responses are discussed in relation to the kinetics of the gas species at the sensor surface and the surface barrier potential.

Key words: SnO₂ gas sensor; modulating temperature; pesticide residue; gas analysis

基于 SnO₂ 气体传感器检测农药残留的表面动态响应特性

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摘要:利用单个 SnO₂ 气体传感器在方波变化的温度条件下实现对敌百虫和乙酰甲胺磷及其混合气体的快速检测和识别。实验结果表明, SnO₂ 气体传感器在温度范围为 250 ~ 300°C、温度变化频率为 20MHz 的工作条件下对敌百虫和乙酰甲胺磷及其混合气体表现出高的灵敏度和清晰的动态响应特征。通过快速傅立叶变换(FFT)实现对敌百虫和乙酰甲胺磷及其混合气体的定量分析。

关键词: SnO₂ 气体传感器; 温度调制; 农药残留; 气体分析

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Pesticide residue had always been the most important problem on food security^[1,2]. In recent years, therefore, considerable effort had been directed towards the detecting techniques of pesticide residue^[1-6]. Although there had been enough precision of analysis, it is well-known that the disadvantages of the conventional detecting method, such as chromatographic detection, is too slow to detect gas sample in situ and affect the timeliness of the analysis. More attention has been focused on the research of rapid test method of pesticide residue. At present, the rapid analyzing techniques include immunoassay^[3], biosensor^[4,5], chromatographic and mass spectrometry^[6], polarographic method^[7] and so on. A simplified indirect method was developed by using adapted versions of molecular emission cavity analysis based on measurements of the intensity of the emission band of indium monochloride at 359.9nm^[8], but in the case of the above mentioned methods there exist some different limitation^[1-7]. Meanwhile, there are very few reports about detecting pesticide residue by using SnO₂ sensor.

SnO₂-based gas sensors had been extensively applied to gases detection^[9]. Well known advantages included their low cost and high sensitivity, and disadvantages concerned their lack of stability and selectivity^[10,11]. In practical applications, several attempts were made to overcome their disadvantages, for example, by using chromatographic columns to separate the components, by operating at different temperatures, by choosing different burning-in procedures, different dopants, and surface chemical modification, measuring frequencies, etc^[9-14]. For common applications of pattern recognition and multi-component analysis of gas mixtures, sensor-arrays^[15,16] which operate at constant temperature were usually chosen. In these cases because of lack of selectivity overlapping sensitivities of different sensors are of advantage^[17,18]. Some authors^[19-22] had indicated that temperature modulation to metal-oxide sensors provides more information from a single sensor than isothermal operation, allows improving research works in gas detection such as CH₄, CO, NO₂. Several investigations had been focused on dynamic sensor measurements obtaining adequate results, nevertheless they used non-commercial sensors and often required sophisticated heater control waveforms^[23,24].

We reported previously that the method employed only a single SnO₂-based gas sensor in a sinusoidal temperature mode to perform the qualitative analysis of binary gas mixture (acephate and trichlorphon) in air, and experimental results show that high selectivity of the sensor present in the temperature range of 250 – 300 °C and modulating frequency 20 MHz^[25].

On the basis of our previous work, we will continuously report the effect of concentration of trichlorphon, acephate and their mixture gases on the response of the single sensor. The resulting output resistance is analysed by Fast Fourier Transformation (FFT). The amplitudes of the higher harmonics of the FFT signal exhibit characteristic changes that depend not only on the species of test gases but also on the concentration of test gases. Nonlinear responses are discussed in relation to the kinetics of the gas species at the sensor surface and the surface barrier potential.

1 Experimental

The thick film sensor consists of a layer of tin oxide film deposited on a ceramics substrate^[26]. The devices were used according to the reference[27]. The preparation of the sensitive material was described elsewhere^[28]. The grain sizes of the materials were around 20 and 50nm. A headspace sample (HP-7694) was used to inject the measured gases into a 2500 mL sensor test chamber, where a single SnO₂ gas sensor was kept. Acephate, trichlorphon gases (Analytical standard, provided by Sigma-Aldrich Laborchemikalien GmbH). and binary mixture of acephate and trichlorphon were measured. A square voltage signal (20 MHz, 25 MHz, 30 MHz, 50 MHz, frequency generator: HP 3325B, power supply: HP 6035A) was applied to the sensor for heating resistor, which allowed to modulate the working temperature of the device in the range 50 – 300 °C. The signal frequency and operating temperature were adjusted to obtain good sensitivities and selectivity for the pesticide gas measuring. The sensor resistance was monitored, and the resistance data were picked up and stored in a PC for further analysis. Fig. 1 shows the experimental set-up. The measurement process was as follows: In measure dry air as carrier gas flows into the chamber at a

constant rate of 10 mmol/sec. Data acquisition had started for 80s before the test gase sample injected into the air-

flow. The sampling rate was set to two data per second and to complete a measure took for minutes.

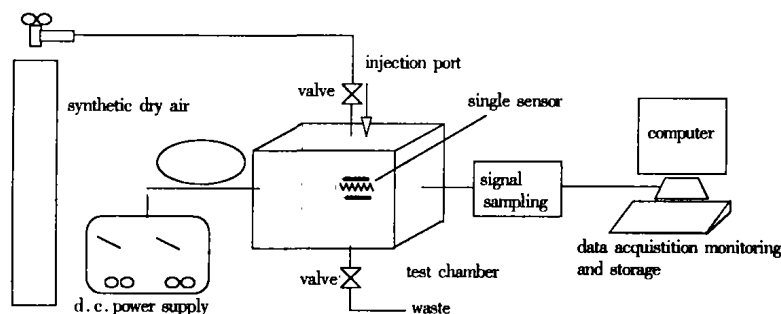


Fig. 1 Experimental set-up

2 Results and Discussion

2.1 Comparative experiments between static and dynamic response

The static responses of 0.1×10^{-6} trichlorphon, acephate gas and 0.2×10^{-6} mixture at 300°C for SnO₂ sensor are reported in Fig. 2 (left). The response time defines the time taken for the sensor to reach 90% of the saturation value after contacting the surface of the sensor by the test gas. In Fig. 2, one can clearly observe that

the sensor exhibit the rapid response upon exposure to the trichlorphon and acephate gas, it is noticed that the response time to both acephate and trichlorphon gas or to 0.2×10^{-6} mixture was only several seconds. It also shows that, however, in addition to the changes of resistance and response time there was no other information about reaction process. In particular, there was no reaction phenomenon but declining of element resistance by comparing to a single pesticide gas, this case can be explained by the fact that the static testing condition:

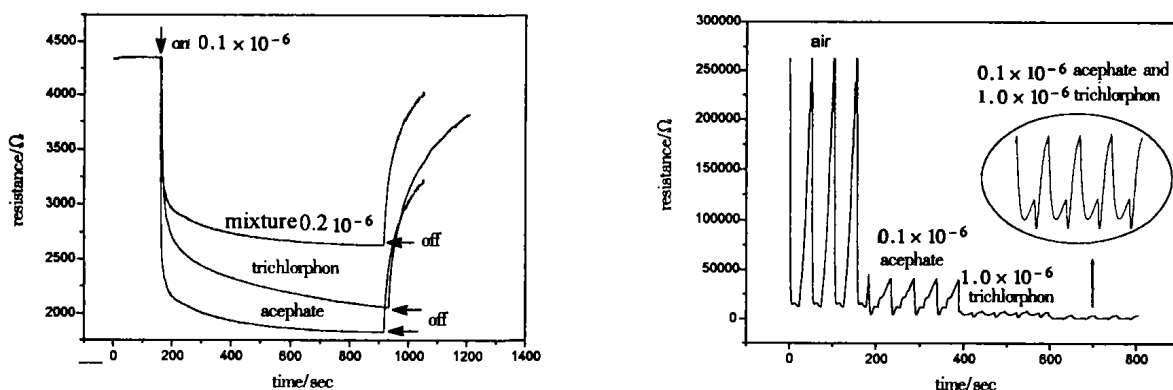


Fig. 2 Time-dependent changes of the resistance of a SnO₂ sensor in synthetic air and during exposure to acephate, trichlorphon and their mixture gases. The left is static response and right is dynamic response.

temperature 250 ~ 300°C; the dynamic testing conditions: temperature modulating frequency was 20 MHz, temperature controlled in the range 250 ~ 300°C, concentration of mixture was larger than that of a single gas. That is to say, during static measurements, we only observe the resistance changes of sensing element of initial and final state, of other changes during reaction process we do not obtain any information. Herein, it is worth to note that there also existed a drift effect due to the self-

instability of SnO₂ sensor and resulted in bad-reproducibility.

Fig. 2 (right) also shows the typical time dependencies of the resistance of the sensor realised with a single SnO₂ sensor, during their exposure to different pesticide gases and mixture under the dynamic measurements. One can easily observe the qualitative difference between the response to pure pesticide gases and that to the mixture. These facts can be also observed by exam-

ining the temperature dependence of resistances, presented in Fig.5 (section 3.3).

During the static measurement process, the adsorbed oxygen results in oxidation of pesticide gases on the surface and in a decrease of chemisorbed oxygen concentration, inducing an increase of the conductance. As seen from Fig.2, it is found that gas identification in a sinusoidal temperature modulated mode is related to the different reaction kinetics of the interacting gases on the tin oxide surface. Although the detailed reaction mechanism of pesticide gases is not clear, it is obvious that, by temperature modulation, it becomes possible to provide the surface oxygen species at constant tempera-

tures, which, in equilibrium conditions, there would not exist. In this way the reacton was dramatically influenced on the response to the pesticide gases at both lower and higher temperature, that is, acephate and trichlorphon gases exhibited in time their characteristic wave shape and to the different oxygen reations at the SnO_2 surface one can not observe the characteristic wave shape of the pesticide gases measuring under to condition of constant temperature.

2.2 The dynamic response to pesticides under different concentration

Plots of dynamic response to acephate and trichlorphon gas as a function of different concentration operated

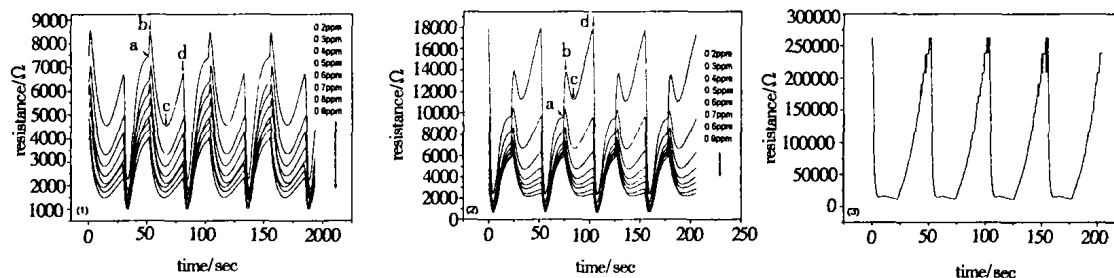


Fig.3 Response of the sensor to different concentration of pesticide gases in the sinusoidal temperature mode of operation in synthetic air. (1) trichlorphon; (2) acephate; (3) air Experimental conditions: temperature $250 \sim 300^\circ\text{C}$, modulating frequency 20MHz

in sinusoidal temperature mode of $250 \sim 300^\circ\text{C}$ and modulating frequency 20 MHz are shown in Fig.3. In order to distinguish the dynamic response features of the trichlorphon and acephate gas clearly, the dynamic response of air under the identical experimental conditions is also plotted at the bottom of Fig.3. As seen in Fig.3, the dynamic responses to pesticide gases are different with that to air, it suggests that the good sensitivity to trichlorphon and acephate gases and sufficient qualitative analysis are achieved. Meanwhile, it is also found that the resistance of the sensor changes regularly with the increase of the pesticide concentration. Besides resistance, at a certain point on the time scale, many other features in the graphs are seen to correlate with the acephate and trichlorphon gas concentration. Such features are the resistance ratios R_b/R_a , R_c/R_a and R_d/R_a . Also, the time periods from a to b and c to d correlates with the acephate and trichlorphon gas, respective-

ly. The dependence of the resistance ratio of R_b/R_a , R_c/R_a and R_d/R_a are depicted in Fig.4 (right) as a function of the pesticides concentration.

In Fig.4 (left), it is found that the resistance of point as shown in Fig.3, decreases with the increase of acephate and trichlorphon concentration with the tendency to a platform. This fact may be explained by taking account of response concentration range. There exists upper and low concentration limit. In connection with the right in the figure, it is found that the response range to acephate is larger than that to trichlorphon under the experimental conditions in this study. Also, in the case of higher concentration, the signal shape does not change (according to changes of the resistance ratios R_b/R_a , R_c/R_a and R_d/R_a) besides the absolute values of resistance. It suggests that the dynamical equilibrium between the surface adsorption and reaction on SnO_2 sensor has reached.

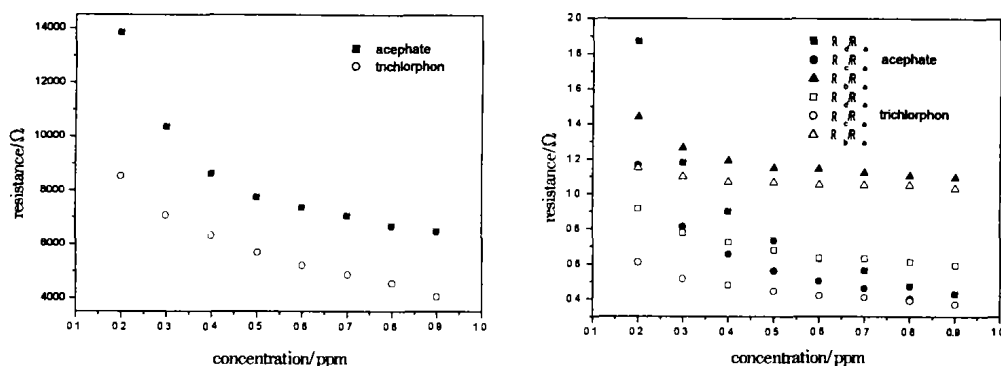


Fig.4 Resistance of point a in Fig.3 (left) and resistance ratios (right) of SnO_2 sensor as a function of the pesticide gases concentration

2.3 Data evaluation and feature extraction

Fig.5 shows the characteristic response curves of resistance versus temperature for air, $0.1 \mu\text{m}$ acephate, 1.0×10^{-6} trichlorphon and mixture of 0.1×10^{-6} acephate and 1.0×10^{-6} trichlorphon gases. The R - T curves for the different gases are apparently different from each other. It is noted that different characteristic responses were given with a single SnO_2 sensor, that is to say, the resistance in dependence on temperature is different with the kind of adsorbed gases by a same SnO_2 sensor in this experimental study. As seen in Fig.5, one can observe the huge sensitization to both acephate and trichlorphon gases, it is also worth to note that their sensitizations are obviously distinguished by controlling the temperature and temperature modulating frequency in this study. The different characteristic responses to gases are attributed to the differences in kinetics of a dsorption or desorption of the test gases and of their oxidizing reaction on the sensing element surface. It is widely accepted that the key process in the response of the semiconductor to a reducing gas involved the modulation of the concentration of adsorbed oxygen species such as O_2^{2-} , O^{2-} or O^{2--} . Although the sensing mechanism during exposure to pesticide gas is not clear, it is affirmative that there existed a complicated kinetics of adsorption or desorption and oxidative reaction on the sensing surface, as seen in Fig.5.

In order to quantitatively evaluate the characteristic changes in the conductance of nonlinear response of gas sensors, the amplitude of the FFT for acephate and trichlorphon gases under different concentration were examined (see (1) and (2) in Fig.6). The analyzed data

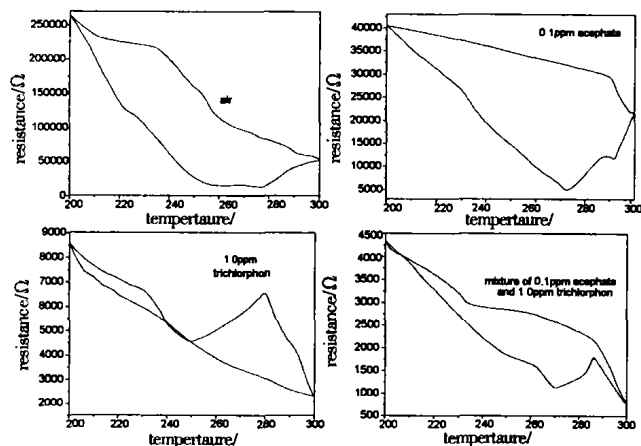


Fig. 5 Characteristic response curve of resistance versus temperature for air, 0.1×10^{-6} acephate, 1.0×10^{-6} trichlorphon and mixture of 0.1×10^{-6} acephate and 1.0×10^{-6} trichlorphon.

correspond to the conductance values in Fig.5. Herein, R_n and I_n denote the real part and imaginary part of the n_{th} harmonic in the FFT respectively. The frequency of the fundamental harmonic (R_1 or I_1) is 40 MHz. The existence of higher harmonic indicates that the experimental system was intrinsically nonlinear. In Fig.6, the concentration-dependence of the second harmonic varies well-regulated between the two pesticide gases. R_2 and I_2 for two species of gas decrease with an increasing in concentration. Meanwhile, R_2 and I_2 for the mixtures of trichlorphon and acephate with different concentration percentage were also here investigated. As shown from the data depicted in Fig.6 (in (3)), we can divide them into three parts and analyzed them one by one. Firstly, R_2 and I_2 decrease with an increasing in the percentage of trichlorphon gas (i.e. 1:1, 1:5, 1:10, 1:15, respectively). Secondly, R_2 and I_2 also decrease

with an increasing in the percentage of acephate gas (i. e. 2:1, 3:1, 10:1, respectively). Third, changes of

R_2 and I_2 are obvious with an increasing of concentration of acephate gas by comparing to the case of 1:5 with that

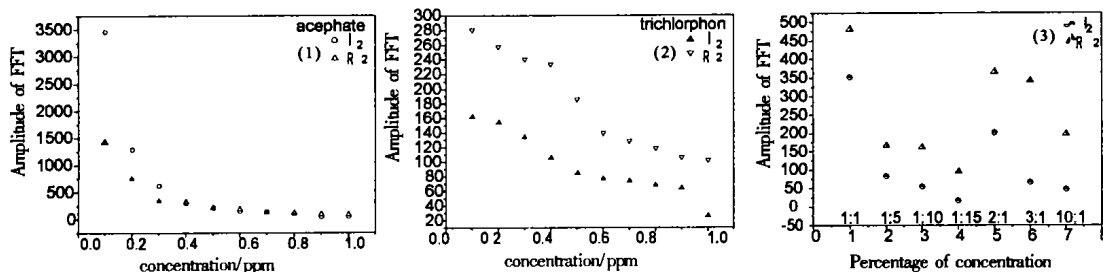


Fig.6 Concentration-dependence of the amplitude of second harmonics in FFT for (1) acephate and (2) trichlorphon gases and (3) mixtures of acephate and trichlorphon gases.

of 2:1 and 3:1. It shows that the effect of acephate gas on R_2 and I_2 was evident comparing with that of trichlorphon gas. This fact can also be verified by other experimental results: resistance-dependent on changes of time during exposure to acephate gas was sharper than that to trichlorphon under the same concentration. Above experimental results suggested that the concentration of pesticide gas can be obtained based on analyzing of the higher harmonics.

2.4 The effect factor of the higher harmonics for FFT in theoretical analysis

We consider that the electrons moving from one particle to another only experience the hindering effect of the barrier. The conductance of a semiconductor gas sensor $G(T)$ at a temperature T may be described by the equation^[29,30]:

$$G(T) = G_0 e^{-\frac{eV_s}{kT}} \quad (1)$$

where G_0 denotes the preexponential factor which includes the bulk intragranular conductance and geometrical effects, e is electronic charge, k is Boltzmann's constant, and T is the absolute temperature (K). It is obvious that $G(T)$ depends on the surface Schottky barrier height V_s and temperature. The surface Schottky

height V_s is given by the surface concentration of ion-sorbed oxygen, as in Eq(2),

$$V_s = \frac{eN_t^2}{2\epsilon_s \kappa_0 N_d} \quad (2)$$

where N_t denotes the surface density of ion-sorbed oxygen, $\epsilon_s \kappa_0$ is the semiconductor permittivity, and N_d is the volumetric density of an electron donor. Eqs (1) and (2) imply that the electron density of the semiconductor surface will increase and the conductance of the sensor will increase too when the reducing gas, is oxidized by ion-sorbed oxygen. Similarly, the conductance of the semiconductor will increase with an increase in temperature.

Eq. (3) is obtained from Eqs(1)and (2) assuming that N_d is significantly larger than N_t :

$$G_{(T)} = G_0 \exp\left(-\frac{V_s C_{O_i^{n-}}^2}{T}\right) \quad (3)$$

Where $C_{O_i^{n-}}$ denotes the surface concentration of ion-sorbed oxygen, O_i^{n-} ($m = 1$ or 2), on the sensor surface, and $V_s = e^2/2\epsilon_s \kappa_0 N_d K$. When the temperature is changed in $T = T_0 + T_a \cos 2\pi ft$, Eq. (3) can be expanded as Eq. (4):

$$G_{(T)} = G_0 \exp\left(-\frac{V_s C_{O_i^{n-}}^2}{T_0}\right) \times \left\{ \left(1 - \frac{V_s C_{O_i^{n-}}^2 T_a^2}{2T_0^3} + \frac{V_s^2 C_{O_i^{n-}}^4 T_a^2}{4T_0^4}\right) + \left(\frac{V_s C_{O_i^{n-}}^2}{T_0}\right) T_a \cos 2\pi ft \right\} + \left\{ -\frac{V_s C_{O_i^{n-}}^2}{2T_0^3} + \frac{V_s^2 C_{O_i^{n-}}^4}{4T_0^4} \right\} \times T_a^2 \cos 4\pi ft + \dots \quad (4)$$

Eq. (4) suggests that the real part of the higher harmonic is related to the surface barrier potential, which depends on the kinds of semiconductor, the catalyst, and the ad-

sorption state of the gas species on the sensor surface.

On the other hand, Eq. (5) is obtained assuming for simplification that the reaction on the sensor surface

progresses as a first-order reaction and the concentration of the reactant, C_{gas} , corresponds to the resistance value of gas sensor, R_{sensor} :

$$\begin{aligned} \frac{dC_{\text{gas}}}{dt} &= \frac{dC_{\text{gas}}}{dt} \approx \frac{dR_{\text{sensor}}}{dt} \\ &= -\kappa R_{\text{sensor}} = -Ae^{-\frac{E}{RT}} R_{\text{sensor}} \end{aligned} \quad (5)$$

$$-\frac{dR_{\text{sensor}}}{R_{\text{sensor}}} = A \exp\left(-\frac{E}{RT_0}\right) \times \left[\left(1 - \frac{ET_a^2}{2RT_0^3} + \frac{E^2 T_a^2}{4RT_0^4}\right) + \frac{E}{RT_0^2} T_a \cos 2\pi ft \right. \\ \left. + \left(-\frac{E}{2RT_0^3} + \frac{E^2}{4R^2 T_0^4}\right) \times T_a^2 \cos 4\pi ft + \dots \right] dt \quad (6)$$

Integration of Eq(6) leads to (7):

$$\ln R_{\text{sensor}} = -A \exp\left(-\frac{E}{RT_0}\right) \left\{ \left[\left(1 - \frac{ET_a^2}{2RT_0^3} + \frac{E^2 T_a^2}{4RT_0^4}\right) t + \left(\frac{E}{2RT_0 \pi f RT_0^2}\right) \times T_a \sin 2\pi ft + \right. \right. \\ \left. \left. \left(\frac{E^2}{16\pi f R^2 T_0^4} - \frac{E}{8\pi f RT_0^3}\right) \times T_a^2 \sin 4\pi ft + \dots \right] \right\} \quad (7)$$

Where R_{sensor} denotes the resistance of gas sensor, Eq. (7) suggests that the imaginary part of the higher harmonics is related to the reaction rate or the activation energy of the reaction on the sensor surface.

3 Conclusion

Experiment found that a very low concentration pesticide gases (acephate and trichlorphon 0.1×10^{-6} , respectively) in the ambient atmosphere were rapidly detected and distinguished clearly by using only a single SnO₂ sensor. The dynamic responses vary well-regulated with different concentrations. The quantitative analysis between the pure pesticide gas and mixture was performed by fast Fourier transformation (FFT). The higher harmonics of the FFT characterized the nonlinear properties of the response at the sensor surface. The amplitudes of the higher harmonics exhibited characteristic changes which depended on the concentration and the kinetics of gas species on the sensor surface. The dynamic nonlinear responses are related to the surface barrier potential and reaction rate of reducing gases on the sensor surfaces. Additional studies are now on the way to extend this approach to identify other pesticide residue gas mixtures with more components and to understand the basic physical phenomena. Future work will also be

Where κ denotes the rate constant, A the preexponential factor, E the activation energy, C_{gas} the concentration of the reactant gas, and R the gas constant. When the temperature can be changed as $T = T_0 + T_a \cos 2\pi ft$, Eq (5) is expanded as Eq. (6):

devoted to the development of appropriate feature extraction procedures for this non-linear frequency-time problem.

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