Selective aqueous benzene detection at ppb level with portable sensor based on pervaporation extraction and UV-spectroscopy

Serge Camou*, Akira Shimizu, Tsutomu Horiuchi and Tsuneyuki Haga

NTT Corporation, Microsystem integration labs, 3-1, morinosato wakamiya, atsugi-shi, kanagawa pref., 243-0198 Japan

Abstract

This paper describes a new portable aqueous benzene sensor that combines UV-spectroscopy detection and benzene extraction from the liquid to gas phase based on pervaporation through a silicone tube. Pervaporation through a silicone membrane provides chromatographic extraction of solutes with compound-dependent time constants, leading to separation of the different compounds at the detection stage. From a benzene/toluene/o-xylene mixture, we demonstrated a three-fold increase of the benzene/toluene ratio, resulting in a decrease of interferences between their overlapping absorption spectra. This aqueous benzene sensor combining portability, sensitivity in the ppb(v/v) range, and selectivity to benzene enables on-site measurements of benzene contamination and represents a potential alternative as an on-site early-alert benzene detection sensor.

Keywords: Aqueous benzene detection, selectivity, pervaporation, UV-spectroscopy

1. Introduction

A few decades ago, benzene was clearly identified as a carcinogenic compound, and strict regulatory levels that benzene concentration should not exceed have since been set in countries all over the world. However, due to its specific properties, it is still widely used in the chemical industry as a precursor or solvent, or as an additive in gasoline. Despite many efforts to find alternative compounds, the concentration in gasoline remains on the order of few percent, which results in air pollution from the car exhaust after gasoline combustion in the engine. Taking into account the mobility of sources and the need for on-site measurement, we then developed a portable system dedicated to airborne benzene monitoring based on UV-spectroscopy detection [1] with a detection limit satisfying the regulatory levels.

Furthermore, leaking storage tanks releases large quantities of benzene, which is a major cause of rivers and ground waters benzene pollution despite its low solubility in water. Starting from our portable airborne benzene sensor, we then further extended its scope to aqueous samples [2]. Despite a good sensitivity to benzene, the system exhibits a limitation in terms of specificity to benzene, which remains an important issue. Theoretically, UV-absorption measurements can perform simultaneous detection of several compounds as long as their reference spectra are identified and taken into account during the analysis process. However, this extensive database is
difficult to build with accuracy, and huge concentration differences of several compounds with overlapping absorption spectra, such as benzene and toluene, can also strongly alter the detection accuracy. We then developed a new system based on pervaporation extraction through a silicone membrane in order to separate the benzene/toluene contributions at the detection stage and thereby provide selectivity to benzene.

2. Materials and Methods

Our portable sensor can be divided into three basic elements: the microfluidic system (pump, tubes) and the extraction and the detection systems.

2.1. Extraction system

We compared two extraction systems for transferring the benzene compound from the liquid to gas phase inside a 1.2L container made of Teflon. For bubbling extraction, the 1.2L tank is filled with 1L of sample solution, leaving some space for air. The extraction mechanism uses evaporation at the air/liquid interface, and bubbling carrier gas inside the sample liquid enables one to drastically increase the exchange area. For the pervaporation system, a silicone tube (inner and outer diameters of 0.5 and 1 mm, and length of 3200 mm) is used to directly connect the inlet and outlet of the Teflon extraction tank, and the 1.2L tank is completely filled with water in order to avoid any liquid/air interface inside it. This time, benzene is extracted by pervaporation through the silicone tube membrane, while the carrier gas flowing inside the silicone tube transfers benzene molecules to the detection cell.

2.2. Sensor parts

The carrier gas flow is provided by a bi-molar pump, which is, like the microfluidic tubes, made of chemically inert material (Teflon) to ensure minimal interaction with the carrier gas constituents. The detection stage is composed of a home-made detection cell based on an uniformly aluminum-covered hollow fiber optical waveguide [3], connected to a compact UV light source (Deuterium lamp) and spectrometer. As a result, our portable sensor fits in an approximately 12L box connected to an extraction tank and a PC, and requires nothing but an external power supply.

3. Results and discussion

3.1. Sensitivity
With a 30-cm detection cell, we first compared the sensitivity provided by the aqueous benzene portable sensor using the two extraction systems mentioned above. With bubbling extraction, we achieved a 50-ppb(v/v) limit of detection (LOD), while the pervaporation extraction led to a 110-ppb(v/v) LOD. This two-fold decrease of the sensitivity can be explained by the exchange surface area/sample volume ratio, which is several times higher in the case of bubbling extraction and thereby results in a faster and more efficient benzene extraction.

3.2. Selectivity

To evaluate the detection selectivity, we used a benzene/toluene/o-xylene mixture at respectively 0.45/3/3 ppm(v/v) concentrations. The three compounds exhibit slightly different characteristic properties (boiling point, solubility in water), and as shown in Fig. 2, their different chemical structures also results in specific absorption spectra in the 230-290 nm range, with a problematic overlapping area especially between benzene and toluene.

![Absorption spectra of the benzene toluene o-xylene compounds in the 230-290 nm wavelength range.](image)

With bubbling extraction, the three compounds are simultaneously extracted (left of Fig. 3), with maximal absorption within the first 400 sec., followed by a linear and constant decrease. In comparison, with pervaporation extraction, the three compounds exhibit specific time responses (right of Fig. 3): the benzene contribution reached a plateau after 1200 sec., while toluene contribution gradually and constantly increased over the first 3200 sec., and the o-xylene contribution remained at a very low level.

![Extraction of respective benzene/toluene/o-xylene contributions from superimposed UV-absorption spectra with (left) bubbling extraction and (right) silicone tube extraction.](image)

However, the results presented in Fig. 3 were obtained from an automatic evaluation based on absorption peak height of at 253, 267 and 272 nm for benzene, toluene, and o-xylene respectively. Therefore, the overlapping spectra (Fig. 2) may lead to overestimation of benzene, a phenomenon also enhanced by the huge concentration differences...
between the three compounds. In order to avoid this artifact, we manually estimated the three compounds’ respective contributions from raw spectra at 800, 1200, 2080, and 3200 sec.

First, the overestimation of benzene contribution was reduced from 100% with bubbling extraction to a maximum of 30% with pervaporation extraction. Second, the manual extraction at four points confirmed the general tendency in Fig. 3: while the benzene/toluene response ratio remains almost constantly equal to 0.16 with bubbling extraction, pervaporation extraction yields a benzene/toluene signal ratio that decreases with time (Fig. 4). These results yield a 3.4-fold selectivity-to-benzene improvement and point to an optimum in the short time response.

![Figure 4](image_url) Evolution of the benzene/toluene ratio versus time, with bubbling (bubb) and pervaporation (perv).

### 3.3. Discussion

The pervaporation extraction then results in both separation improvement and sensitivity deterioration. However, the limit of detection remains in the low-ppb range, which satisfies the wastewater regulatory levels in Japan and makes the sensor competitive for field measurements. Concomitantly, the chromatographic extraction ability renders possible the separation of benzene, toluene and o-xylene contributions despite their closely related chemical composition and physical properties. When dealing with real sample solution, we can then reasonably expect separation of many other potential unknown compounds that may interfere with benzene measurements, leading to better robustness for on-site measurements.

In terms of separation efficiency, the results point to an optimum in the short-time regime. However, measurements based on the absorption spectra before benzene response reaches its plateau will also result in a decrease of the sensor sensitivity to benzene (i.e. lower SN level). A compromise may then be found between sensitivity and selectivity to benzene in the short-response-time regime whenever the application requires it.

### 4. Conclusions

We described a portable sensor based on pervaporation through a 0.25-mm-thick silicone tube and dedicated to aqueous benzene measurements. Combined with a 110-ppb(v/v) LOD, we also demonstrated a significant enhancement of selectivity to benzene from a benzene/toluene/o-xylene mixture due to chromatographic extraction of diluted compounds, which remains an important issue for on-site applications.

### References