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Qualitative and quantitative analysis of organophosphorus pesticide residues using temperature modulated SnO_2 gas sensor

Xingjiu Huang[a,b], Jinhuai Liu[a,c,*], Zongxin Pi[a], Zengliang Yu[c]

[a] *Hefei Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, 230031, PR China*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei, 230026, PR China*
[c] *Institute of Plasma Physics, Chinese Academy of Sciences, Hefei, 230031, PR China*

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Abstract

Qualitative and quantitative analysis of organophosphorus pesticide residues (acephate and trichlorphon) using temperature modulated SnO_2 gas sensor were studied. The testing method employed only a single SnO_2-based gas sensor in a rectangular temperature mode to perform the qualitative analysis of pure pesticide vapor and a binary vapor mixture in the air. Experimental results showed that in the range 250–300 °C and at the modulating frequency of 20 mHz the high selectivity of the sensor could be achieved. The quantitative analysis of the pure pesticide vapor and their mixture were performed by fast Fourier transformation (FFT). The higher harmonics of the FFT characterized the non-linear properties of the response at the sensor surface. The amplitudes of the higher harmonics exhibited characteristic variations that depend on the concentration and the kinetics of pesticide species on the sensor surface.

Keywords: SnO_2 gas sensor; Modulating temperature; Pesticide residue; Qualitative and quantitative analysis

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1. Introduction

SnO_2-based gas sensors had been extensively applied to gases detection [1]. Present well-known advantages included their low costs and high sensitivities; well-known disadvantages concerned their lack of stability and selectivity [2,3]. 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, and by choosing different burning-in procedures, dopants, surface chemical modification, measuring frequencies, etc. [1–6]. For common applications of pattern recognition and multi-component analysis of gas mixtures, arrays of sensors [7,8] were usually chosen which operated at constant temperature. In these cases a lack of selectivity and overlapping sensitivities of different sensors was of advantage [9,10]. Some authors [11–14] had indicated that temperature modulation of metal-oxide sensors provides more information from a single sensor than isothermal operation, allowing improved research works in gas detection such as CH_4, CO, and NO_2. Several investigations had been focused on dynamic sensor measurements obtaining adequate results, and nevertheless, they used non-commercial sensors and often required sophisticated heater control waveforms [15,16].

Pesticide residue had always been the most important problem on food security [17,18]. In recent years, therefore, considerable efforts had been directed towards the detecting techniques of the pesticide residue [17–22]. Although there had been precision of analysis, it was well known that the disadvantages of the conventional detecting methods, such as chromatographic detection, were too slow to detect gas samples in situ and had affected the timeliness of the analysis. So, more attention had been focused on the research of rapid test methods of pesticide residues. At present, the rapid analyzing techniques includes immunoassay [19], biosensor [20,21], chromatography and mass spectrometry [22], polarographic method [23], and so on. A simplified indirect method has been developed using adapted

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[*] Corresponding author. Tel.: +86-551-5591142; fax: +86-551-5592420.
E-mail address: jhliu@iim.ac.cn (J. Liu).

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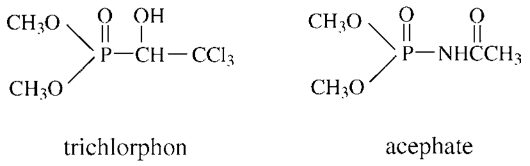

Fig. 1. Structures of the pesticides investigated in this study.

versions of molecular emission cavity analysis based on measurements of the intensity of the emission band of indium monochloride at 359.9 nm [24], but, respectively, the above-mentioned methods have some limitations [17]. So far, few reports about detection of pesticide residue detecting by using SnO_2 sensor have been made. In the present study, a modulated temperature operation mode has been chosen as a new approach to identify the two pesticide vapor and their mixture. The quantitative analysis of the pure pesticide vapor and their mixture are performed by fast Fourier transformation (FFT). We have also reported the amplitudes of the higher harmonics of the FFT signal exhibited characteristic changes depending not only on the species of but also on the concentration of the pesticide vapor.

2. Experimental

The thick film sensors were made by depositing thick films of tin oxide on ceramics substrates [25]. The devices were used according to reference [26]. The preparation of the sensitive materials was described elsewhere [27]. The grain sizes of the materials were around 20 and 50 nm. A headspace sample(HP-7694) was used to inject the gases measured into the 2500 mL sensor test chamber, where a single SnO_2 gas sensor was kept. Acephate, trichlorphon (Analytical standard, provided by Sigma-Aldrich Laborchemikalien Gmbh) and their mixtures were measured. The analytes whose structures are shown in Fig. 1 were chosen on the basis of their wide use in PR China. A square voltage signal (20, 25, 30, and 50 mHz; frequency generator: HP 3325B, power supply: HP 6035A) was applied to the sensor heating resistor, which allowed the working temperature of the device to be modulated in the range 50–300 °C. The signal frequency and operating temperature settings were adjusted to obtain adequate sensitivities and selectivity on the pesticide gases measuring. The sensor resistance was monitored, acquired and stored in a Personal Computer for further analysis. Fig. 2 showed the experimental setup. The measurement process was as follows: dry air at a constant flow rate of 10 mL s^{-1} was used as carrier gas. Data acquisition started 80 s before the injection of the test gases sample into the air-flow. The sampling rate was set at two samples per second and the whole process took 8 min to complete.

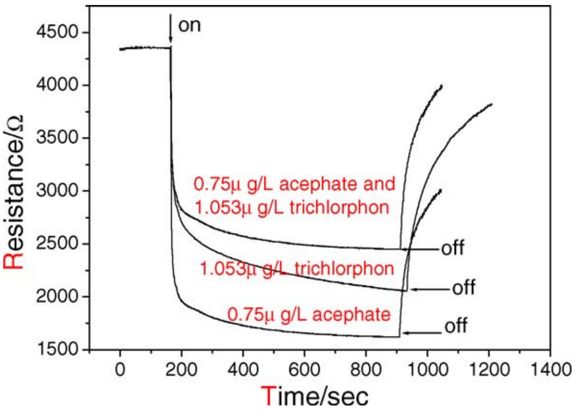

Fig. 3. Static response characteristics of the sensor to trichlorphon, acephate and their mixture (operating temperature: 300 °C).

3. Results and discussion

3.1. Static response of the sensor to the trichlorphon and acephate vapor

The SnO_2 sensor responses to the 1.053 $\mu g\,L^{-1}$ trichlorphon, 0.75 $\mu g\,L^{-1}$ acephate gases and their mixture at 300 °C are reported in Fig. 3. The response time defines the time taken by the sensor to reach 90% of the saturation value after contacting with the test gas at the surface of the sensor. In Fig. 3, one can clearly observe that the sensor has exhibited a rapid response upon exposure to the trichlorphon and acephate gas. We have noticed that the response time to both acephate and trichlorphon gases and to their mixture is only several seconds. It also shows however, that no other information except the changes in resistance and response time, appears in the reaction process. In particular, the decrease of the element's resistance in the case of the

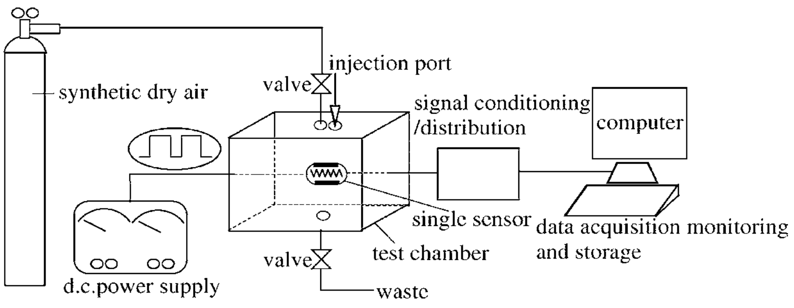

Fig. 2. Experimental set up.

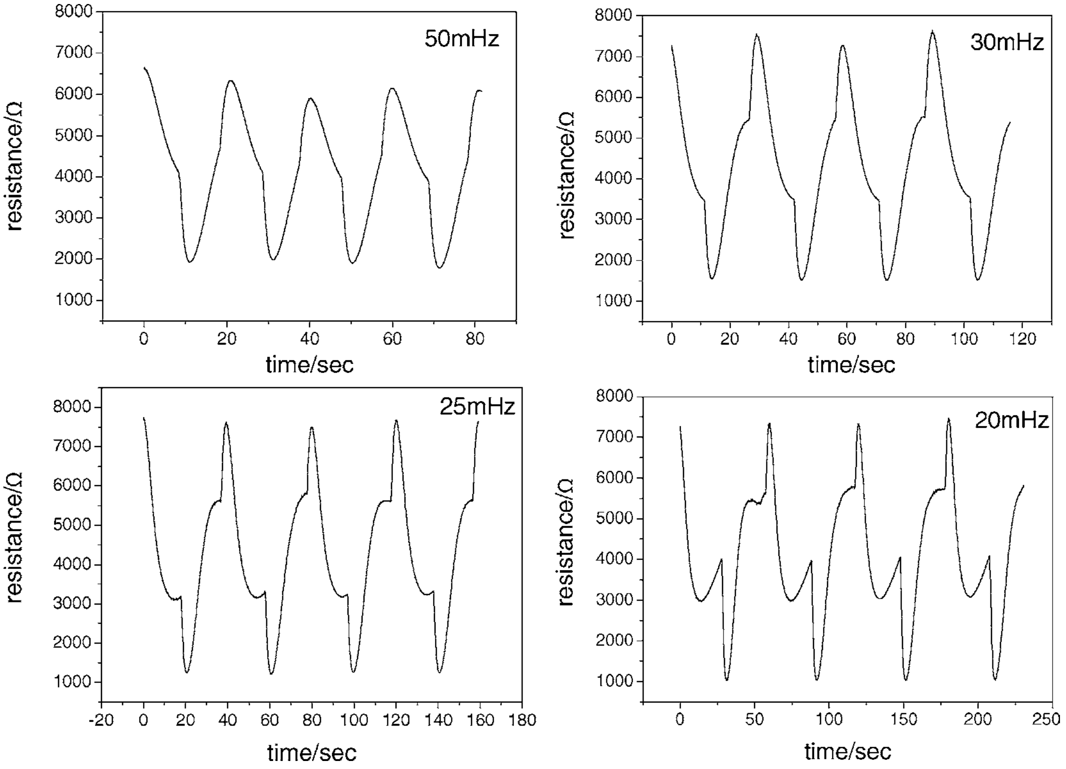

Fig. 4. Effect of modulating frequency on the response to 1.053 μg L^{-1} trichlorphon.

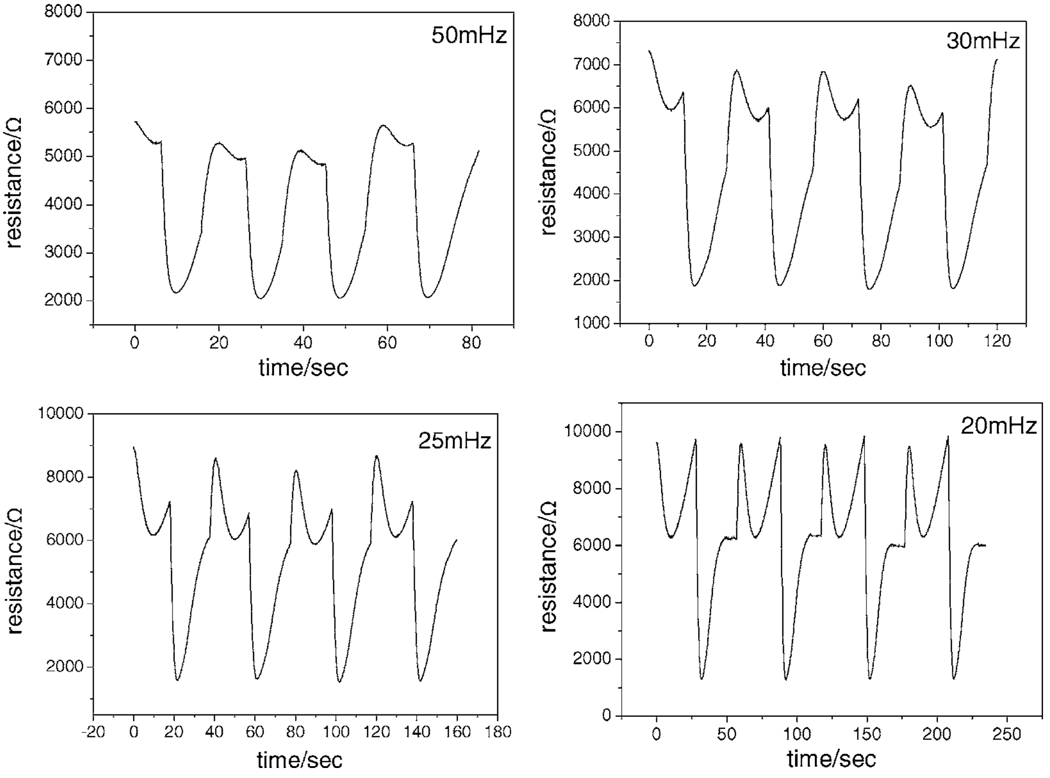

Fig. 5. Effect of modulating frequency on the response to 0.75 μg L^{-1} acephate.

mixture is more pronounced compared to a single pesticide gas, which can be explained by the fact that the concentration of the mixture is higher than that of a single gas, i.e., during static measurements, we have only observed the resistance changes of the sensing elements at the initial and final states, while in the case of the other changes during reaction process we did not obtain any other information. Herein, it is worth noting that there also exists a drift effect due to the self-instability of SnO_2 sensor and results in bad reproducibility.

3.2. Effect of modulating frequency on the response of pesticide vapor

Figs. 4 and 5 clearly show the time-dependence changes shape the of the sensor resistance in the presence of trichlorphon and acephate vapor in air under different tem-

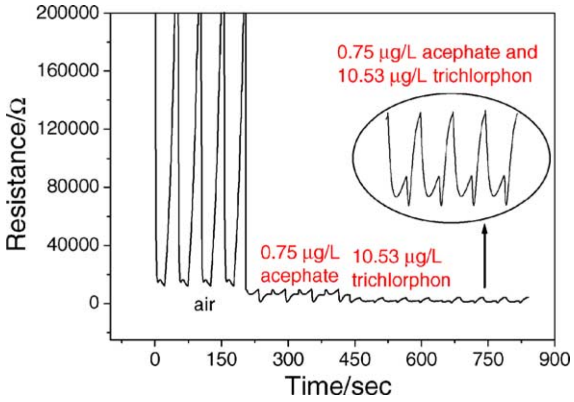

Fig. 7. Time-dependent changes of the resistance of a SnO_2 sensor in a synthetic air and upon exposure to 0.75 μg L^{-1} acephate, 10.53 μg L^{-1} trichlorphon and their mixture. Experimental conditions: modulating frequency 20 mHz, temperature controlled in the range of 250–300 °C.

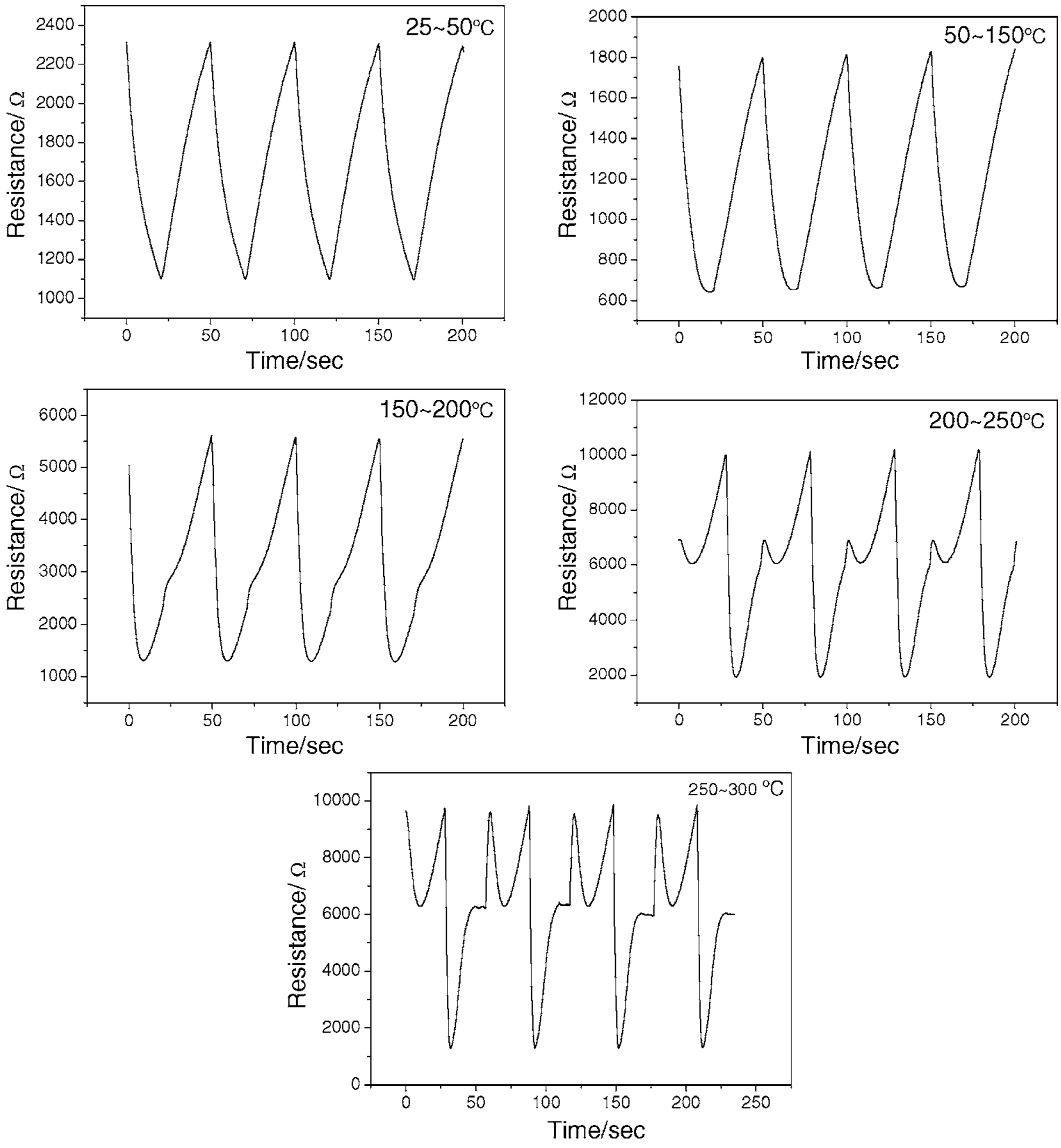

Fig. 6. Effect of temperature on the response to 0.75 μg L^{-1} acephate gas at frequency of 20 mHz.

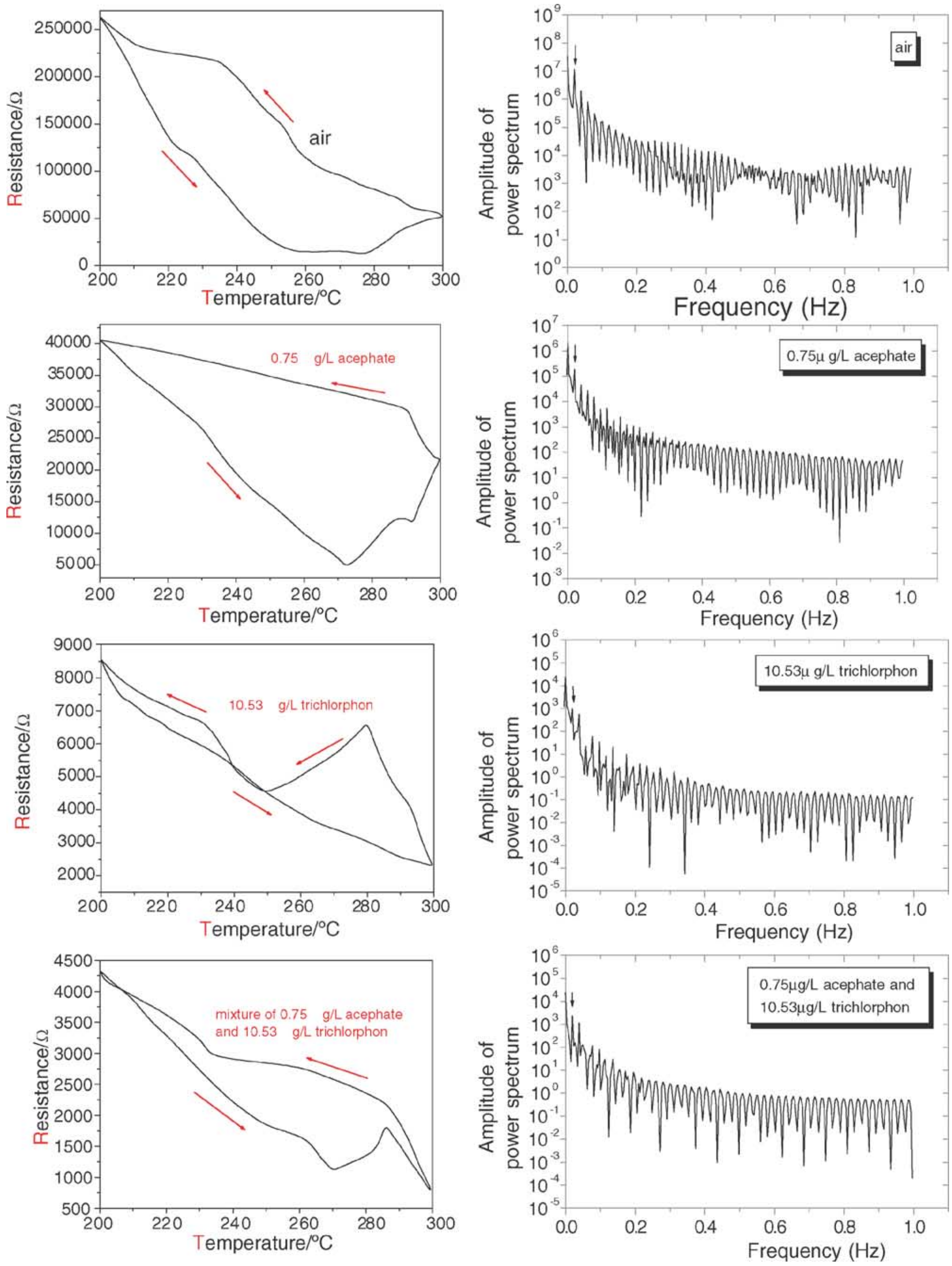

Fig. 8. Characteristic resistance response vs. temperature curves (left) and their corresponding power spectrum (right, the downward arrow is the fundamental frequency, the analyzed data correspond to the resistance values in Fig. 7) for air, 0.75 μg L^{-1} acephate, 10.53 μg L^{-1} trichlorphon and their mixture with a square voltage ($f = 20$ mHz) applied to the heater of the sensor and the temperature varied approximately between 200 and 300 °C.

perature modulating frequencies by controlling temperature range 250–300 °C. Obviously, temperature modulating frequencies has a significant effect on the sensing behavior of the sensor. With the decrease of the modulating frequency we can clearly observe that the sensing characteristics of the sensor, which remain more or less the same in further experimental process (frequency <20 mHz), had been exposed to both acephate and trichlorphon vapor.

3.3. Effect of temperature at a constant frequency of 20 mHz

In order to reduce drift effect and optimize the selectivity of a temperature modulated sensor, it is necessary to obtain a relationship between a given temperature and its conductance response in the presence of pesticide vapor. Fig. 6 shows the effect of a given temperature on the response to 0.75 μg L^{-1} acephate at a constant modulating frequency of

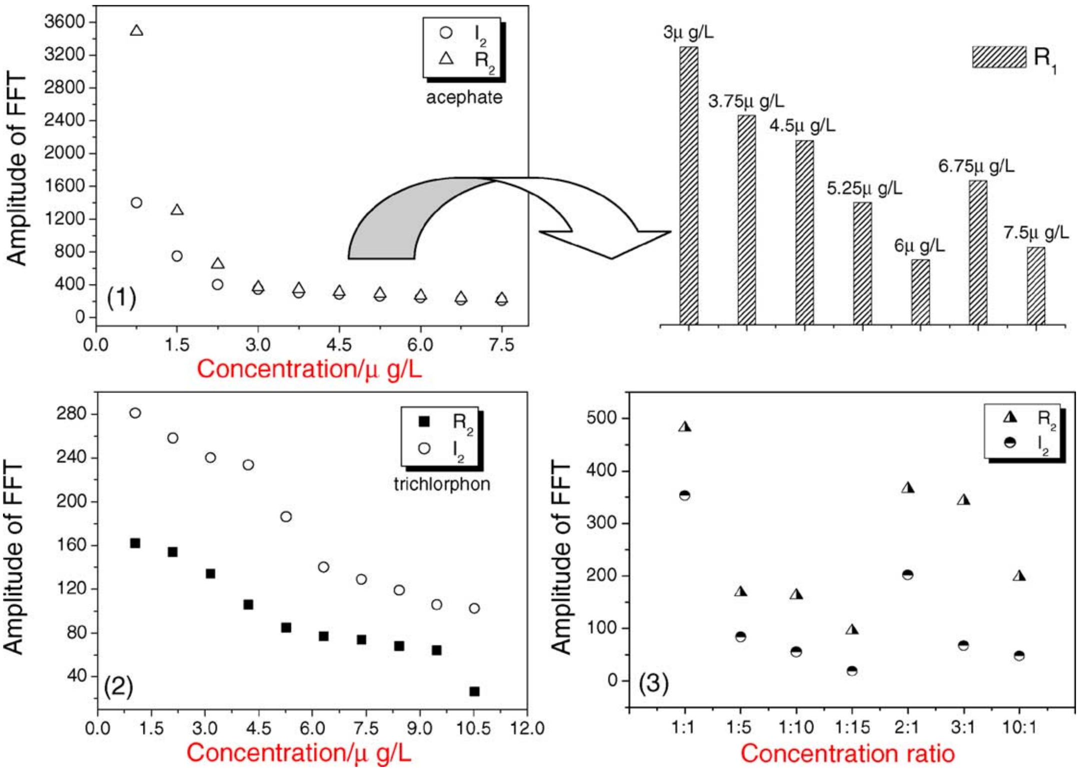

Fig. 9. Concentration-dependence of the amplitude of second harmonics in FFT of acephate (1) and trichlorphon gases (2) and their mixtures (3). R_2 and I_2 denotes the 2nd harmonic (real and imaginary part) in the FFT, respectively. The frequency of the fundamental harmonic (R_1 or I_1) is 20 mHz.

20 mHz. From the figure, one can easily observe the evident different signals with different temperature ranges, which indicates that, with temperature increasing, the sensor exhibits an enhanced selectivity to acephate vapor. So, we suggest that acephate vapor can be identified by means of a relatively complete response signal between 250 and 300 °C at a constant frequency of 20 mHz. During the cooling and heating of the sensor, fluctuations of the resistance are discovered. Obviously, the surface mechanisms of the reactions between acephate vapor and chemisorbed oxygen under different temperature ranges are different.

3.4. Dynamic response to the pure pesticide vapor and their mixture

Fig. 7 shows the typical time dependencies of the sensor resistance realized by a single SnO_2 sensor during their exposure to different pesticide vapor and their mixture. One can easily observe the qualitative difference between the response to pure pesticide vapor and their mixture, which can also be observed by examining temperature dependence of the resistances as presented in Fig. 8.

3.5. Data evaluation and feature extraction

To give a clearer intuitive view of the different shapes of the curves, the characteristic resistance response versus temperature curves and their corresponding power spectrum evaluated by FFT for air, 0.75 $\mu g\,L^{-1}$ acephate, 10.53 $\mu g\,L^{-1}$ trichlorphon and their mixture are investigated, as indicated in Fig. 8. The *R*–*T* curves for the different pesticides and their corresponding power spectrum are apparently different from each other. It is noted that different characteristic responses are given by a single SnO_2 sensor, i.e., the sensor conductance are different in temperature dependence in the presence of the adsorbed gas under

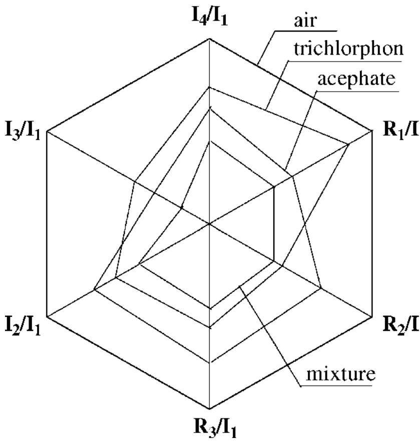

Fig. 10. Characteristic response of the relative intensities of the higher harmonics. R_i and I_i are the real and imaginary components of the *i*th higher harmonic. The analyzed data correspond to the resistance values in the concentration of 1.053 $\mu g\,L^{-1}$ trichlorphon, 0.75 $\mu g\,L^{-1}$ acephate and their mixture.

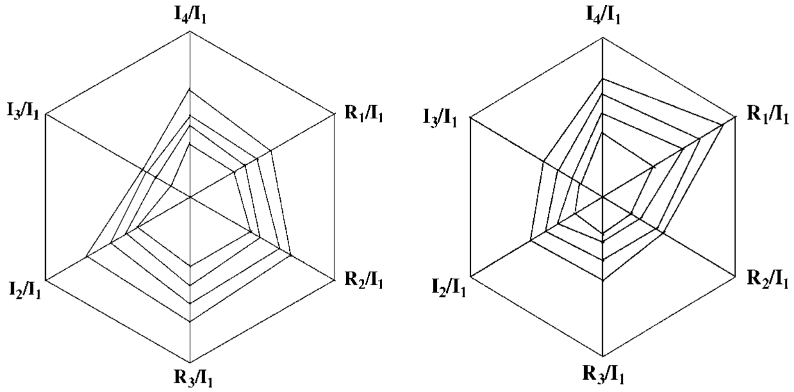

Fig. 11. Effect of concentration of pesticide vapor on the relative intensities of the higher harmonic. The concentration from inside to outside are 0.75, 2.25, 3.75, 5.25 $\mu g\,L^{-1}$ and 1.053, 3.159, 5.265, 7.371 $\mu g\,L^{-1}$, respectively. Left: acephate, right: trichlorphon.

the experimental conditions in this study. In Fig. 8, one can observe the huge sensitization to both acephate and trichlorphon vapor. And it is also worth noting that, by controlling the temperature and modulating frequency, acephate, and trichlorphon vapor are obviously distinguished in this study. On the other hand, the characteristic response to each vapor is attributed to the difference in the adsorption or desorption kinetics and the oxidative reaction kinetics of the test vapor on the sensing element surface. It is widely accepted that the key process in the semiconductor's response to a reducing gas consisted of the modulation of the adsorbed oxygen species (such as O_2^-, O^-, or O^{2-}) concentration. Although the sensing mechanism upon exposure to pesticide vapor is not clear, it is affirmative that there exists a complicated adsorption/desorption or oxidative reaction kinetics on the sensing surface, as seen in Fig. 8.

In order to quantitatively evaluate the characteristic changes in the non-linear response of gas sensors, the amplitude of the FFT for acephate and trichlorphon vapor under different concentrations are examined (see (1) and (2) in Fig. 9). The existence of higher harmonics indicates that the experimental system is intrinsically non-linear. In Fig. 9, the varying rules of the concentration dependence of the second harmonics of the two pesticide vapor can be easily detected. As their concentration increases, R_2 and I_2 for two pesticides decrease. As for acephate vapor with concentrations 3–7.5 $\mu g\,L^{-1}$, it becomes possible to distinguish among these concentrations based on R_1, shown to the right of (1). Meanwhile, R_2 and I_2 for the trichlorphon and acephate mixtures with different concentration ratios are also investigated, as can be seen from the data depicted in Fig. 9 (shows in (3). Here, three situations are analyzed. First, as the concentration ratio of the trichlorphon vapor (i.e., 1:1, 1:5, 1:10, 1:15) increases, R_2 and I_2 decreases. So is the case with acephate vapor (i.e., 2:1, 3:1, 10:1) in our second experiment. In the third experiment, we compare R_2 and I_2 changes at different concentration ratios of trichlorphon and acephate, and find that the acephate is more effective over the resistance than trichlorphon. This fact can also be verified by other experimental results: time-dependent resistance varies upon exposure to acephate vapor is more obviously than that of trichlorphon with the same concentration. As mentioned above, we suggest that the pesticide vapor concentration ratio can be obtained based on the changes of the higher harmonics.

We know that there are six sensor variables in the FFT,i.e., the amplitude corresponding to 0 Hz frequency, the amplitude corresponding to the fundamental frequency, and the first four harmonics. In order to minimize the experimental error and to give a much clearer illustration for the quantitative analysis of the pesticide gases, the relative intensities of the higher harmonics are used herein, i.e., the intensities of the 2nd, 3rd, and 4th harmonics which is the first four harmonics in the FFT are normalized in association with that of the imaginary component of the first harmonic I_1. The diagram is shown in Fig. 10. It is apparent that, through measuring the changes of the relative intensities, the identification of the pesticide vapor became possible. We have also been investigated the effect of concentration change on the relative intensities, as presented in Fig. 11. As noted, the general trend was that the main effect of the concentration change was to change the area of the diagram, while its shape tended to remain essentially the same.

4. Conclusions

Experimentally we found that very low concentrated pesticide vapor (0.75 $\mu g\,L^{-1}$ acephate and 1.053 $\mu g\,L^{-1}$ trichlorphon) in the atmosphere could be rapidly detected and clearly identified only through operating a single SnO_2 sensor in the rectangular temperature mode. The optimum temperature range and modulating frequency were 250–300 °C and 20 mHz, respectively. The quantitative analysis of the pure pesticide vapor and their mixture was performed by FFT. The higher harmonics of the FFT characterized the non-linear properties of the response at the sensor surface. The amplitudes of the higher harmonics exhibited characteristic changes depending on the vapor concentration ratio and the kinetics on the sensor surface.

We consider that it will become a significant exploratory development in the pesticide residue vapor rapid detection. Additional studies are now under way to extend this approach to identify other pesticide residue vapor mixtures with more components and to decode their basic chemi-physical mechanism. Future work will also be devoted to the development of appropriate feature extraction procedures for this non-linear frequency–time problem.

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References

[1] W. Gopel, K.D. Schierbaum, Sens. Actuators B 26–27 (1995) 1.

[2] K. Ihokura, J. Watson, Stannic Oxide Gas Sensors, Principles and Applications, CRC Press, Boca Raton, FL, 1994.

[3] P. Moseley, B. Tofield, Solid State Gas Sensors, Adam Hilger, Bristol, 1987.

[4] J.-H. Liu, X.-J. Huang, G. Ye, et al., Sensors 3 (2003) 110.

[5] U. Weimar, W. Gopel, Sens. Actuators B 26 (1995) 13.

[6] K. Wada, M. Egashira, Sens. Actuators B 53 (1998) 147.

[7] T. Maekawa, K. Suzuki, T. Takada, T. Kobayashi, M. Egashira, Sens. Actuators B 80 (2001) 51.

[8] D.-S. Lee, J.-K. Jung, J.-W. Lim, Sens. Actuators B 77 (2001) 228.

[9] H.V. Shurmer, J.W. Gardner, Sens. Actuators B 8 (1992) 1.

[10] K.D. Schierbaum, U. Weimar, W. Gopel, Sens. Actuators B 2 (1990) 71.

[11] A. Ortega, S. Marco, A. Perera, T. Sundic, A. Pardo, J. Samitier, Sens. Actuators B 78 (2001) 32.

[12] A. Heilig, N. Barasan, U. Weimar, M. Schweizer-Berverich, J.W. Gardner, W. Gopel, Sens. Actuators B 43 (1997) 45.

[13] A.P. Lee, B.J. Reedy, Sens. Actuators B 60 (1999) 35.

[14] L. Ratton, T. Kunt, et al., Sens. Actuators B 41 (1997) 105.

[15] R.E. Cavicchi, J.S. Suehle, K.G. Kreider, M. Gaitan, Sens. Actuators B 33 (1996) 143.

[16] M. Schweizer-Berberich, M. Zdralek, U. Weimar, W. Gopel, et al., Sens. Actuators B 65 (2000) 91.

[17] C.M. Torres, Y.J. Manes, J. Chromatogr. A 754 (1996) 301.

[18] P. Lea, F. Mladen, Biosens. Bioelectron. 18 (2003) 1.

[19] V.Z. Anatoliy, B.D. Boris, N.T. Janna, Anal. Chim. Acta 347 (1997) 131.

[20] D. Barcelo, S. Lacorte, J.L. Marty, TrAC, Trends Anal. Chem. 14 (1995) 334.

[21] T. Marek, L.H. Michael, TrAC, Trends Anal. Chem. 15 (1996) 38.

[22] J.S. Hans, J. Chromatogra. A 892 (2000) 347.

[23] Zh. Jiao, L.-F. Bian, J.-H. Liu, Chin. J. Funct. Mat. 32 (2001) 67.

[24] V.I. Rigin, Anal. Chim. Acta 291 (1994) 121.

[25] A.J. Reviejo, A. Sampron, J.M. Pingarron, L.M. Polo, Electroanalysis 4 (1992) 268.

[26] Zh.-Y. Zhang, Y.-H. Zhang, Zh. Jiao, J.-H. Liu, Chin. J. Sens. Actuators 2 (2000) 106.

[27] Zh.-Y. Zhang, J.-H. Liu, Y.-H. Zhang, Chin. J. Sens. Actuators 1 (2000) 13.