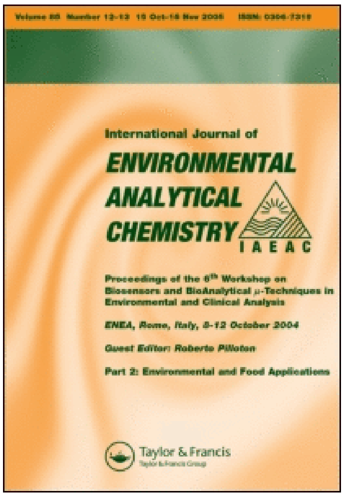

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Fung, Y. S. and Wong, Y. Y.(2000) 'Development of a Piezoelectric Crystal Sorption Detector for Monitoring of Total Organic Compounds in Air', International Journal of Environmental Analytical Chemistry, 78: 3, 397 — 412

To link to this Article: DOI: 10.1080/03067310008041356

URL: http://dx.doi.org/10.1080/03067310008041356

Intern. J. Environ. Anal. Chem., Vol. 78(3-4), pp. 397-412
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DEVELOPMENT OF A PIEZOELECTRIC CRYSTAL SORPTION DETECTOR FOR MONITORING OF TOTAL ORGANIC COMPOUNDS IN AIR

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(Received 16 November 1999; In final form 19 May 2000)

A light and portable organic vapours monitor has been developed using piezoelectric (P/Z) quartz crystal to determine Volatile Organic Compounds (VOCs) commonly found in workplace air. Out of the eight coating material studied, High Vacuum Grease (HVG) was found to be the best for determining commonly encountered organic vapours such as 1,1,1-Trichloroethane, Chloroform, Benzene and Toluene in room air. The optimised coating weight was 23 μg HVG at a flow rate of 200 mL/min. Moisture was found to interfere and the use of a Nafion gas dryer was found to reduce the relative humidity to a constant 37 % for room air with 43 – 81 % relative humidity. Under optimised conditions, a mean sensitivity of 1.9×10^{-2} Hz/ppm was obtained for total VOCs with 17.2% RSD variation towards different VOCs. Excellent linear working ranges were obtained from 40 to 2400 ppm (v/v), with response time and recovery time within one minute up to 500 ppm (v/v) of analyte. High and relatively constant response factors were obtained for different VOCs. The reliability of the method has been established by parallel method comparison using established GC-FID method. The P/Z detector developed could also be used to monitor individual VOCs.

Keywords: Portable organic vapour monitor; piezoelectric quartz crystal detector; volatile organic compounds; moisture interference

INTRODUCTION

Due to the increasing use of volatile aromatic and halogenated organic compounds as solvent, degreaser and thinner in paints, lacquers, adhesives and cleaners at home and for industrial uses[1] and many of these compounds have been identified as toxic substances and suspected carcinogens[2], it has generated a Volatile Organic Compounds (VOCs) problem that requires frequent monitoring

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at workplace for health protection and at offices/home for assessing indoor air quality. As VOCs are often present in air at ppm level and the results are needed urgently, the analytical methods required must be sensitive, portable and capable of giving results immediately at the monitoring site.

Many existing instrumental methods such as GC [3,4] are not suitable for field monitoring and those available for field monitoring such as Dräger tubes [5] are operated in a batch mode with monitoring of a single organic compound at a time. A sensitive and portable detector capable of continuous determination of multiple VOCs at ppm levels is needed for monitoring workplace air for health protection and for assessment of indoor air quality, an issue of increasing world-wide concern in many urban cities.

A coated piezoelectric quartz crystal (P/Z crystal) sorption detector has been developed to provide a sensitive detector for VOCs analysis.[6–11] The detector is light-weighed, sensitive, simple to operate, requiring low power and hence supported by battery and portable for field use. The operation of the detector is based on the principle that the oscillating frequency of the P/Z crystal is decreased by the absorption of a foreign material on its surface. Application of the frequency-to-mass relationship of P/Z crystal was first employed by Sauerbrey in 1959. [12–15] For AT-cut P/Z crystal vibrating in the fundamental thickness shear mode, the resonant frequency can be expressed as:

$$F_o = V_{tr}/2t \tag{1}$$

where F_0 is the resonant frequency; V_{tr} is the velocity of propagation of a traverse wave in the plane of the crystal and t is the thickness of the crystal. A relationship of thickness and mass is:

$$t = M/A\rho \tag{2}$$

where M, A and ρ are the mass, surface area and density of the crystal respectively. From Eq. (1) and (2), it indicates that the resonant frequency is inversely proportional to the mass of the crystal and an expression for the change in frequency when the thickness is increased by a differential amount is obtained as:

$$\Delta F/F_o = \Delta t/t = -\Delta M/tA\rho \tag{3}$$

The negative sign indicates that an increase in the mass of the quartz crystal causes a decrease in its oscillating frequency. For pure shear-mode vibrations in air or vacuum, the strains are all zero at the principal faces. Sauerbrey assumed that of the plate was divided into an infinite number of parallel planes along the plate surface. Only those planes close to the surface would affect the frequency through their mass and not through their elastic character. Thus, the frequency change resulting from the deposition of a thin, uniform film of any foreign sub-

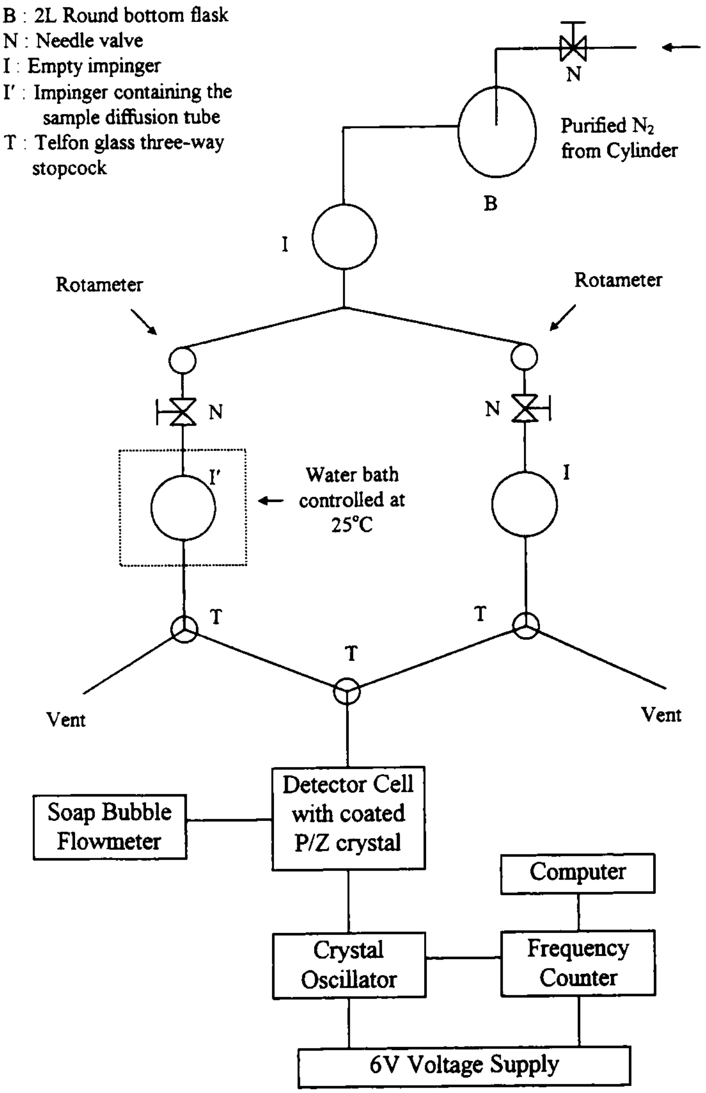

FIGURE 1 A schematic diagram of the flow system with the P/Z crystal detector for testing coating materials

stance is equivalent to that of a layer of quartz crystal itself and the frequency change obtained from Eq. (3) becomes:

$$\Delta F/F_o = -\Delta M_s/tA\rho \qquad (4)$$

where ΔM_s is the mass of film of any substances coated on the crystal surface. Substituting Eq. (1) into Eq. (4), the expression is:

$$\Delta F/F_o = -\Delta M_s/A\rho(2F_o/V_{tr}) \qquad (5)$$

For a AT-cut quartz crystal, with $\rho = 2650$ kg/m^3 and $V_{tr} = 3340$ m/s, and substituting values into Eq. (5), the Sauerbrey's equation is obtained:

$$\Delta F = -2.3 \times 10^6 F_o{}^2 \Delta M_s/A \qquad (6)$$

where ΔF is the change in frequency due to the addition of coating (Hz); F_o is the oscillating resonant frequency of the P/Z crystal (MHz); ΔM_s is the mass of coating adsorbed (g) and A is the area coated (cm^2). The factor 2.3×10^{-6} is an inherent constant for the quartz crystal due to the density and velocity of propagation of the traverse wave in the plane of the crystal and it is useful to calculate the sensitivity of the quartz crystal towards the intended analyte. The Sauerbrey's equation describes quantitatively the relationship between the frequency shift and the mass change on the crystal, and it predicts that a commercially available 10 MHz P/Z crystal would have a mass sensitivity of about 10^{-9} g/cm^2 for 1 Hz frequency shift. Using an appropriate coating material on the crystal surface to adsorb the organic gaseous pollutant, the concentration of the organic vapours can be determined quantitatively.[16–26]However, most of the work done in the development of P/Z crystal sorption detector is focussing on the monitoring of a single organic compound, which is suitable for industrial monitoring. For assessing indoor air quality, providing results for clearance of enclosed spaces after spillage of organic solvents, and for screening and identifying hot spots with potential health problems due to VOCs, a portable monitor or sensor capable of determining total volatile organic compounds is needed.

In this paper, the development of a total organic vapour monitor for determining ppm levels of VOCs in air based on piezoelectric crystal sorption detection will be given. The selection of coating materials, the development and optimization of the VOCs sensor towards different types of organic vapours, the effect of interference and the performance of the VOCs sensor developed will be described and discussed.

METHODS AND PROCEDURES

Reagents and coating material

The coating materials used consisted of eight gas-liquid chromatography coatings: Squalane and Silicone 550 (E. Merck Darmstadt, Germany); DC High Vacuum Grease (HVG) (Dow Corning Corp., Midland, MI); Apiezon Grease L (AG) (GEC Alsthom Ltd., Manchester England); Poly(ethylene glycol) 400 and 1000 (PEG 400 & PEG 1000) (Aldrich); Carbowax 20M (Aldrich); Dioctyl Phthalate (Aldrich). All organic chemicals used were analytical reagent grade (except 1,1,1-trichloroethane at GPR grade) and were used as received.

Equipment and apparatus

The P/Z crystals used were AT-cut 10 MHz quartz crystals with about 1.2 cm diameter, 0.5 mm thickness and silver-plated on both faces of the electrodes (C&Y Trading Co., Ltd., Hong Kong). The instrumentation consisted of a laboratory built electronic oscillator circuit, a 6V dc regulated power supply and a frequency counter (Model 8220R Universal Counter) with accuracy ± 1 Hz. The frequency signal was acquired from the oscillator circuit by a PC via a RS-232 cable and was monitored as a function of time.

The evaluation of different coatings was done in the laboratory using nitrogen as carrier gas. The flow system as shown in Figure 1 was used. The flow rate of nitrogen was controlled and measured by a rotameter (Model FL-3802SA-HRV, Omega Engineering, Inc. Stamford, CT 06907) calibrated by a soap bubble flowmeter. For studying the performance of the quartz crystal detector for analysing VOCs in the field, the flow system as shown in Figure 2 was used. Air was drawn at 0–0.5 L/min by a pump (Model GS-III, Shanghai, China). Hydrocarbon-free air was generated by passing the air through activated charcoal tubes and the moisture interference in air was reduced by passing through a Nafion gas dryer (95 mm × 60 mm × 25 mm, up to 500 mL/min) containing about 60 g 13X molecular sieve as the desiccant prior to detection. In the validation study, the GC (Hewlett Packard 5890) was equipped with a flame ionization detector and an integrator (Hewlett Packard 3395) for data acquisition and plotting of the chromatogram. Helium at 145 mL/min was used as the carrier gas and the oven temperature was maintained at 70°C.

Analytical procedure

Coating materials were dissolved in suitable solvents and the solution was applied onto the entire surface of the electrode on both sides of the P/Z crystal using a microsyringe. The crystal was then placed in an oven at about 50°C for several hours to evaporate the solvent. An atmosphere of known relative humidity was generated by passing the carrier gas through an impinger containing saturated inorganic salt solutions and the relative humidity of the gaseous stream was

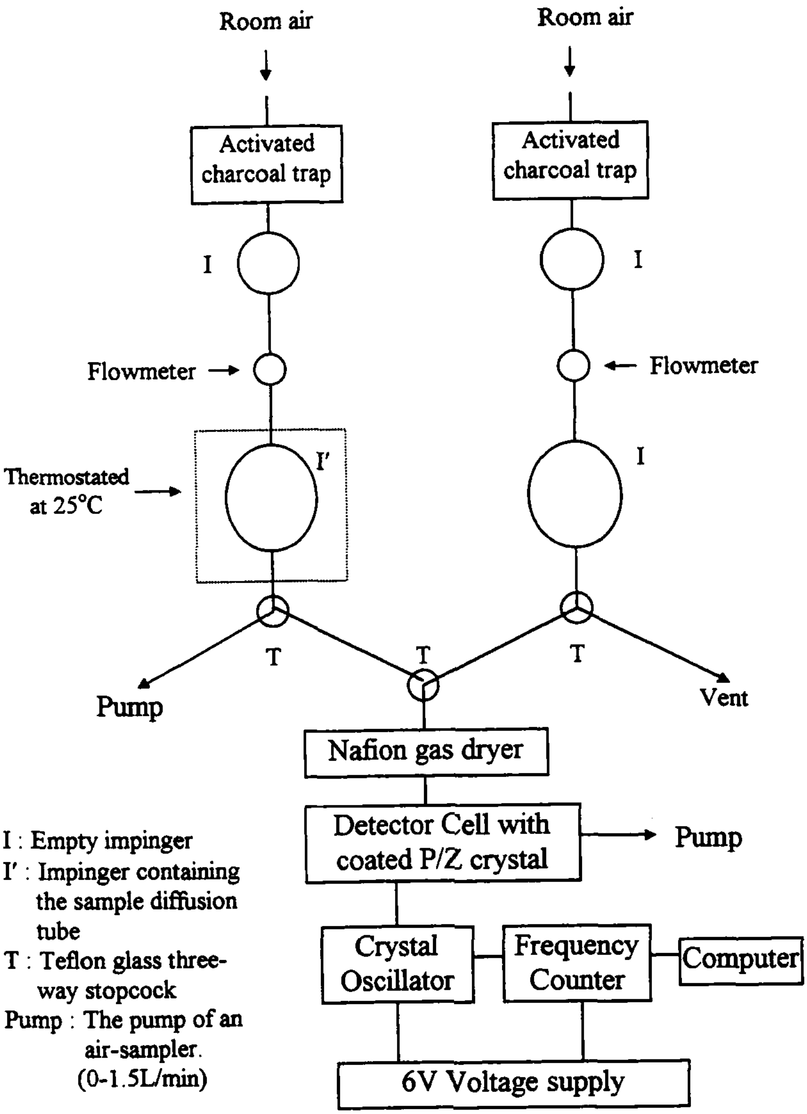

FIGURE 2 A schematic diagram of the flow system with the P/Z crystal sorption detector for analysing VOCs in room air

measured by a hygrometer placed in an enclosed chamber. For studying the sensitivities of the coated crystals, the sample gas was generated continuously by a diffusion tube placed inside an impinger (500 mL) immersed in a water bath at 25°C. The organic solvent reservoir in the tube was swept by nitrogen (40 % relative humidity and 260 mL/min flow rate) as given in Figure 1. For investigation of the applicability of the P/Z crystal detector for analysing VOCs in room air, the flow system is shown in Figure 2. Room air (65 % relative humidity) was used as the carrier gas and the P/Z detector was calibrated by VOCs generated by diffusion tubes onsite. The concentration of the vapour generated was adjusted by using different diameter and length of a glass capillary inserted at the diffusion tube. The VOCs concentration were calculated based on the gas flow rate and the weight loss over the experimental period. After at least two hours for stabilization, the vapour generated was introduced to the VOCs sensor in a steady state. The frequency of the oscillation was recorded and the difference in frequency between the baseline and the absorption equilibrium was taken as the analytical response.

RESULTS AND DISCUSSION

Testing of coating materials

In search for suitable coating material for total VOCs monitoring, the following eight gas-liquid chromatography coatings were selected based on their known interaction with different types of organic vapours: Squalane and Silicone 550, DC High Vacuum Grease (HVG), Apiezon Grease L (AG), Poly(ethylene glycol) 400 and 1000 (PEG 400 & PEG 1000), Carbowax 20M and dioctyl phthalate. For testing the interaction of VOCs with the selected coating materials, the following four organic compounds were selected: 1,1,1-trichloroethane, chloroform, toluene and benzene as they are differed in polarities and functional groups, readily availability and found in ambient air and workplaces atmosphere, with known toxicity for aromatic and halogenated vapours, and they are often monitored onsite for assessing ventilation system, occupational health and indoor air quality for the protection of workers in an enclosed environment. The experimental flow system for testing the interaction between coating material and VOCs is shown in Figure 1. Nitrogen was used as the carrier gas. At the detector cell, the carrier gas was split into two equal streams with each passing through a 3 mm diameter hole before direct contact with both sides of the coated electrodes in order to enhance the sensitivity of the detector.

The results showing the sensitivity of the coated P/Z crystals after exposure to various organic vapours at 150 ppm (v/v), which is the medium concentration of the Threshold Limit Value of many VOCs, are given in Figure 3. From Table I, the mean value is the mean sensitivity of each coating material to the four selected VOCs and the variability for different VOCs is the relative standard deviation of sensitivity of each coating materials to these four VOCs which represent the response uniformity to the VOCs investigated. To monitor total VOCs, the coatings should give non-selective and sensitive response to various organic vapours and show low drifting in baseline, as the bleeding of coating material could shorten the detector lifetime. For the response towards individual VOCs, PEG 1000 was found to give the best uniform response (Figure 3). However, the mean of its sensitivity to these four selected VOCs is much lower compared to other coating materials (Table I). Both Silicon 550 and Squalane gave very high sensitivity, but suffered from high bleeding rate and non-uniform responses. For AG, HVG and Dioctyl Phthalate, they show high sensitivity and acceptable uniform response towards different VOCs. However, the bleeding rates for AG and Dioctyl phthalate are much higher as compared to HVG. Thus, HVG was selected for detailed investigation and optimisation.

TABLE I The overall sensitivity of different coating materials to various VOCs using N_2 as the carrier gas. Temperature: 22°C; Flow rate of N_2: 260 ml/min; Relative humidity: 40%

Coatings	*Bleeding rate (Hz/min)*	*Sensitivity*		*Variability[a] for different VOCs (%)*
		Mean[b]	*SD*	
		(Hz/ppm/μg × 10–4)		
(1) AG	0.3	18.9	14.3	75.7
(2) HVG	0.1	23.5	14.9	63.4
(3) Silicone 550	1.5	24.4	19.1	78.3
(4) Squalane	0.7	21.5	21.2	98.6
(5) PEG 400	0.5	14.7	7.5	51.0
(6) PEG 1000	0.3	6.0	3.3	55.0
(7) Dioctyl Phthalate	0.7 (<10μg) 3.3 (>20μg)	22.1	13.0	58.9
(8) Carbowax	20M 0.3	5.2	3.6	69.2

a. Variability for different VOCs is the relative standard deviation of the sensitivity of each coating materials to four selected VOCs.

b. Mean of sensitivity is the arithmetic mean value of each coating materials for four selected VOCs including Toluene, Benzene, Chloroform and 1,1,1-Trichloroethane.

Optimization study

To optimise the response of the P/Z crystal detector, 1,1,1-trichloroethane was used for testing, as its sensitivity is in the middle of the VOCs investigated. The effect of different amounts of HVG to 150 ppm (v/v) 1,1,1-trichloroethane under

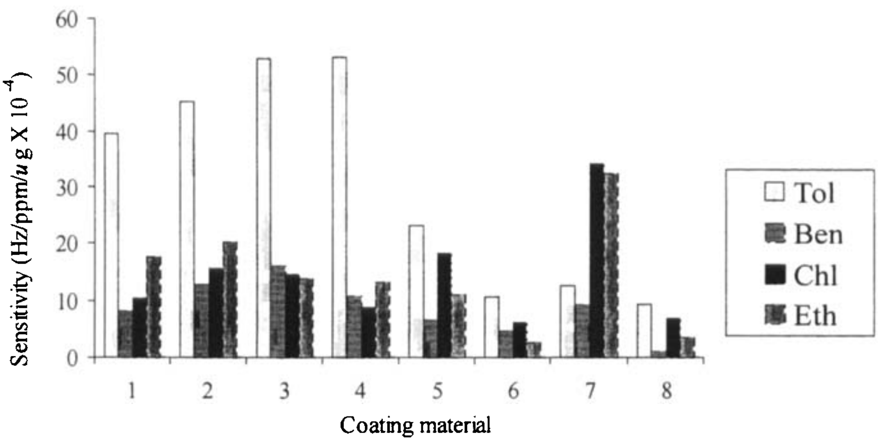

FIGURE 3 The sensitivity of the coating material to individual VOCs using N_2 as the carrier gas. Temperature: 22°C; Flow rate of N_2: 260 ml/min; Relative humidity: 40 %. Note: Same coating material and VOCs are used as described in Table I.

nitrogen was shown in Figure 4. The change in frequency was found to increase with the coating weight and 23 μg HVG was found to give the optimum results. For very high coating mass, it will lead to overloading of the crystal, leading to ceasing of oscillation. For low coating mass, it will give a poor sensitivity due to the low concentration of active sites at the coating surface. The increase of coating will lead to an increased response as the coverage of the surface of the crystal by the coating material is increased until a complete coverage at 23 μg HVG, above which, the response goes to a plateau region (Figure 4) with a variation of ± 1 Hz, as the increase in coating mass does not increase the active sites at the surface of the coating material.

Figure 5 showed the effect of gas flow rate on the sensitivity of HVG coated P/Z crystal at 250 ppm (v/v) 1,1,1-trichloroethane under room air in the flow system described in Figure 2. From the principle of the piezoelectric sorption detector for determining a particular analyte with a selective coating material in gas phase derived by Janghorbani and Freund [27], the frequency response increase with decrease in the flow rate of the carrier gas. It predicts a higher response was obtained using a lower gas flow rate, as the contact time between the analyte and coating would be longer at a lower gas flow rate. From flow rate ranging between 100 and 500 mL/min, the optimum flow rate was found to be at 200 mL/min. The reason for the decrease in response at flow rate less than 200 mL/min may due to the adsorption loss along the flow line at low gas flow rate.

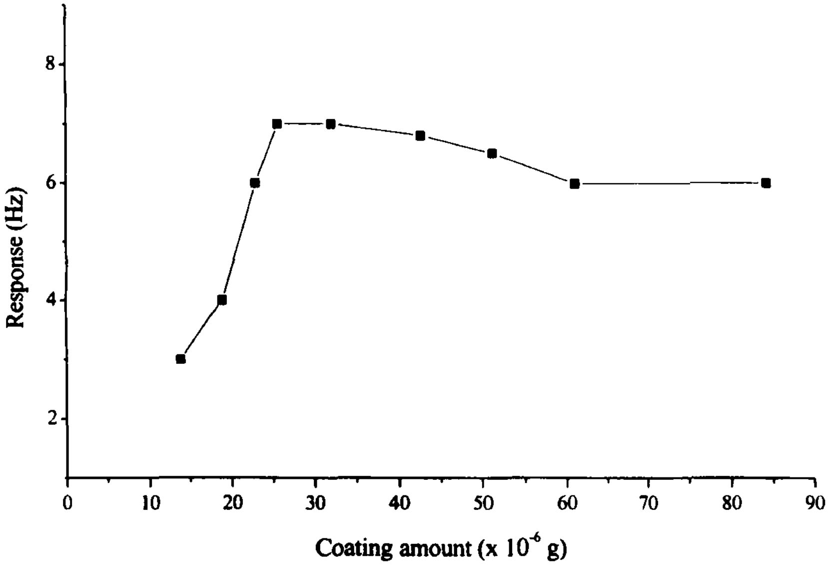

FIGURE 4 The effect of different amount of coating material on the response of HVG coated P/Z crystal at 150 ppm 1,1,1-Trichloroethane using N_2 as the carrier gas. Temperature: 22°C; Relative humidity: 40 %; Flow rate of N_2 : 260 ml/min

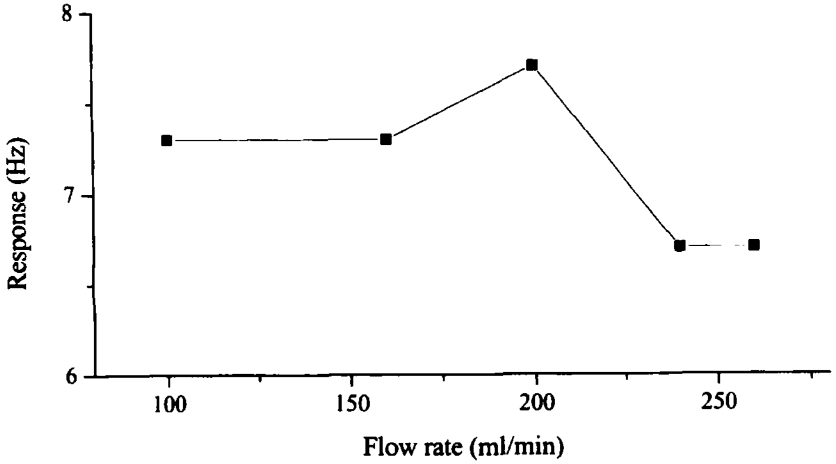

FIGURE 5 The effect of gas flow rate on the response of HVG coated P/Z crystal at 250 ppm 1,1,1-Trichloroethane

Interference study

As the occurrence of high humidity in indoor air interfered with the response of the P/Z crystal due to the competition of water molecules for the adsorption site on the coating, the water vapour in the room air sampled must be reduced to an acceptable level. A Nafion dryer tube was used to control the relative humidity of air with different moisture contents.

Gases with different relative humidity were generated by passing the carrier gas through impingers containing different inorganic salt solutions at controlled temperatures. Gases with relative humidity ranging from 43 to 81 % were generated to test the efficiency of the Nafion gas dryer under 8 hours continuous operation. The results were shown in Table II. A constant relative humidity at 37 % was found to maintain for room air after 8 hours continuous operation without the need to replace the desiccant when the relative humidity at the air inlet was varied between 43 % and 81 %. Thus, the interference effect of moisture on the P/Z crystal detector could be reduced with the use of the Nafion gas dryer, as a constant relative humidity was maintained.

TABLE II The effect of the Nafion Dryer Tube on the relative humidity of air with different moisture content. Temperature: 25°C; Flow rate of the pump: 200 ml/min

Salt	*Temperature (°C)*	*Relative humidity (%)*	
		before Dryer	*after Dryer*
$K_2CO_3 \cdot 2H_2O$	24.5	43	37
$Ca(NO_3)_2 \cdot 4H_2O$	24.5	51	37
NH_4Cl	25	79	37
$(NH_4)_2\,SO_4$	25	81	37

The effect of moisture on the response of the HVG coated P/Z crystal to 1,1,1-Trichloroethane was shown in Table III. Under low VOC concentration and high relative humidity, the response of the P/Z crystal was mostly affected by moisture. 100 ppm (v/v) 1,1,1-trichloroethane could only be detected after reducing the humidity from 65 % to 37 % with the use of the Nafion gas dryer. Under different constant levels of relative humidity (65 % vs 37 %), the response of the P/Z crystal detector was found to increase with increasing concentration of 1,1,1-trichloroethane. However, at the same concentration of VOC, a better repeatability and a higher responses were obtained at lower moisture content. Thus, the use of the Nafion gas dryer was found to improve the performance of the P/Z crystal detector for VOC monitoring.

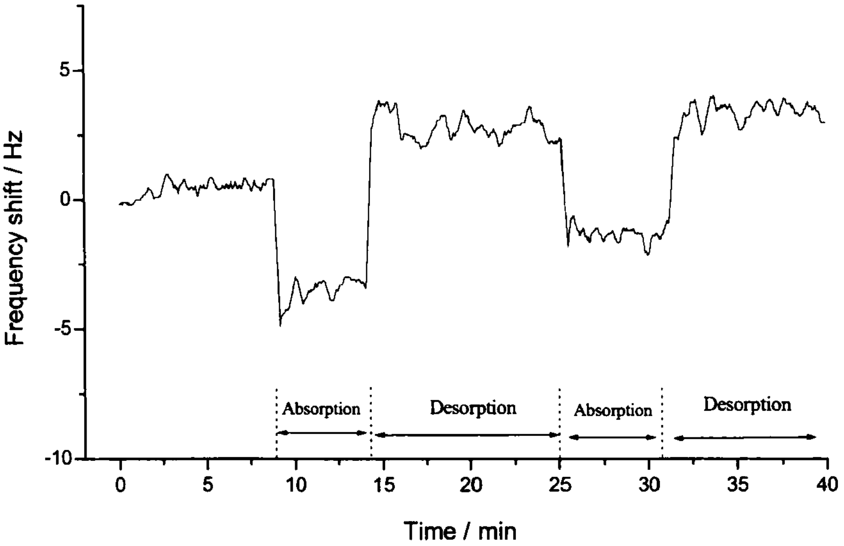

FIGURE 6 Frequency changes of the VOCs sensor as a function of time upon interaction with 150 ppm (v/v) 1,1,1-Trichloroethane

TABLE III The effect of moisture on the response of the HVG coated P/Z crystal. Temperature: 22°C; Relative humidity of room air: 65%; Flow rate of the pump: 200 ml/min; n = 3

	Response of P/Z crystal detector			
1,1,1-Trichloroethane (ppm v/v)	*with dryer*		*without dryer*	
	Mean (Hz)	*RSD (%)*	*Mean (Hz)*	*RSD (%)*
100	3	17.5	0	
200	5	10.9	2	34.0
300	8	7.5	4	13.5
500	11	5.4	10	6.0
700	12	4.9	10	6.0
1000	21	2.9	18	3.3

Analytical performance of P/Z crystal detector

The analytical performance of the P/Z crystal detector for monitoring total VOCs is shown in Table IV. It is suitable for concentrations in the ppm range and gives satisfactory response and recovery time with reasonable variability in response for different VOCs (RSD = 17.2 %). The P/Z crystal detector could also be used to monitor individual VOCs if they are known to be present in air. A plot of frequency response of the detector towards 150 ppm (v/v) 1,1,1-trichloroethane against time is given in Figure 6. When using a Nafion gas dryer, the detector showed good stability and repeatability with short response and recovery times. The analytical performance of the detector for the determination of 1,1, 1-trichloroethane, chloroform, toluene and benzene is shown in Table V. The linear working ranges were found to vary from 40 to 2400 ppm (v/v) for different VOCs and a typical calibration curve is shown in Figure 7. The response time and recovery times were found to be within one minute up to an analyte concentration of 500 ppm (v/v). High and relatively constant response factors were obtained for different VOCs. No observable change in the sensitivity was recorded after two weeks of continuous operation.

TABLE IV The analytical performance of the P/Z crystal detector for monitoring Total Volatile Organic Compounds

1. Working range (ppm v/v)	40 – 2400
2. Response time (s)	10 – 60
3. Recovery time (s)	20 – 50
4. Sensitivity	
Mean[a] = 1.9×10^{-2} Hz/ppm	
RSD[b] = 17.2 %	

a. n = 4
b. Variability amongst different VOCs

TABLE V The analytical performance of the P/Z crystal sorption detector for individual VOCs

	Tol	*Ben*	*Chl*	*Eth*
(1) Working range				
lower (ppm)	40	75	120	100
upper (ppm)	350	930	2400	1000
Correlation coefficient	0.99350	0.99862	0.99896	0.99497
(2) Response time / Recovery time (s) at				
– 100ppm	10/20	10/30	10/20	20/30
– 500ppm	60/50	10/40	10/30	20/50
(3) Sensitivity (Hz/ppm × 10^{-2})	2.5	1.7	1.7	1.8

Tol = Toluene, Ben = Benzene, Chl = Chloroform, Eth = 1,1,1-Trichloroethane

To ascertain the reliability of the sensor developed, a field study was carried out for determining toluene in a class room after recent painting work. Parallel method comparison was carried out using the established GC-FID method for determining unknown concentrations of toluene generated and sampled by the P/Z crystal detector. From Figure 8, it can be seen that both methods produce comparable results for toluene within the concentration range from 25 to 180 ppm (v/v) with a correlation coefficient between the two methods equal to 0.9919 and a slope close to 1.

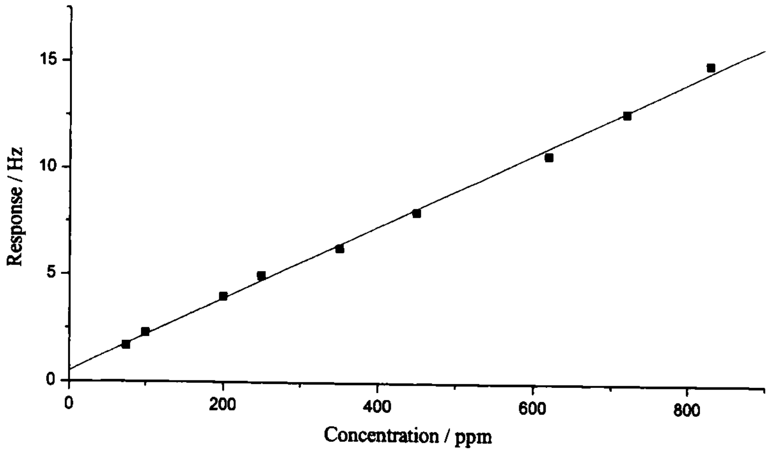

FIGURE 7 Relationship between the frequency response of the HVG coated P/Z crystal detector and the concentration of Benzene.(n=3)

CONCLUSIONS

Amongst the 8 coating materials studied, HVG was found to be the best coating material for P/Z crystal detector for monitoring total volatile organic vapours in air. The optimised coating weight was found to be 23 μg HVG at a flow rate of 200 mL/min. Moisture was found to interfere with VOC determination, particularly at the lower concentrations. The use of a Nafion gas dryer was found to reduce the relative humidity to a constant 37 % for incoming air with relative humidity ranging from 43 % to 81 %. Under optimised conditions, the P/Z crystal detector was found to give a mean sensitivity of 1.9×10^{-2} Hz/ppm for total VOCs with 17.2 % RSD variation towards different VOCs. The linear working ranges were found to vary from 40 to 2400 ppm (v/v) with excellent linearity. The response time and recovery time were found to be within one minute up to

500 ppm (v/v) of analyte. High and relatively constant response factors were obtained for different VOCs. No observable change in the sensitivity was recorded after two weeks of continuous operation. The reliability of the method was established by comparison with the established GC-FID method for the determination of toluene concentrations ranging from 25 to 180 ppm (v/v). The P/Z detector developed could potentially be used to monitor individual VOCs such as 1,1,1-trichloroethane, chloroform, toluene and benzene if they are known to occur alone. In summary, the P/Z crystal detector developed was shown to provide a sensitive, light-weighed and portable monitor suitable for the analysing of VOCs in industrial air and indoor environment.

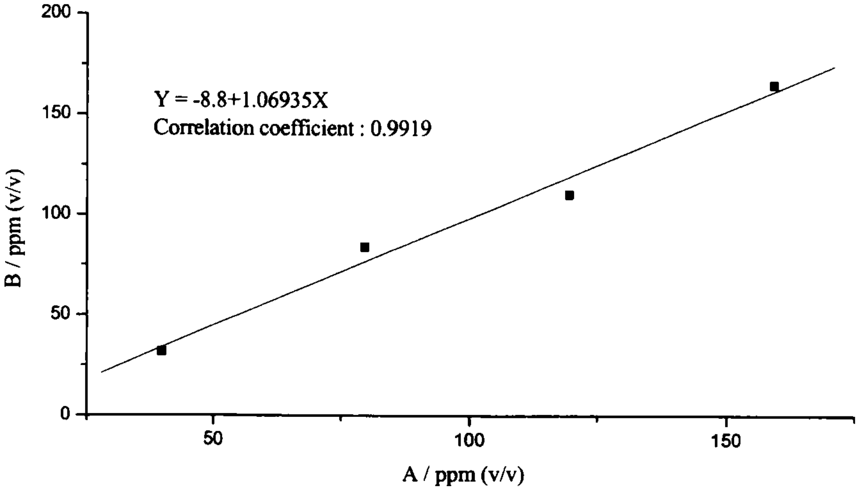

FIGURE 8 Comparsion of the results of using HVG coated P/Z crystal detector (A) and GC-FID detection (B) with Toluene as analyte

Acknowledgements

The authors would like to acknowledge the financial support from the Hong Kong University Committee on Research and Conference Grants and the Research Grants Council of the Hong Kong Special Administrative Regions, China (HKU 496/96P) on the above project.

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