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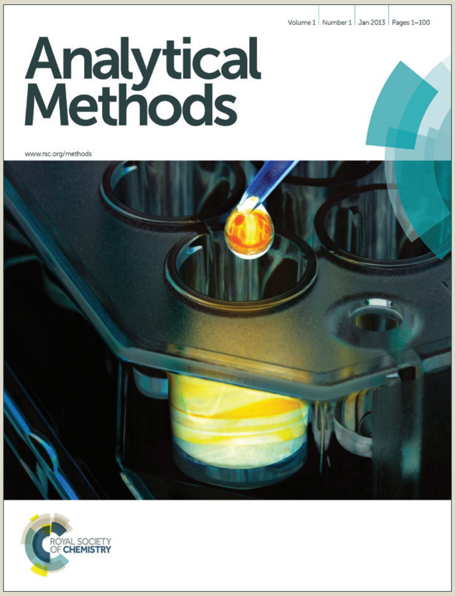

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Paper

The response comparison of a hydrogen-bond acidic polymer to sarin, soman and dimethyl methyl phosphonate based on surface acoustic wave sensor

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A hydrogen-bond acidic (HBA) polymer, poly{methyl[3-(2-hydroxyl, 4,6-bistrifluoromethyl)phenyl]propylsiloxane}(DKAP), was coated on a 434 MHz surface acoustic wave (SAW) device, and subsequently tested against sarin (GB) and soman (GD) vapour along with dimethyl methyl phosphonate (DMMP) at concentrations below 10 mg/m^3. A direct detection of GB and GD in the sub mg/m^3 range, indicating high sensitivity of the sensor, was demonstrated by the corresponding sensor which showed high reproducibility as well. However, the response of the sensor to the real agents was relatively smaller and slower than to the simulant DMMP. Towards the real agents, the time to reach an adsorption equilibrium was considerably long (~16 min) and a time-dependent linear response was observed in the initial >3 min for both the adsorption and the desorption process. The sensor was also compared with other HBA polymer coated SAW sensors in terms of response characteristics, with emphasis on the kinetic response behaviour. The slow adsorption and desorption property of the DKAP sensor toward the real chemical agents were attributed to the analytes size effect and hydrogen-bond strength.

1. Introduction

Organophosphorus nerve agents are a group of lethal chemical compounds that poses a great threat to the military as well as the civilian. Up to now, there are a variety of technologies for nerve agents detecting, in which analytical methods[1-3] (e.g. gas chromatography and mass spectrometry) are studied firstly and show high sensitivity, precision and reliability. However, these techniques require expensive equipments and professional personnel, as well as time consuming and unsuitable for on-site detection. In response to these problems, there is an urgent demand for highly sensitive and selective sensors.

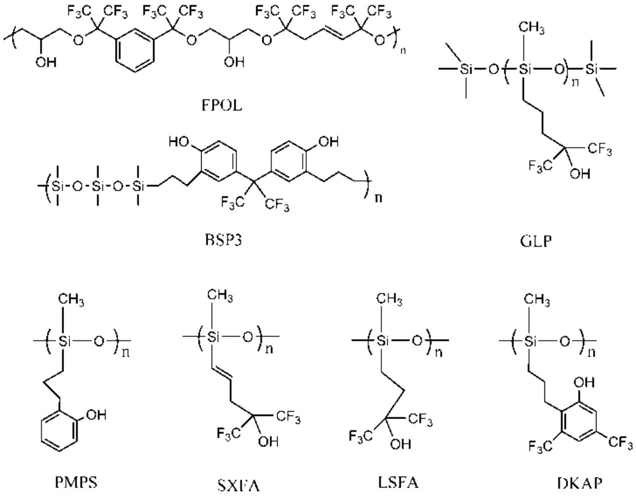

Fig. 1 Structures of some typical HBA polymers

Surface acoustic wave (SAW) sensor[4-6], ion mobility spectrometry[7-9], and acoustic resonant chemical sensor[10, 11] were promising technologies. Among them, the SAW sensors were intensively studied, wherein a sorptive coating was required to deposit on the surface of the SAW transducer. Hydrogen-bond acidic (HBA) polymers[6, 12-17], functionalized by fluorinated alcohol or fluorinated phenol groups, such as FPOL, SXFA, BSP3, GLP, PMPS and LSFA shown in Fig. 1, were predominately utilized as the sorbent coatings because they could selectively interacted with the target analytes by hydrogen bond. Most of the HBA polymers were constituted with polysiloxane or polycarbosilane backbone, thus exhibited a low glass to rubber transition temperature (T_g) and a high thermal stability. A lower T_g was beneficial to the permeation of an analyte into the polymer. Until now, about 30 HBA polymers have been designed and synthesized. However, the sensing properties of these polymers towards nerve agents were typically tested by simulants such as dimethyl methyl phosphonate (DMMP) or diisopropyl methylphosphonate (DIMP)[18], only in a few cases responses to real chemical agents such as GB (sarin) or GD (soman) were reported[19-23]. For a FPOL coated 158 MHz delay line sensor, signals of up to 200 Hz and 200-300 Hz were recorded at 0.1 mg/m^3 of DMMP and 0.5 mg/m^3 of GD, respectively, indicating FPOL had about 3-fold higher sensitivity to DMMP as compared to GD [19]. GLP also showed a 2.3 times higher response to DMMP than to GB as demonstrated by Zimmermann et al[20]. However, BSP3 synthesized by Chen et al was within 20% more sensitive to DMMP relative to GB, while PTFP (a fluorinated polymethyldrosiloxane whose molecular structure was not given in details) was even less sensitive to the simulant with respect to the real agent[23]. Thus, remarkable response differences towards the simulant and the real agents were demonstrated and the differences differed widely from one polymer to another. Therefore, vapor exposing tests under the real chemical warfare agents (CWA) were inevitable necessary for developing a CWA sensor.

In our previous work[24], a HBA polymer DKAP (initially dubbed as PMTFMPS) was synthesized. As shown in Figure 1, the polymer was a polysiloxane with pendant 3,5-bis(trifluoromethyl)phenol functional groups. Excellent sensing property of DKAP to DMMP was confirmed based on an 8 MHz QCM sensor. In this paper, to further investigate its sensitive performance, DKAP was coated on a 433.94 MHz SAW sensor and tested against real agents GB and GD as well as simulant DMMP. The sensor response details to the real agents and the mimic were compared, which was the focus of this paper.

2 Experimental

The SAW test platform was constructed in the following procedure.

The 434 MHz SAW two-port resonator devices were purchased from Shenzhen Luguang electronics, China. DKAP was synthesized in our laboratory, then dissolved in chloroform and spray-coated onto a bare SAW device by the airbrush apparatus. After film deposition, frequency shift of 1.2 MHz was recorded. The coated SAW device had a Q value of 3500 and an insert loss of -14 dB, measured by a network analyzer (E5070B, Agilent Technologies). The coated device, as well as a bare SAW device, was mounted onto a printed circuit board. Each device was excited individually in an oscillator loop. Then, the frequency difference between the coated device and the bare device was obtained by a mixer, and recorded by a SS7200A general counter (Suin Digital Instruments, China).

The test platform of the sensor to analyte vapors is shown in Figure 2. The flow rate in the platform was controlled by two mass flow controllers (MFC) and one float flow controllers (FFC). A small amount of the analyte solvent was injected into the vaporizing chamber by a microsyringe. The vaporized solvent was fluxed by pure N_2 and stored in a gas bag, and subsequently diluted by another pure N_2 stream to get a test concentration. The diluted vapor was injected into a small test chamber made up of aluminum alloy, which mounted gas tightly on the sensor printed circuit board. Since the flow rate has an influence on the response of the sensor, the stream injected into the chamber was controlled by the FFC at a constant of 1 L/min, and the redundant was discharged out. All the tests were carried out at room temperature of about 20 ^{o}C.

3. Results and discussion

The sensitive property of the sensor was investigated by exposing it to the analyte vapors for 3 to 4 min, followed by 3-4 min of pure nitrogen, and a 6-8 min cycle corresponded to one sharp peak in the following figures.

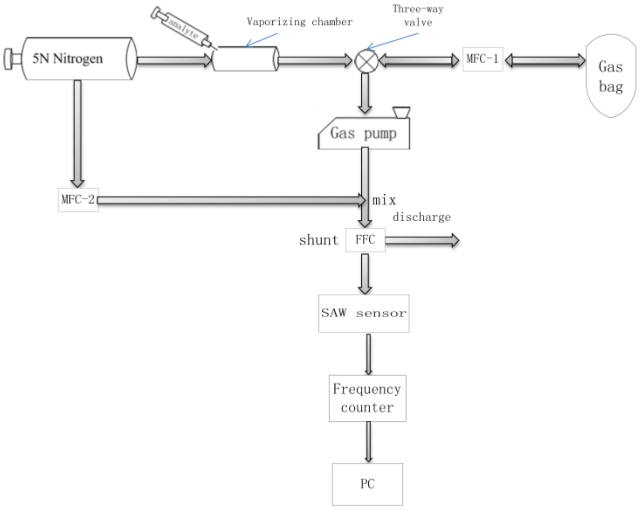

Fig. 2 Test platform of the SAW sensor to the analytes

Fig. 3a shows the response of DKAP sensor to DMMP ranging from 1 to 20 mg/m^3. The response changed immediately when the test chamber was injected with DMMP vapor and the rising trend quickly flattened with the purging of DMMP vapor. The response time T_{80}, defining as the time interval between the vapor on and the frequency shift f reaches to 80% maximum, was about 40 s at the highest tested concentration of 20 mg/m^3 and increased considerably with the decreasing of the vapor concentration, finally reached 150 s at 1 mg/m^3. When pure nitrogen entered the chamber three minutes later, the response fell down and recovered to the original value more rapidly. The desorption time (D_{80}) were only about 25 s regardless of the vapor concentration. Each sorption-desorption cycle exhibited a square-wave like curve especially at a higher DMMP concentration. Inset of Fig. 3a is the response of the sensor as a function of the DMMP concentration, a parabola is obtained after polynomial fitting although the second derivative was relative small.

Fig. 3b shows the real-time response of the DKAP sensor for GB detection ranging from 0.2 to 10 mg/m^3. As can be seen, the response of the sensor increased almost linearly with the exposure time of the GB vapor with a time-dependent sensitivity of 190 Hz/min at 0.2 mg/m^3, indicating the DKAP coating couldn’t reach an equilibrium state of adsorption within 3 minutes (actually the T_{80} was 13 min for 10 mg/m^3 GB as shown in Fig. 3d, the sensor reached an equilibrium state in about 16 min and the response value was 73.5 kHz). Three minutes later, the chamber was purged into pure nitrogen, desorption occurred gradually and the response could return to the original value after purging for 3-4 min. Thus, the real-time response of the sensor to GB exhibited a triangular-wave curve for each sorption-desorption cycle which was totally different from the square-wave behavior of the sensor responded to DMMP. At the lowest tested concentration of 0.2 mg/m^3, the response of the sensor could reach 570 Hz at the end of 3-min duration, and response of 28 kHz was recorded at 10 mg/m^3. Inset was the calibration curve by plotting the 3-min response in terms of the GB concentration.

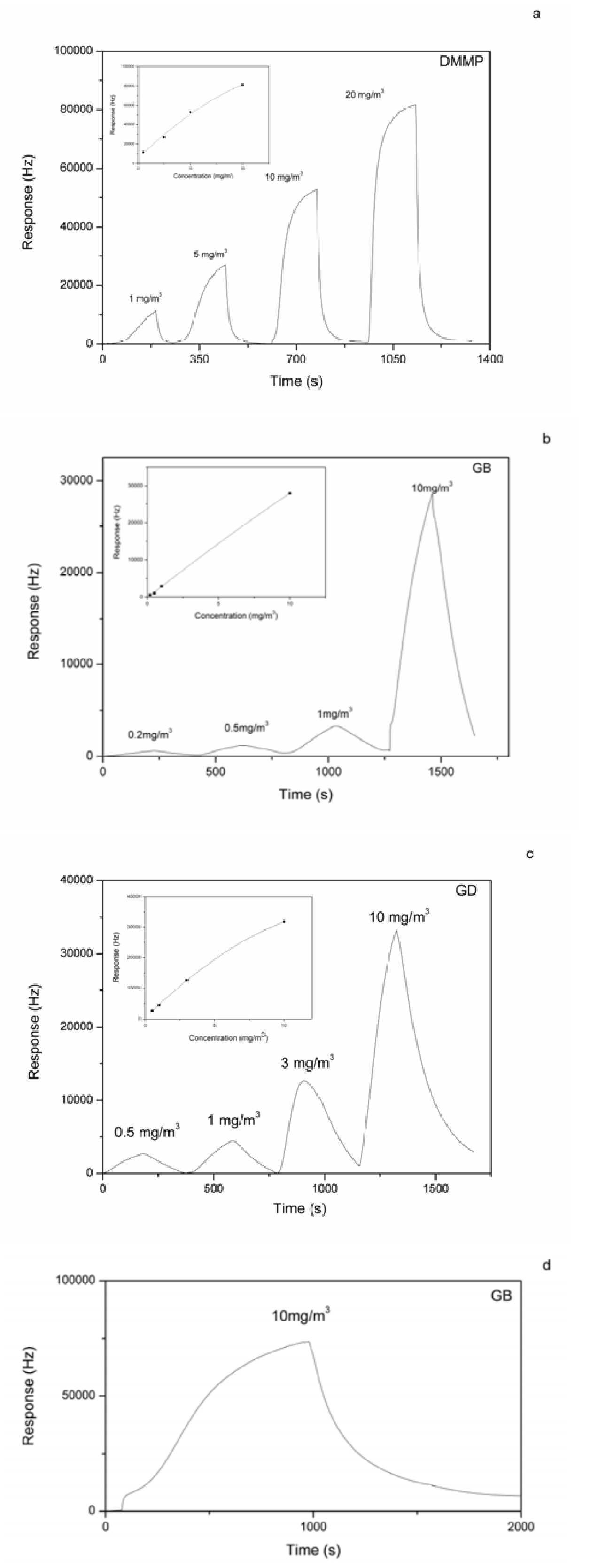

Fig. 3 Responses of DKAP sensor to DMMP (a), GB (b,d) and GD (c), insets are the responses of the sensors as a function of the analyte concentration

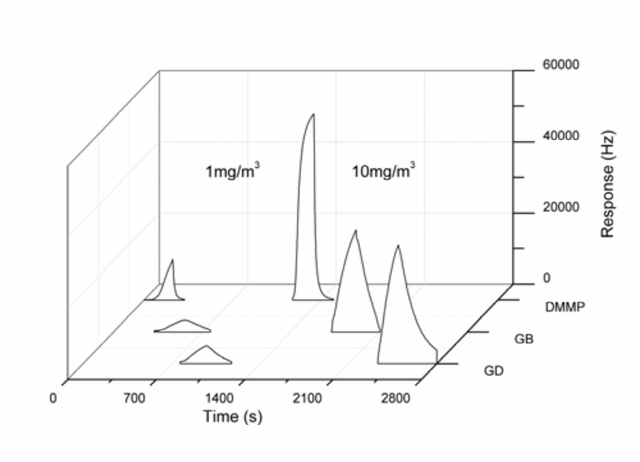

Fig. 4 Responses of the sensor to GB, GD and DMMP at 1 mg/m^3 and 10 mg/m^3

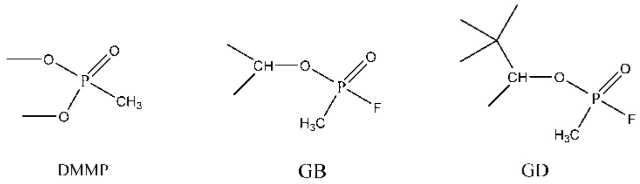

Fig. 5 Molecular structures of the analytes

A linear fitting was obtained with a slope of 2801 Hz/mg·m^{-3} and a correlation coefficient R^2 of 0.99969.

Response of the sensor to GD in the range of 0.5 to 10 mg/m^3 is shown in Fig. 3c. The curve exhibited a similar tendency as to GB vapor. The response of the sensor reached a value of 2.7 kHz to GD vapor at 0.5 mg/m^3, and response of 32.3 kHz was recorded to the highest tested concentration of 10 mg/m^3. Unlike the response to GB, the sensor had a parabolic calibration curve to GD, as showed in the inset of Fig. 3c.

To make a comparison of the DKAP SAW sensor responded to GB, GD and DMMP, a vivid curve was obtained at the concentration of 1 mg/m^3 and 10 mg/m^3, shown in Fig. 4. It was obviously that the response of the sensor to the simulant was higher and faster than to the real agents, indicating a better diffusion of DMMP into the polymer than those of GB and GD. To make a possible explanation, it is possible to give some hypothesis from the differences of their molecular structures. As shown in Fig. 5, the two groups –OCH$_3$ in DMMP were replaced by the group –O–C$_3$H$_7$ and a fluorine atom for GB, and replaced by the group –O–C$_6$H$_{13}$ and a fluorine atom for GD. Thus, the GB and GD molecules occupied larger volumes than the DMMP molecule and were consequently harder to diffuse into the sorptive coating. As a result, much slower sorption processes of the sensor to GB and GD than to DMMP were present. Furthermore, compared with the group –OCH$_3$ bonded to phosphorus atom in DMMP, the fluorine atom in GB and GD molecules showed stronger electron-withdrawing ability. This made the real agents more active and exhibited stronger hydrogen-bond basicity than DMMP, which led to much slower desorption processes of the sensor toward G series agents than to the simulant.

The sensitive property of DKAP to DMMP was also investigated by Lee et al[10] using a capacitive micromachined ultrasonic transducer (CMUT). In principle, CMUT was an array of electrostatically actuated resonators working at several tens of MHz, all electrically connected in parallel and individually backed with a vacuum-sealed cavity. At DMMP concentrations ranging from 1 ppm down to 10 ppb (0.05-5 mg/cm^3), the DKAP coated CMUT sensor showed an average response time T_{90} of 117 s, which was in good agreement with our result, reflecting the kinetic response nature of the DKAP polymer which was independent on the sensor platform. Roukes et al[25] drop-coated DKAP polymer on a NEMS cantilever and mounted the sensor at the downstream of a miniaturized gas chromatography (GC) system. The polymer based detector could separate 8 analytes (primarily the organophosphates) within a 5 s time window, presenting sharp peaks which were comparable to a FID detector. For the narrowest peak, the 90% recovery time was <40 ms, indicating ultrafast desorption process could occur when the DKAP coating was far from saturation during exposing to the short duration of the GC eluted analytes. However, the sensing performance of DKAP to the real nerve agents, to the authors' knowledge, was not reported before in the literature. We found a much slower sorption and desorption behavior of this polymer to GB and GD as a comparison to DMMP. The unexpected result indicated that the sensitive property of the sensor towards the real agents could not fully predict by a simulant.

Except DKAP, the sensing properties of other HBA polymers toward the real nerve agents were seldom reported in the previous papers, let along the kinetic response, which was the most concern of this paper. In these very few reports, the GLP coated ~ 115 MHz Love wave devices were tested in details to GB as well as DMMP vapor by a French group[20]. The real time responses of the sensor to 0.5-5 ppm GB revealed that the frequency shifts increased with exposure time gradually rose linearly at the initial 4-8 min and reached 80% full responses at 20-25 min. Thus, a good agreement with our DKAP sensor was demonstrated. However, the response time of the GLP sensor to DMMP was even longer with respect to the response time to GB by a factor of 2, which was in contradiction with our result but the authors did not gave an explanation for this phenomenon. The same team also investigated the response details of FPOL SAW sensor to GB in the concentration range of 0.5-10 ppm[26]. They found the response time was significantly affected by the temperature. At a temperature below the T_g (30 ^{o}C), the 90% response time was 40 min for a 1 ppm GD; while at a temperature above the T_g (40 ^{o}C), the response time dramatically decreased to about 6 min. Our DKAP sensor was tested at a much lower temperature of 20 ^{o}C, that's the main reason we believed, according to the previous report, why the DKAP sensor responded to GB slowly. To achieve fast response, the sensor would need to test under an elevated temperature by an integrated heater, which is part of our future work.

The reproducibility of the sensor was investigated to GB and GD vapor of 1 mg/m^3. As can be seen in Fig. 6, the four exposure cycles for each agent exhibited very similar curves, indicating the consistency and reliability of the tested results and good reproducibility of the sensor. It was also clearly that the sensor was 1.6-fold higher sensitive to GD than to GB. For GB vapor, an average baseline shift of < 50 Hz/min was observed, while the response of the sensor was 900 Hz/min in average,which was more than 18 times larger. As for GD vapor, the baseline shift of the sensor was much smaller and could be negligible as shown in Fig. 6.

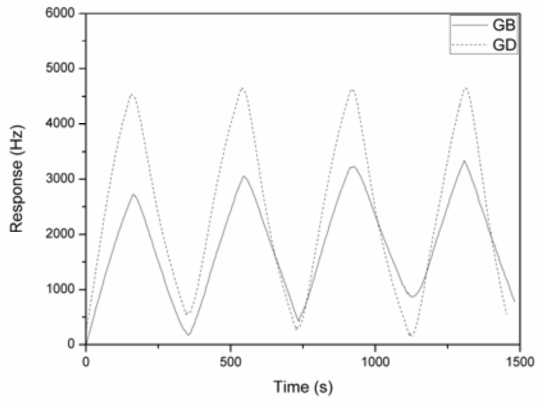

Fig. 6 Reproducibility of the sensor for GB and GD detected at 1 mg/m^3

4 Conclusion

In the past, DMMP was widely used as simulant for nerve agents detection. In this paper we verified, however, that the sensitive performance of a sensing material to the real agents could not fully predict by a simulant and a considerable difference might occur. The sorbent we investigated was a HBA polymer, DKAP, which was spray-coated on a 434 MHz SAW device. The corresponding sensor showed much higher and faster response towards the simulant DMMP than to GB and GD. We believed that the slow response of the polymer interacted with the real agents was induced by the size effect, while the slow desorption process was attributed to the strong hydrogen bond. The sensitive characteristics of DKAP were compared with that of other HBA polymers, wherein high agreement was demonstrated.

Acknowledgements

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Notes and references

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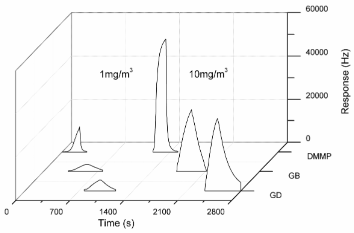

Fig. 4 Responses of the DKAP coated SAW sensor to GB, GD and DMMP at 1 mg/m^3 and 10 mg/m^3