Water monitoring system for oil contamination using polymer-coated quartz crystal microbalance chemical sensor

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Abstract A water monitoring system with a new chemical sensor for oil contamination was developed. The sensor had an organic polymer film on a quartz crystal microbalance (QCM). The organic film was a hydrocarbon polymer and had high affinities for the organic compounds of petroleum products such as gasoline, kerosene, diesel oil and fuel oil. The monitoring system was composed of a sampling part, a purging part, a humidity control part and a sensor part. The oil in contaminated river water could be detected whose threshold odour number (TON) was less than three. The detecting time was less than 5 min depending on the oil kindness. This system was tested using artificially contaminated river water with the oils, to be found that the sensitivity was kept steady for longer than 6 months with 400 detections of diesel oil and heavy oil. Moreover, the oil kind could be discriminated with only one sensor device by analyzing the desorption response curves obtained by flowing a clean air on the sensor instead of the purging air.

Keywords Chemical sensor; odour sensor; petroleum; water plant; water pollution

Introduction Odour and taste in drinking water are major concern to water utilities because many consumers complain about them even though the unpleasant odour and taste do not necessarily indicate that the water is unsafe (Khiari et al., 1999). Many naturally or artificially occurred accidents pollute raw water for water plants to cause odour problems. The odour problems by some of the major odourants such as geosmin have recently been improved by ozonation (Atasi et al., 1999). The other kind of major odourants is petroleum products (oils), which may pollute water by car accident or illegal waste. Oils such as gasoline and heavy oil have bad odours but there is no efficient method to remove them from water. Moreover, there is no efficient method to detect the oil pollution. Therefore, at present, the only method to prevent oil from contaminating tap water is monitoring the water by using a human nose and removing oil by addition of activated carbon or stopping using the polluted water. Quick detection of oil in the source water before it invades water plants should lead to overcoming this problem. Since Sauerbrey found that the resonant frequency of a quartz crystal resonator is very sensitive to the mass variation on the surface at the nanogram level, chemical sensors have been developed using QCM (Sauerbrey, 1959; Nakamoto and Moriiizumi, 1990). The key device for an oil detection system is, therefore, a QCM and a sensing film whose affinity for oil molecules is high (Urabe et al., 1998; Sugimoto et al., 1998). The essential properties necessary for the system are: (1) high sensitivity, (2) quick response (real-time monitoring), (3) high selectivity and (4) long life time. In this paper, we report an oil monitoring system superior on these key properties with a chemical sensor having a new sensing film.
Four kinds of oils were used for artificial contamination. Kerosene, diesel oil and fuel oil were used as purchased. A part of gasoline was evaporated by heating it at 60°C to reduce the final volume to one third of the original before using it. The concentrations of their water solutions were shown in the results and discussion, whose TONs were about 2. The 30 µg-TOC/L solution was prepared by diluting a 300 µg-TOC/L solution (base solution) with water. For a long-term test, the 300 µg/L solution of diesel oil or fuel oil was prepared every 1 to 10 days (normally 7 days) and diluted to 30 µg-TOC/L, where industrial water was used which was river water treated only by coagulation and sedimentation (used as distributed from an industrial water plant). For other experiments deionized water was used. Raw river water was also used for a selectivity test of the sensor.

The schematic illustration of the oil detecting principle is shown in Figure 1. The oil odour molecules in water is purged out by air bubbles and then flown over a QCM covered with a sensing film, which has affinity to the oil molecules. The weight of the film is slightly changed following adsorption of the oil molecules, which causes the decrease of the resonant frequency of the QCM. Thus, the oil contamination can be known by monitoring the resonant frequency with a recorder or a personal computer.

The experimental apparatus is shown in Figure 2. This system is composed of a sampling part, a heater, purging part, a humidity control part using a Peltier device and a sensor part. The sensor part was composed of a QCM chemical sensor, an oscillator circuit and a Peltier device which controlled the sensor temperature. The QCM was an AT-cut quartz crystal whose resonant frequency was ca. 9 MHz and was coated with a hydrocarbon polymer by dropping and drying the polymer solution in toluene. The resonant frequency was monitored with a frequency counter and the digital data were recorded on a personal com-
puter. Monitoring of the frequency change was performed as follows: non-contaminated water was sent to the purging bottle, into which filtered air was blown at 100 mL/min through a glass filter to make bubbles. The purging gas was then sent to the humidity control part. The gas was then passed to the sensor part whose temperature was controlled to be constant. The water in the purging bottle was then switched to a sample solution which was an aqueous solution of oil if necessary and the frequency change was monitored. For starting the desorbing process of the chemical sensor, the water in the purging bottle was returned to the non-contaminated water. The desorbing response curves were analyzed by fitting an equation with an exponential to them and the obtained time constants were compared. For a long term test, the system was set up as shown in Figure 3. The water was pre-heated before entering the purging bottle, while the water was heated in the purging bottle in a water bath for other experiments.

Results and discussion

Response of polymer-coated QCM chemical sensor to oils

The response curves of the QCM chemical sensor to the oils in water were investigated. Because gasoline is a mixture of organic compounds whose volatility is in a wide range, some of them are thought to be evaporated quickly after contaminating the water and others to remain for a rather long time. Thus, the gasoline was heated and compounds with very high volatility were removed before preparation of a gasoline-contaminated water sample. Figure 4 shows the response curves of the four petroleum products in water. These results shows that the sensor had the following characteristics: (1) [oil dependence] The sensitivity was dependent on the kind of oil. For highly volatile kerosene, a quicker response was
observed. Very similar response curves were observed for diesel and fuel oils, although the response to fuel oil was much less than to diesel oil. This is because the concentration of the former was half that of the latter, which is due to both solutions having the same value of TON (ca. 2); (2) [high sensitivity] the 15-min responses to all of the four oils having very weak odour were higher than 15 Hz; (3) [quick response] the sensor responded to four oils quickly and the response reached the 5Hz-line in 5 min (Table 1). Because the noise level of the frequency was less than 2 Hz, we could set the alarm level at 5 Hz (dashed line in Figure 4). Thus the system could sound the alarm in a shorter time than 5 min for the 2–5 TON of contamination; (4) [high selectivity] although data were not shown, this sensor responded neither to highly volatile compounds with very low boiling point, such as methane or chloroform, nor to hydrophilic compounds, such as ethanol and organic acids. The sensor did not respond to raw river water without oil contamination.

Long-term performance

One of the key properties of a water monitoring system is the long life of a sensor. Otherwise, the maintenance cost becomes so high that real-time monitoring cannot be realized. We investigated the long-term performance of the system using artificially contaminated industrial water which was river water treated only by coagulation and sedimentation. The artificial 15-min contaminations occurred three times a day (every 8 hours). This test was performed from February to August 2000. Figure 5 shows the response curves on one day. Although eight hours was not long enough to remove the adsorbed oils on the sensing film, the sensor recovered to detect another oil contamination. Figure 6 shows the

<table>
<thead>
<tr>
<th>Oil kind</th>
<th>Conc. (µg-TOC/L)</th>
<th>Response time (min)</th>
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<tbody>
<tr>
<td>Gasoline</td>
<td>30</td>
<td>2.0</td>
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<tr>
<td>Kerosene</td>
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</tr>
<tr>
<td>Diesel oil</td>
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</tr>
<tr>
<td>Fuel oil</td>
<td>15</td>
<td>3.5</td>
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</table>

Table 1  Response time for 5 Hz response for 2–5 TON oil contaminated water

Figure 5  Response curve to diesel oil in water on one day for long-term monitoring test. The arrows show the start point of oil contamination

Figure 6  Time course of the maximum response height to diesel oil or fuel oil in water. Only the response for the first test after exchange of a diesel oil base solution was shown
time course of the maximum response height of the first test after the exchange (every 1 to 10 days) of the base oil solution. The sensor repeated showing the constant response curves to the contaminations, although the response height fluctuated in the range of 60–120 Hz. This fluctuation may be due to the fluctuation of the water flow rate into the purging bottle and to unexpected contamination in the water by unknown compounds on repairing the pipe from the industrial water plant. During the operation, some sediment was observed in the purging bottle and tubes, which did not affect the response. Although the plots were shown only for the first responses after preparing the base solution, only one sensor device responded to the more than 400 artificial contaminations occurred in this test period without changing sensitivity, which means that the sensor has a long life time.

Though at present, the maintenance period of other parts than the QCM such as filters and tubes is unclear, an automatic system to stop oil-contaminated water flowing into the detecting system, which is considered to be equipped, will make the maintenance period much longer. Another consideration is being done for a long-period (e.g. 1 week) oil pollution. The detecting system compares periodically a filtered sample water with raw sample water after the first detection, enabling the system to determine the end of the pollution.

**Discrimination of oil**

The kind of oil in the contaminated water is useful information for the drinking water treatment plant because it may lead to the clarification of the contaminant source. Because of the difference of adsorption and desorption constants for the components of oils, the response curve shape depends on the kind of oil, which means the analysis of response curves might lead to the estimation of the kind of oil. Since the concentration of oils in water is afraid to fluctuate, however, the sensor response will also fluctuate, which makes it difficult to analyze the response curve on adsorption. To overcome this problem, we analyzed the desorption response curves. Figure 7 shows the normalized response curves for gasoline, kerosene and diesel oil. Normalization of the response curves was performed by dividing the raw data by the minimum datum and by multiplying them by $-1$. The concentrations and adsorbing time is summarized in Table 2. The time constants as a fitting parameter of a one-exponential equation are also shown in Table 2. Figure 8 shows an example of the fitting curve. Although good agreement between the real response curve and the fitting curve was observed only in the short range, the time constants (3.1–5.7 min) for the kerosene desorption for several different conditions were much different from those for gasoline (1.9 min) and diesel oil (58–81 min). These results indicate that the analysis of desorption response leads to the discrimination of the kind of oils in any conditions. In order to improve the agreement, we fit an equation of a sum of 2 or 3 exponentials to the data, and it improved the agreement. However, it did not lead to better discrimination, which indicates that only the data for the first several minutes are necessary for effective discrimination.

**Figure 7** Normalized response curves of the sensor to gasoline, kerosene and diesel oil. Meaning of symbols is shown in Table 2.
Conclusions

We have developed a water monitoring system for oil contamination using a hydrocarbon polymer coated quartz crystal microbalance chemical sensor. This system has the following key properties. (1) High sensitivity; it can detect oil contamination with TON of less than 3. (2) Quick response; it can raise the alarm within 5 min after contamination. (3) High selectivity; it can detect gasoline, kerosene, diesel oil and fuel oil, and hardly responds to raw river water, high volatile compounds or hydrophilic compounds. (4) Long life time; one sensor device could work longer than half a year and detect 400 fuel oil contaminations with almost constant response height and shape. Moreover, the discrimination of oils was realized by the desorption analysis.

References


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<th>Adsorbing time (min)</th>
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<th>Symbols</th>
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Figure 8 Curve fitting (——) to the response curve (○) for kerosene-contaminated water. Kerosene was 300 µg-TOC/L.

Table 2 Experimental conditions and time constants of desorption responses

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