Determination of Volatile Chloroorganic Compounds Using Quartz Crystal Microbalance

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Introduction

In recent years, a large amount of chloroorganic compound, such as trichloroethylene (TCE) and tetrachloroethylene (PCE) have been used. These compounds have caused severe contamination in groundwater. In addition, the contamination of surface water in wide aria and air pollution becomes serious problems. To prevent such pollution rapid and on-site monitoring method for these compounds is strongly needed.

Usually, these compounds are determined by gas chromatography with an electron capture detector (GC-ECD), but its operation needs skillful technique and long time per one measurement. On the other hand, detector tube method is simple and easy but the sensitivity is not enough. With either method, a portion of sample solution must be taken from a monitoring point, and therefore, an on-line continuous monitoring is impossible.

We have investigated the continuous monitoring method using the lipid coated Quartz Crystal Microbalance (QCM) type gas sensing system.

The QCM has for long time been used as an *in-situ* high sensitive weighing device. It consists of a thin disk of single-crystal quartz, with a deposited metal (gold) electrode on each side. The principle of operation as an *in-situ* microbalance is that mass adsorbed on or desorbed from the surface of electrode(s) induces a frequency shift, Δf, related to the mass change, Δm.

In this study, specific adsorptions of volatile chloroorganics on a synthetic lipid film were detected by observing frequency changes of a lipid coated QCM.

Material and Method

Synthetic lipids, purchased from Sogo Pharmaceutical, used without further purification. The molecular structures were shown in Fig. 1. These lipids, dissolved in dichloromethane, were cast on a gold electrode of the QCM and then dried in air for immobilization. Standard gases of TCE, PCE and 1,2-dichloroethane (DCE) at approximately 1000 ppm (calibrated) were purchased from Takachiho (Tokyo). Other standard gases were prepared by a gas generator PD-1B (Gastec, Yokohama) utilizing the diffusion tube method.

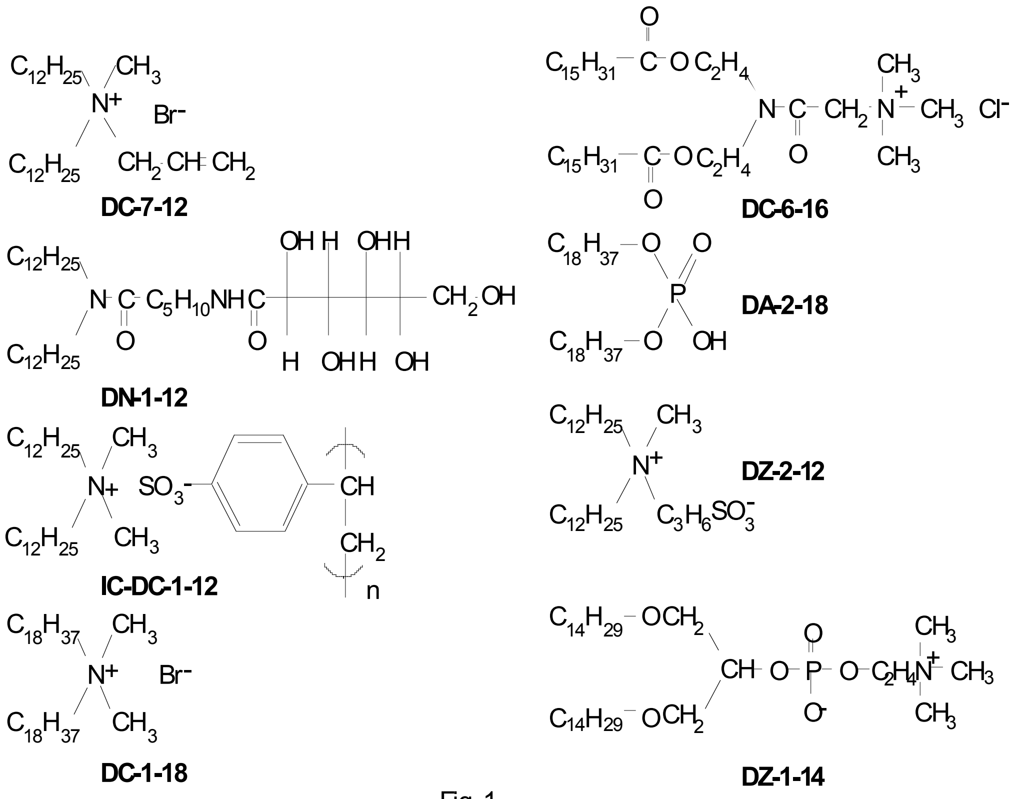

Fig. 1

A schematic diagram of the QCM sensing system is shown in Fig. 2. A sensor unit, which consists of four quartz crystal probes and a flow cell, was purchased from Sogo Pharmaceutical Co., Tokyo. It was placed in a temperature control chamber SU-220 (Tabai Espec, Osaka). The frequency of QCM was measured by a frequency measurement device SF-105 (Sogo Pharmaceutical). The data were recorded and converted into ASCII format with Oscillographic Recorder OR100 (Yokogawa, Tokyo), and then transferred to a microcomputer system for further processing. The concentration and the flow rate of the standard gases were independently controlled by changing the mixing ratio of standard gases and nitrogen gas using mass flow controllers. Nitrogen was used as a blank gas. AT-cut type crystal units were purchased from Kinseki (Tokyo). The diameter was 5 mm and the basic frequency was 9 MHz. Calibration of the QCM used in this system showed that a frequency change of -1 Hz corresponds to a mass increase of about 1 ng (9 MHz, AT-cut).

Results and Discussion

Adsorption of volatile chloroorganics

Fig. 3 shows the frequency change of the different type of synthetic lipid film coated QCMs responding to trichloroethylene (TCE). The frequency were shift down in the case of DC-7-12, DN-1-12 and IC-DC-1-12, but in other lipids, the shift down were less than 100 Hz.

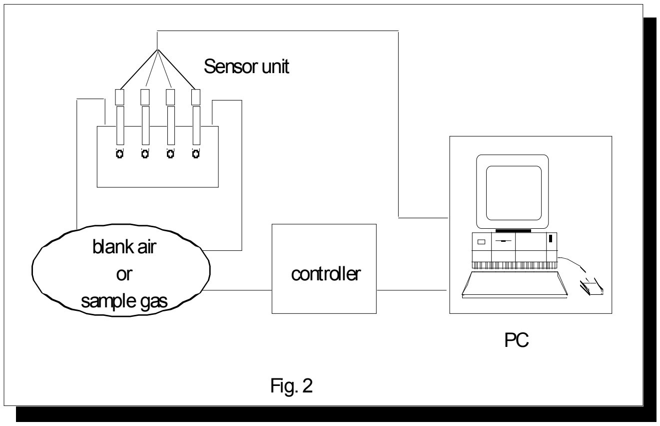

Fig. 2

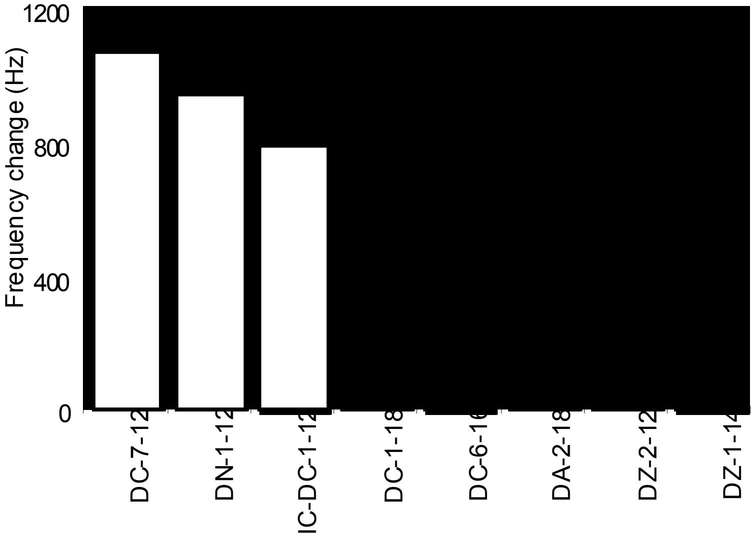

Fig. 3 Relative responses to TCE(Saturated in air)

Fig. 4 shows the frequency change of four types of QCMs to TCE at 1000 ppm. The response was reversible and by using IC-DC-1-12 coated QCM the time to reach 90% of the steady-state signal was about 96 s when increasing the concentration up from the blank to 1000 ppm of TCE and about 86 s when decreasing the concentration down to the blank.

The responses of three different kinds of lipid coated QCM to several kinds of organic gases was shown in Fig. 5. From this Figure, not only the chloroorganic compound but also other organic compounds, such as alcohol and hydrocarbon, gave rise to frequency changes. This is probably because the lipid film works as hydrophobic layer and it dissolves many kinds of organic compounds. However, this does not mean that the lipid coated QCMs have no selectivity to gases. The difference of the selectivity pattern appears to be based on the molecular interaction between the volatile chloroorganic compound and the lipid. The lipid, having different functional groups, modified the surface of the QCM, and it would form the layer with a high affinity for chloroorganic compound.

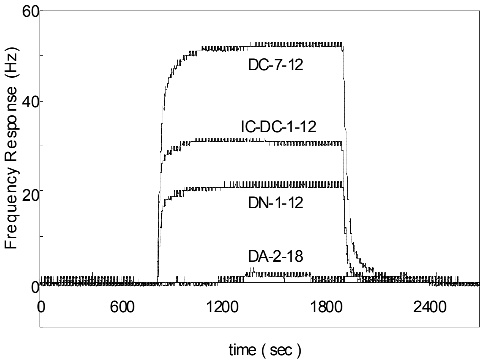

Fig. 4 Characteristics of the frequency response

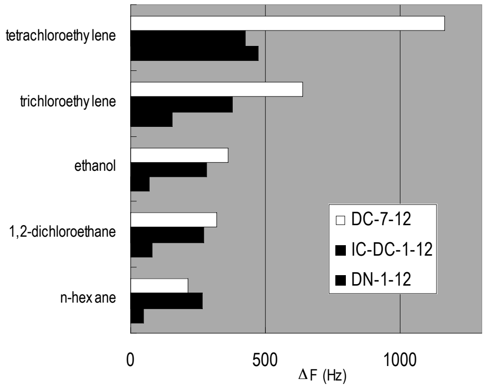

Fig. 5. Response patterns to several kinds of organic compounds obtained with three different lipids coated QCMs.

The detection limit for trichloroethylene (TCE) was 870 ppb/Hz. Contrary to the detector tube method, the QCM sensor enable the continuous monitoring of volatile chloroorganic compounds, and therefore, it would be applied to the continuous monitoring of these compounds in the factory.

Acknowledgements

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Reference

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