Sensitivity Improvement in the Detection of Trichloroethylene by Applying Oxidizing Agents to the Quartz Crystal Microbalance Method

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A new quartz crystal microbalance-based method has been developed for high-sensitivity detection of trichloroethylene. The method uses oxidizing agents such as lead dioxide and sulfuric acid, by which trichloroethylene is converted into hydrogen chloride, which in turn reacts directly with a copper electrode placed on the quartz crystal surface. The new method enables the measurement of very low concentrations of trichloroethylene, and has a detection limit comparable to the Japanese Environmental Standard (0.2 mg·m^{-3}).

Highly sensitive detection of trichloroethylene (TCE) in soil is an important aspect of soil pollution control. The Quartz Crystal Microbalance (QCM) technique,[1–3] originally developed by Sauerbery,[4] is based on the detection of changes in the resonant frequency of a quartz crystal oscillator due to increased inertia caused by the adsorption of substances onto the oscillator surface. In our previous experimental survey,[5] we used a conventional method that applies a lipid membrane as a sensing layer on a QCM oscillator surface. However, the detection limit of this method for TCE was about 1 ppm, more than 30 times the environmental standard in Japan (0.2 mg·m^{-3}, equivalent to about 30 ppb).

To improve the sensitivity, we have developed a new QCM-based method. The new method is based on the reaction used in a gas detecting tube[6] for TCE sensing. The gas-detecting tube converts TCE to HCl by reaction with oxidizing agents (PbO_2 and H_2SO_4, weight ratio is 1:4). A gas converter containing oxidizing agents is placed upstream of the QCM sensor, as shown in Figure 1. The resulting HCl gas reacts with the copper electrode to form a copper chloride layer on the quartz crystal surface. The formation of copper chloride then induces a change in resonant frequency. For comparison, gold and silver electrodes were also investigated.

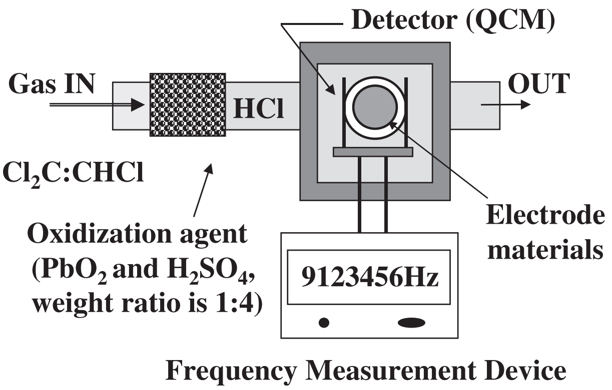

Figure 1. The basic experimental equipment.

A QCM oscillator with a copper electrode (diameter: 6 mm, thickness: 200 nm) was prepared by sputtering copper onto one side of a gold electrode on a quartz crystal surface. In this method, QCM sensor is disposable because the time degradation is considered.

TCE standard gas (100 ppb, balance: nitrogen gas) or nitrogen gas (six-nine grade purity) was supplied from a 1000 mL Tedlar bag, whose internal surface had been coated with Teflon. The bag was connected to an oxidizing converter and QCM sensor and a suction pump system (GSP-200, Gastec Corporation) attached to the other side of the bag to supply TCE standard gas or blank gas to the measurement device.

The detector section was immersed in a thermostatic chamber [300 (H) × 300 (W) × 260 (D) mm, SH-220, Tabai Espec Co., Ltd.] enabling temperature control. In the data processing section, the output signals reflecting the frequency change of the quartz oscillator (WN-AR-101, Hokkaido Toka Fine Technic Co., Ltd.) are displayed as real-time trends and are recorded using a PC-based system. Experiments were conducted, typically under the following conditions: amount of oxidizing agent: 0.1 g, temperature: 30 °C, concentration of TCE standard gas: 100 ppb, gas supply flow rate: 100 mL/min, QCM oscillating frequencies: 9 MHz and 12 MHz.

Table 1 shows the effect of the chemical composition of the electrode materials on the detection characteristics. The copper electrode element shows the largest frequency change. This result is due to its higher reactivity with HCl gas. The gold and silver electrodes show a very small frequency change since they are unreactive with HCl gas. These electrode elements show virtually no response to the blank gas.

Table 2 shows the dependence of the detection sensitivity on the fundamental oscillating frequency of QCM sensors. A much higher sensitivity (2.25 times) attained by using a QCM with a higher fundamental oscillating frequency. This sensitivity improvement is greater than the calculated one (1.78 times) from Sauerbery's equation:

Table 1. Detection characteristics of various electrode materials

Electrode materials[a]	Δf/Hz[b]
Gold	2
Silver	3
Copper	12

[a] AT-cut type device (Hokuto Denko Corporation) has small temperature dependence characteristics. The fundamental oscillation frequency is 9 MHz. [b] Using 0.1 g of an oxidization agent (PbO_2, H_2SO_4), the experiments were conducted under the following conditions: the temperature 30 °C; TCE standard gas 100 ppb; gas supply flow rate 100 mL/min; frequency change is observed 8 min after switching to the sample gas.

Table 2. Detection characteristics

Oscillator[a]	$\Delta f/\mathrm{Hz}$[b]
9 MHz	12
12 MHz	27

[a] AT-cut type and copper element. [b] Using 0.1 g of an oxidization agent (PbO_2, H_2SO_4), the experiments were conducted under the following conditions: temperature 30 °C; TCE standard gas 100 ppb; gas supply flow rate 100 mL/min; the frequency change is observed 8 minutes after switching to the sample gas.

$$\Delta f = -\Delta m \cdot F^2/(N \cdot S \cdot r) \quad (1)$$

where Δf is the change in frequency, Δm is the change in QCM oscillating mass caused by adsorption etc., F is the fundamental oscillating frequency of QCM, N is the frequency constant (AT-cut is 167 cm·kHz), S is the surface area, and r is the density of the crystal ($2.65\ \mathrm{g\cdot cm^{-3}}$). The frequency changes at the ratio of $0.27\ \mathrm{Hz\cdot ppb^{-1}}$ (fundamental oscillating frequency: 12 MHz) was linearly correlated to TCE concentration in the ranging from 0 to 100 ppb. The environmental standard for TCE in Japan is about 30 ppb ($0.2\ \mathrm{mg\cdot m^{-3}}$), and the degree of frequency change at this concentration is about 9 Hz using QCM with an oscillating frequency of 12 MHz.

The conventional method[5] using a lipid membrane as the gas adsorbent directly detects TCE that is physically adsorbed onto the membrane. In contrast, the newly developed method detects HCl that is converted from TCE by the oxidation agents. The converted HCl reacts chemically with the copper electrode to form copper chloride on the electrode surface. The experimental result for TCE sensing using a lipid membrane shows a sensitivity of $1.3\ \mathrm{Hz\cdot ppm^{-1}}$, whereas the new method using the copper element shows a sensitivity of $300\ \mathrm{Hz\cdot ppm^{-1}}$. This means that the newly developed method has a 200 times higher sensitivity than the conventional method, and features ppb-level sensitivity.

The new method has several advantages over the conventional version. Because the conventional QCM system using a lipid membrane as the sensor membrane is susceptible to the influence of humidity, it needs a system to offset this influence. In addition, the process of coating the quartz crystal electrode surface with a lipid membrane is the time-consuming. However, the new method, which is based on direct reaction with the electrode material, eliminates both these disadvantages. Gases that react with the copper electrode could interfere the TCE detection. However, no interference is expected for the measurement in the environmental atmosphere since it scarcely contains copper-reacting gases. We have confirmed that the new method is less sensitive to humidity than the conventional version,[7] allowing the sensing element to be used without additional treatment.

In conclusion, we have developed a simple method for measuring TCE as an application of QCMs. This method is characterized by the use of oxidization agents for the pretreatment of TCE, and the direct reaction of the produced HCl gas with the electrode material of the quartz crystal element. The weight change caused by this reaction, which forms copper chloride, is detected as a change in frequency. Sensitivity can be improved further by raising the fundamental frequency. Our results show that the new method is able to measure low concentrations of TCE comparable to the environmental standard in Japan of $0.2\ \mathrm{mg\cdot m^{-3}}$.

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