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Ppt-level Detection of Aqueous Benzene with a Portable Sensor based on Bubbling Extraction and UV Spectroscopy

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1. Introduction

Benzene (EPA, 1993), sometimes also referred to as part of BTX or BTEX, which stands for benzene, toluene, ethylbenzene, and xylenes, is widely used in industrial activities despite being a known carcinogen that can easily contaminate different media (gas, water, and soil). It can be inhaled, ingested, and absorbed through the skin and therefore represents a potential threat to human health, even at trace levels. With respect to benzene toxicity, national regulations have been established in an effort to minimize its impact on human health. Water regulations cover drinking water and wastewater, with levels varying from one country to another but falling within the same order of magnitude. Wastewater regulations give the maximum concentration allowed for disposal, about a few hundred parts per billion (ppb) (Volume) (110 ppbV in Japan (Ministry of the Environment in Japan, 2008)). Below this level, the impact on the environment is assumed to be negligible. This level is sometimes referred to as the alarm level. Drinking water regulations, which are aimed at water for human consumption, stipulate permissible levels in the low ppbV range, two orders of magnitude lower than for wastewater (11, 5 and 1 ppbV in Japan, America, and Europe, respectively (Ministry of Health, Labour and Welfare in Japan, 2003) (EPA, 2006) (European Council, 1998)).

Laboratory procedures for detecting benzene concentrations in water involve several consecutive steps: (i) extraction by inert-gas stripping or heating to transfer benzene to the vapor phase, (ii) trapping to enhance the concentration, and (iii) detection by gas chromatography combined with either flame ionization, photo-induced detection or mass-spectrometry (respectively GC/ FID, GC/ PID, and GC/ MS) (Martinez *et al.*, 2002) (Serrano & Gallego, 2004) (Richardson & Ternes, 2005). The detected thresholds far exceed the requirements, but the procedures are complex and involve the use of expensive equipment. The required apparatuses are also not compatible with the requirements for on-site measurements, which means samples have to be collected in the field and sent to a laboratory for analysis (Richardson & Ternes, 2005). To prevent contamination of samples or changes in their characteristics due to long contact-exposure to the container (with transportation time to the laboratory varying from a few hours to a few days), complex and error-prone procedures have been established (Namiesnik *et al.*, 2005), which, depending mainly on the potential contaminants, include choosing an appropriate container material,

dilution with organic solvent, and avoiding headspace. Recent disasters in 2005/ 2006 (chemical plant explosions in China; hurricane Katrina in America) point to an urgent need for on-site, real-time monitoring of pollutant contamination to prevent dramatic impacts on the local population's health, making response time a crucial factor.

A suitable on-site sensor should then exhibit robustness, sensitivity in the low-ppbV range for drinking water regulation levels, and response time of about a few minutes or less. A few studies have examined portable sensors dedicated to on-site benzenic-compounds measurements from water samples. Those devices use alternative detection techniques, and, though the sensitivity is relatively low, exhibit several advantages over conventional methods in cost, protocol and data analysis, and size. In addition, they do not require any inert gases, such as the carrier gas used in gas chromatography-based measurements, which improves portability.

These sensors can be classified into direct measurements systems, which directly measure pollutant concentrations in the liquid phase, and indirect measurements ones, which require pre-conditioning of a sample before its characterization.

Among the direct methods, mid-infrared (MIR) evanescent field spectroscopy has been largely utilized. The sensing element is a polymer-coated optical fiber or an attenuated-total-reflection (ATR) crystal. The polymer coating provides selective enrichment of compounds to be detected within the depth penetration of evanescent wave in the aqueous media. Silver halide fibers and various polymer coatings have been used to measure hydrocarbons in water (Hahn *et al.*, 2001) (Krska *et al.*, 1993) (Steiner *et al.*, 2003) (Beyer *et al.*, 2003), though the limit of detection (LOD) is in the low ppmV range and measurement time is longer than an hour. Systems based on coated quartz-glass optical fibers and detection in near infrared (NIR) spectral range have been reported (Burck *et al.*, 2001) (Zimmermann *et al.*, 1997). A recent system on ATR crystal (Karlowatz *et al.*, 2004) has demonstrated a LOD to benzene of about 45 ppbV with a 20-min measurement cycle. Although the simultaneous detection of five compounds has been demonstrated at low concentration levels, consecutive measurements using the same apparatus may take longer because the equilibration time to water diffusion through the coating (about several hours) for stabilizing the baseline is not included in the measurement time and because enrichment reversibility, i.e., the refreshment of sensing system, is a slow process limited by the partition coefficient and diffusion through the polymer coating. As a potential improvement of evanescent wave spectroscopy, Tobiska *et al.* (Tobiska *et al.*, 1998) proposed bending the fibers to increase the evanescent field intensity. Mohacsi *et al.* (Mohacsi *et al.*, 2001) described a sensor based on photo-acoustic detection principle with a 300-ppbV LOD and a 40-min response time. To achieve high sensitivity, aromatic compounds are detected in the vapor phase after the molecules have been selectively transferred from the liquid phase through a semi-permeable membrane surrounding the acoustic cavity. Vogt *et al.* (Vogt *et al.*, 2000) proposed direct and simultaneous detection of hydrocarbons in water with a system based on UV derivative spectrometry. This approach offers a fast response time of few minutes and a LOD to benzene below 50 ppbV. However, turbidity is expected to strongly bias the results, which limits the applicability of such a sensor to specific on-site measurements.

In comparison with direct measurements, indirect ones require sample extraction from the liquid phase. Yang *et al.* combined gas-stripping (Yang & Her, 1999) or headspace (Yang & Tsai, 2002) techniques to transfer aromatic compounds from the liquid to the vapor phase and performed detection by MIR evanescent wave spectroscopy. The reported LOD is in the few-hundred ppbV range. Measurements are faster, typically less than thirty minutes all steps included, from sample introduction to complete regeneration, but the sensor gains in

complexity because of the large number of connected elements. Solid phase micro extraction (SPME) combined with IR (Heglund & Tilotta, 1996) or UV (Lamotte *et al.*, 2002) spectroscopy has also been used to quantitatively and qualitatively determine benzenic compounds diluted in water. Since only the disposable SPME matrix is in direct contact with the sample, the contamination risk to the re-usable detection setup is almost negligible, making the regeneration step unnecessary. However, because enrichment is based on diffusion through the SPME matrix, the sensitivity is directly proportional to exposure time. In order to reach a LOD in the hundreds of ppbV range, enrichment time exceeding one hour is then common.

Field-test validation has been carried out successfully for high pollutant concentration levels (Krska *et al.*, 1993) (Steiner *et al.*, 2003), indicating the proposed sensors offer alternatives to laboratory equipment at the alarm-level threshold. However, with the drinking water regulation level as the final target, none of those devices fulfill the requirements in terms of sensitivity.

This chapter then describes the design of portable aqueous benzene sensor based on UV-spectroscopy with a sensitivity in the pptV range. Starting from our portable BTX sensor dedicated to air monitoring (Ueno *et al.*, 2001) (Camou *et al.*, 2006, a), we extended its use to aqueous sample solution by adding an extraction module into the inlet to transfer the benzene compound from the liquid to the vapor phase (Camou *et al.*, 2008). However, the concentration cell developed for the airborne system, which provides benzene concentration enhancement prior to the detection cell, could not be used. As a consequence, the sensor demonstrated a LOD in the hundred ppbV range, several times higher than the requirements (Camou *et al.*, 2008). Since the concentration stage is a key component for achieving high sensitivity, we developed a new one, taking into account the carrier gas specific properties after extraction, and demonstrated pptV range measurements. These results open the door to potential on-site and high sensitive measurements of aqueous benzene concentrations and make the presented sensor a viable alternative to standard methods.

2. Airborne benzene portable system

Figure 1 shows the schematic view of our portable airborne BTX sensor, which is mainly composed of detection and concentration cells connected to external elements.

As the detection principle, we chose UV spectroscopy because it offers several advantages for on-site and real-time monitoring: portability and simultaneous detection of several compounds if the wavelength range has been selected appropriately. The output spectrum results from summation of all contributions of solutes absorption weighted by ponderation coefficients proportional to their respective concentration. This method can therefore provide qualitative and quantitative measurements of complex mixtures if every compound that significantly contributes to the final spectrum has been identified and their reference spectra are taken into account in the data analysis process (Ueno *et al.*, 2002). Regarding the three BTX compounds, they exhibit specific and characteristic absorption spectra in the 235 – 275 nm range, whereas water (and especially water vapor), as a potential interferant, shows no peak absorption.

For BTX mixtures in ambient air, we previously demonstrated the accuracy of UV spectroscopy detection in the low-concentration range when the micromachined detection
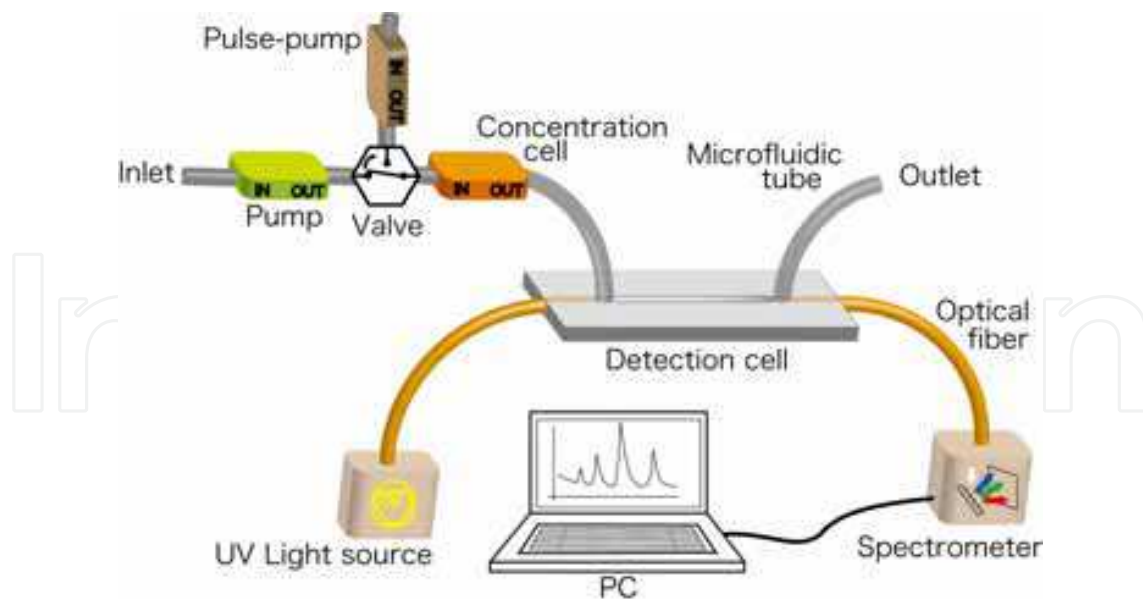
Fig. 1. Schematic view of the airborne BTX portable monitoring system, including the concentration and detection cells with pumps and a few external elements.

cell shown in Fig. 2 was used. The cell's fabrication process is described in detail elsewhere (Camou *et al.*, 2006, b), but can be briefly summarized as follows. A hollow fiber whose inner side-wall has been uniformly covered with an aluminum reflective layer (Souken Co., 2005) acts as an optical waveguide. It is sandwiched between two patterned Pyrex glass wafers, which are anodic-bonded to each other through a silicon nitride thin film. A multi-step dicing process produces trenches with various depths and shapes, providing excellent optical alignment between optical fibers and the hollow fiber in the plane perpendicular to the optical axis. Finally, sealing the different parts with UV resin yields good mechanical stability and prevents gas leaks. By separating mechanical parts (alignment of optical fibers in regards to the hollow fiber, microfluidic connections, etc) from optical parts (waveguide optical efficiency), we were able to fabricate a 10-cm-light-path detection cell with high coupling efficiency using conventional equipment for four-inch wafer processing.

The fabrication process for the concentration cell shown in Fig. 2, which is also described elsewhere, used classical microfabrication processes combined with sand blasting for the patterning of a trench with arbitrary shape in the Pyrex glass. After completing the concentration cell, the adsorbent material is inserted through the inlet by aspiration from the outlet.

The measurement sequence can then be described as follows. First, the ambient air is pumped at a high flow rate through the concentration cell during the so-called concentration time. The adsorbent, characterized by its high active surface/ volume ratio, then selectively adsorbs the BTX compounds at its surface.

Meanwhile, since most of the BTX compounds are trapped by the adsorbent, spectrometer calibration measurements are performed. At the end of concentration time, the pump stops, and BTX compounds trapped by the adsorbent are desorbed by heating the concentration cell. After switching the valve, the pulse-pump precisely transfers the resulting high-density sample gas from the concentration cell to the detection cell, where simultaneous and efficient detection of BTX compounds are performed by UV-absorption-based

measurements. Among the several benzene absorption peaks in the studied wavelenght range, we chose the main peak located at 253 nm to perform quantitative measurements.
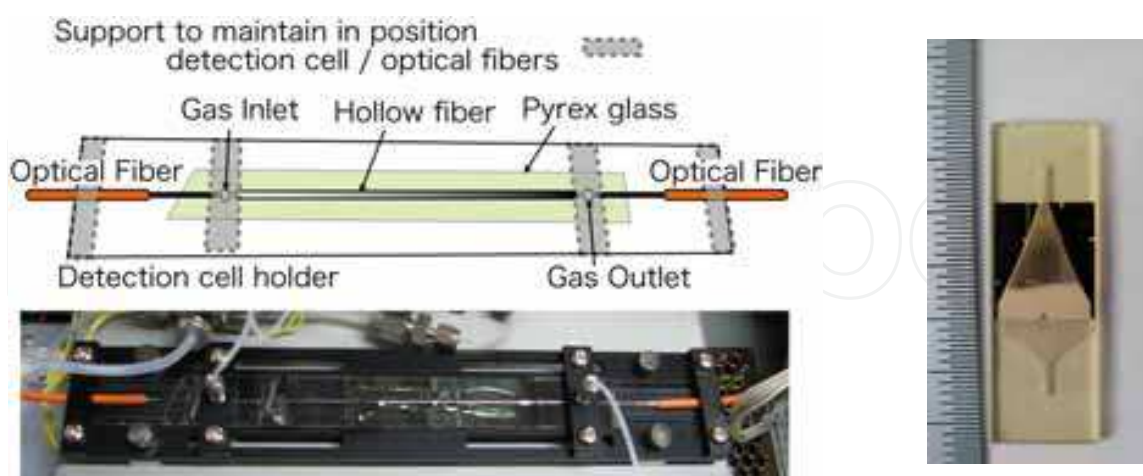

Fig. 2. Pictures of (left) the detection cell (10-cm-long light path) on its holder and (right) a micro-fabricated concentration cell half-filled with adsorbent (platinum heater electrodes on the rear side).

Figure 3 shows the sensor response versus benzene calibrated gas concentration for concentrations varying from 0 to 10 ppbM and with a concentration time of fifty minutes. The sensor exhibits linear response over more than one order of magnitude, with a detection limit of about 1 ppbM. These characteristics are consistent with our primary objectives, but improvements in the detection limit are still necessary in order to really claim accurate and reproducible measurements at 1 ppbM benzene concentration.

Meanwhile, due to the high toxicity of benzene diluted in water despite its low solubility, we also started the development of a portable, high-sensitivity aqueous benzene sensor based on our technology.
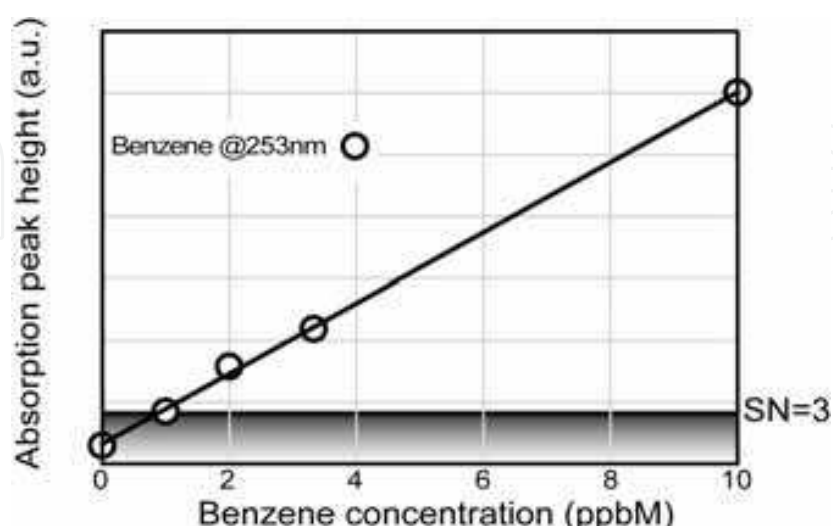

Fig. 3. Sensor response versus benzene concentration of calibrated gas mixture in dried nitrogen.

3. Extension of portable sensor usage to aqueous samples

The airborne system was designed to deal with gaseous samples. To extend the portable sensor's use to aqueous sample, an extraction module based on a bubbling method – sometimes also referred to as gas stripping- was added as shown in Fig. 4.
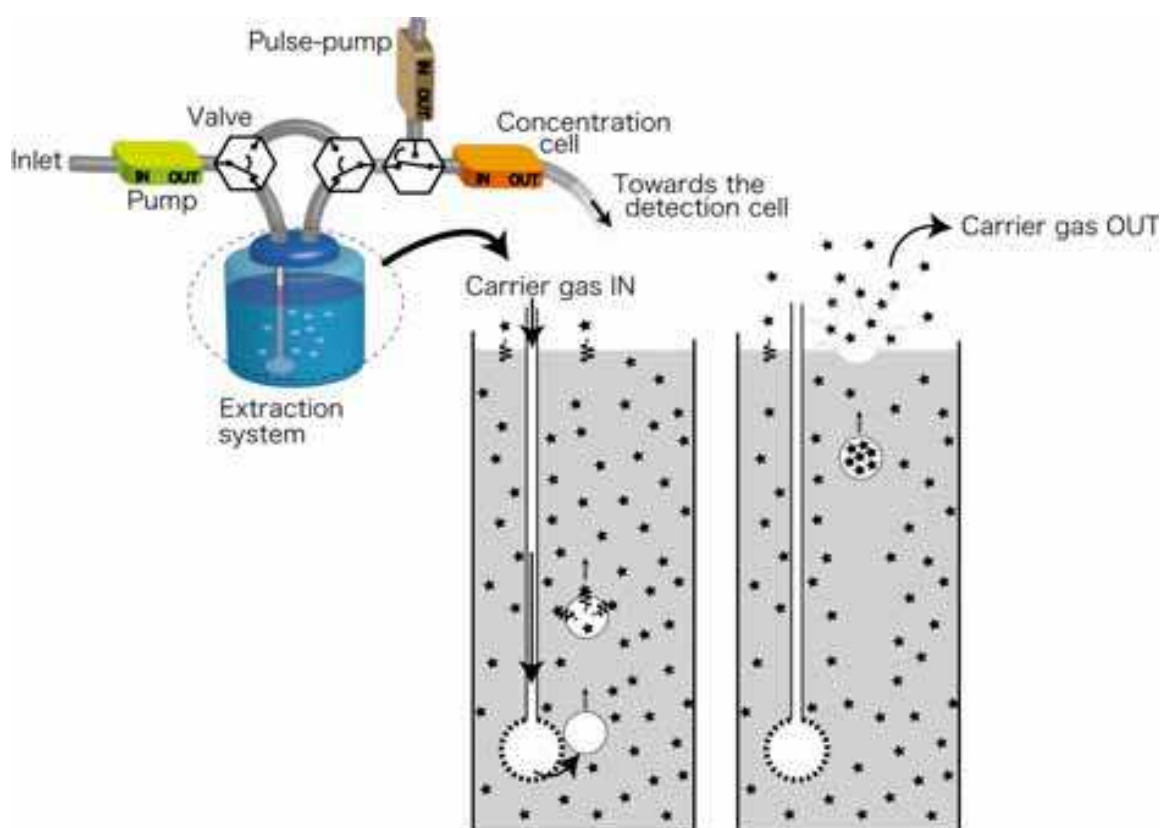

Fig. 4. Schematic view explaining the basic concept of aqueous benzene extraction by bubbling, with the black stars representing benzene molecules.

3.1 Extraction system: transfer of benzene from liquid to gas phase

Thanks to two compound-specific properties of benzene -a low boiling point (80.1 degrees C) and a low solubility in water (1.79 g/ l at 25 degrees C) (EPA, 1993)- bubbling is a very efficient way to extract benzene diluted in aqueous solution. Standard methods based on chromatography sometimes use bubbling extraction, where an inert gas flows through the sample solution. This is known as "purging" from the so-called "purge and trap" technique (EPA,, 2003). This method, also used by Yang *et al.* (Yang & Her, 1999), does not require any additional components (actuators, heaters, etc) and provides easy and robust benzene extraction from aqueous samples.

The bubbling method is briefly described as follows. Due to the low solute-solvent interaction of benzene diluted in water, benzene naturally evaporates at the air–water interface. By generating air bubbles inside the liquid, we can greatly increase the air-liquid interface area so that gas exchange can proceed at a faster rate. Since the main gas exchange is considered to be benzene evaporation, the bubbles take in a large amount of benzene from the solution while rising and then release it in the gas volume over the sample solution.

This sample gas is then transferred to the next stages, where its benzene concentration is finally determined by UV spectroscopy.

However, a major drawback of bubbling extraction is a lack of selectivity. When air is bubbled through an aqueous sample, most diluted compounds as well as water itself will evaporate with a compound-specific efficiency and flow through the concentration/ detection cell. As a result, the sample gas measured will also contain a high relative humidity (RH) ratio, estimated to be over 90%.

3.2 Without concentration stage

Figure 5 shows the set-up without a concentration stage and the corresponding measurement sequence. While the spectrophotometer calibration measurements are performed, ambient air flows through the detection cell thanks to the valve positioning.
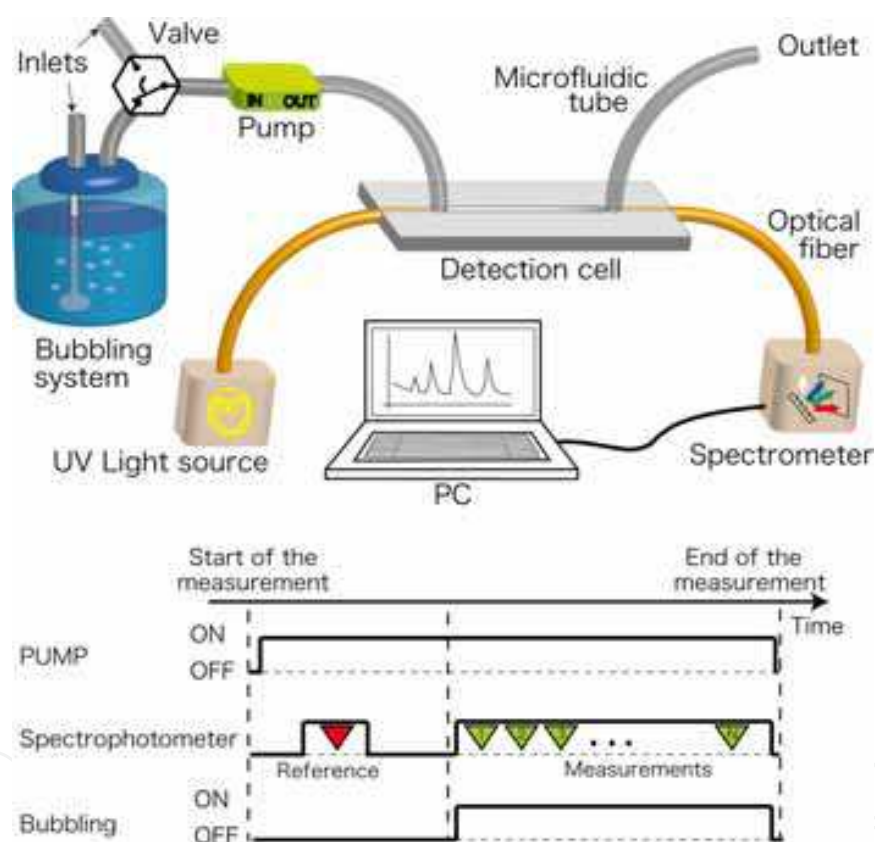

Fig. 5. Schematic view of the experimental set-up (top) and the corresponding measurement sequence (bottom)

Then, the valve switches and simultaneously bubbling through the sample solution occurs and spectra acquisition starts. As the benzene compound is extracted from the liquid phase (with a certain efficiency) and passes through the optical detection cell mixed with the carrier gas (ambient air), spectra in the specific UV range are captured continuously and the results are displayed on the computer screen in real time.

This set-up has several advantages compared to previously reported technologies. The proposed system does not require any enrichment or regeneration. This reduces the measurement time to less than 10 minutes, from sample collection to the reading of the

results on the computer display. Also, the UV absorption-based method is a relative measurement. Therefore, by using ambient air as the carrier gas for both spectrometer calibration and bubbling extraction, the contribution from compounds in ambient air should then cancel each other out and leave the output spectra free of interference.

With measurement every 80 seconds, plotting the peak heigh at 253 nm versus time leads to the characteristic response shown in left part of Fig. 6. After a fast increase of benzene absorption within the first two measurements and a narrow plateau, the absorption signature of benzene decreased at a stable and slow pace. Using the plateau value as the measurement, we then investigated the sensor response to benzene solution whose concentrations vary from 0.1 to 3 ppmV (right, Fig. 6).
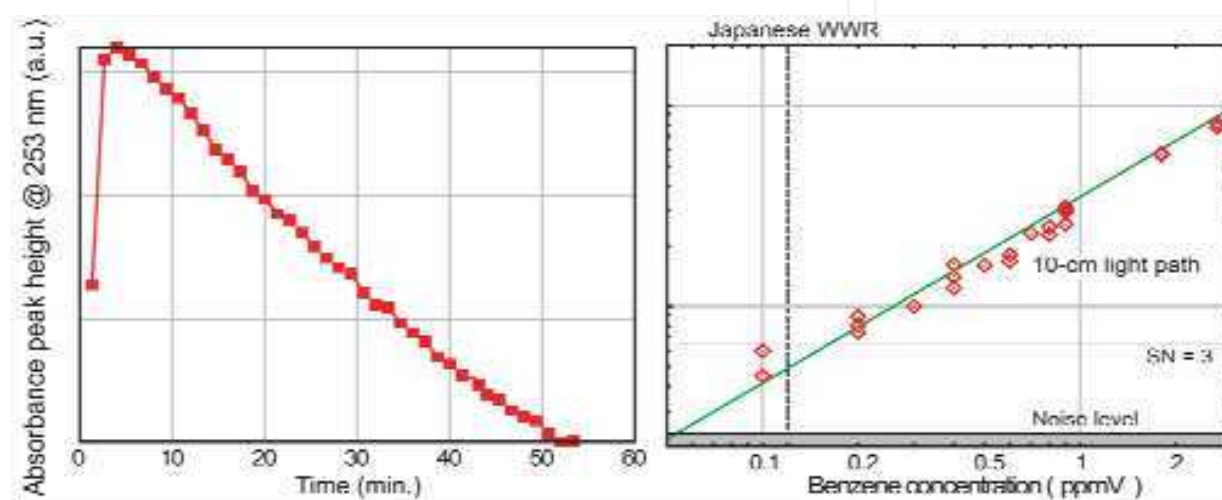

Fig. 6. Benzene main peak absorption amplitude at 253 nm versus time (left) and sensor response versus aqueous benzene concentration (right) (Camou *et al.*, 2008)

First, the sensor exhibits a linear response in the 0.2 - 3 ppmV range, which is more than one order of magnitude. This range may be extendible; however the high concentration range is not of much interest regarding the final application.

Concerning the actual detection limit, with a S/N ratio of 3 as our minimum requirement for extracting reliable data from the spectra, the LOD was estimated to be about 150 ppbV.

Experiments at lower concentrations were carried out, but the low S/N prevented a precise estimation of peak heights, as the points slightly diverged from the linear fit in Fig. 6.

As a result, with a LOD in the 150-ppbV range and ease of operation, this sensor represents an alternative suitable for on-site alarm-level measurements. In comparison to other relevant sensors, it exhibits similar sensitivity to benzene, while the time needed per measurements is shortened to just 10 minutes.

Nevertheless, the drinking-water regulation levels remain about two orders of magnitude below the reported LOD (5 ppbV in both America and Japan; 1 ppbV in Europe), and gaining two orders of magnitude in sensitivity requires drastic modifications. Previously, in the framework of the air monitoring system, the concentration stage led to a gain in sensitivity of about three to four orders of magnitude. The concentration stage then remains the key technology for reaching the drinking-water regulatory levels, typically in the high pptV levels.

3.3 Results with airborne system

We first equipped the airborne system (Fig. 1) with bubbling-extraction module (Fig. 4) and tested its ability to detect high-aqueous-benzene-concentration [several ppmV] solutions. During these preliminary experiments, two problems occurred that allowed us to identify the major difference between airborne and aqueous benzene detection: the carrier gas relative humidity.

Figure 7 depicts the first five consecutive raw spectra obtained in this experiment. Despite absorption peaks at wavelengths characteristics of benzene compounds, the raw spectra exhibited unusual shapes. After a positive first response characterized by peak amplitudes drastically lower than first expected, the second spectrum exhibited no peak, and from the third spectrum, the benzene signature appeared negative. A decrease of the absorption peak amplitude with time, where time is equivalent to increasing spectrum number, is normal due to the diffusion of concentrated gas within the fluidic system. As a result, when the benzene molecules remaining within the optical light path lead to absorption below the noise level, the output and reference spectra become comparable and free of absorption due to benzene. Thus, the raw spectra tend to a flat baseline around 0 as the spectrum number increases. The results of Fig. 7 then clearly indicated that the reference spectrum had been corrupted. In fact, silicate adsorbent active sites also exhibit strong affinity to water molecules, even stronger than that to benzene molecules. Thus, water molecules have the ability to remove and replace benzene molecules adsorbed at the active sites while the reverse reaction can hardly occur. As a consequence, competition between water and benzene molecules resutls in random release of benzene molecules in the carrier gas that can potentially alter the reference spectrum. This explanation elucidates the negative peaks seen in Fig. 7 and also corroborates some previous results.
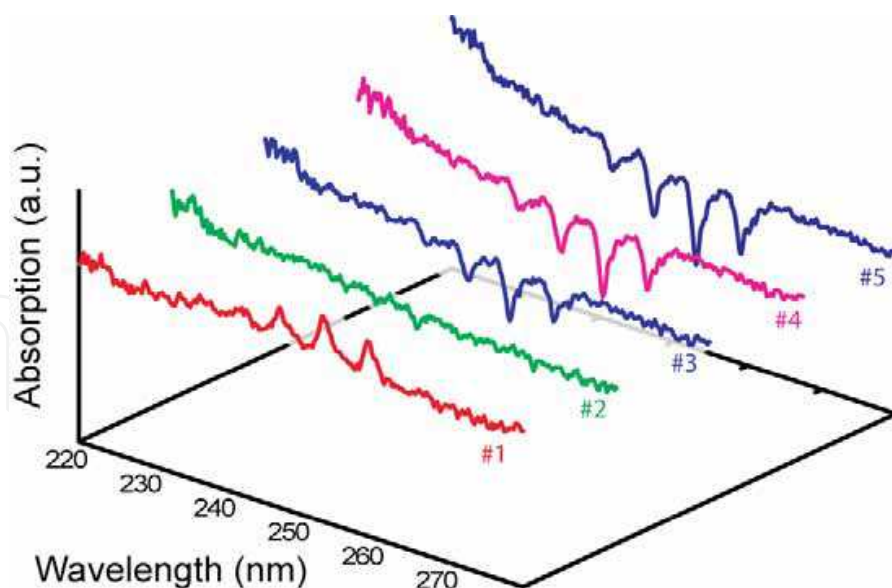

Fig. 7. First five consecutive raw spectra obtained with sensor combining bubbling extraction and a concentration cell filled with silicate adsorbent.

Second, while carrier gas containing benzene molecules flowed through the concentration cell, we observed a continuous decrease of the flow rate. Furthermore, at the end of this experiment, the recovery/ refresh process of the adsorbent required an unusually large

number of thermal cycles at high temperature before the flow rate would return to reference value. These phenomena come from capillary condensation of water, which is due to the combination of carrier gas containing high RH levels with the nano-sized structure of silicate adsorbent.

The high RH value of carrier gas after the extraction exerts two side effects that make the approach inefficient. However, replacing the silicate adsorbent with another compound is not sufficient because of the capillary condensation. Indeed, we are facing here two contradictory properties. The active sites of the adsorbent are localized at its surface. In order to optimize the number of active sites within a finite volume, high surface/ volume ratios are a prerequisite for an efficient concentration enhancement. As a consequence, all the potential adsorbents exhibit dense structures through pores whose sizes vary greatly but always in the range where 90% RH carrier gas leads to capillary condensation. Whatever adsorbent material we use, the relative humidity of carrier gas flowing through the concentration cell should exhibit lower levels. Extraction systems based on different mechanism and with lower efficiency have been tested, but the RH levels of the carrier gas remained over 80%, leaving the issue intact.

3.4 New concentration stage

We then developed a new concentration stage that could provide benzene concentration enhancement prior to the detection cell despite interference due to water molecules. As shown in Fig. 8, the new stage is composed of a passive drying system (Nafion tube), which decrease RH to a level where capillary condensation doesn't occur, and a concentration cell filled with a zeolite adsorbent, which exhibits weaker affinity to water molecules.
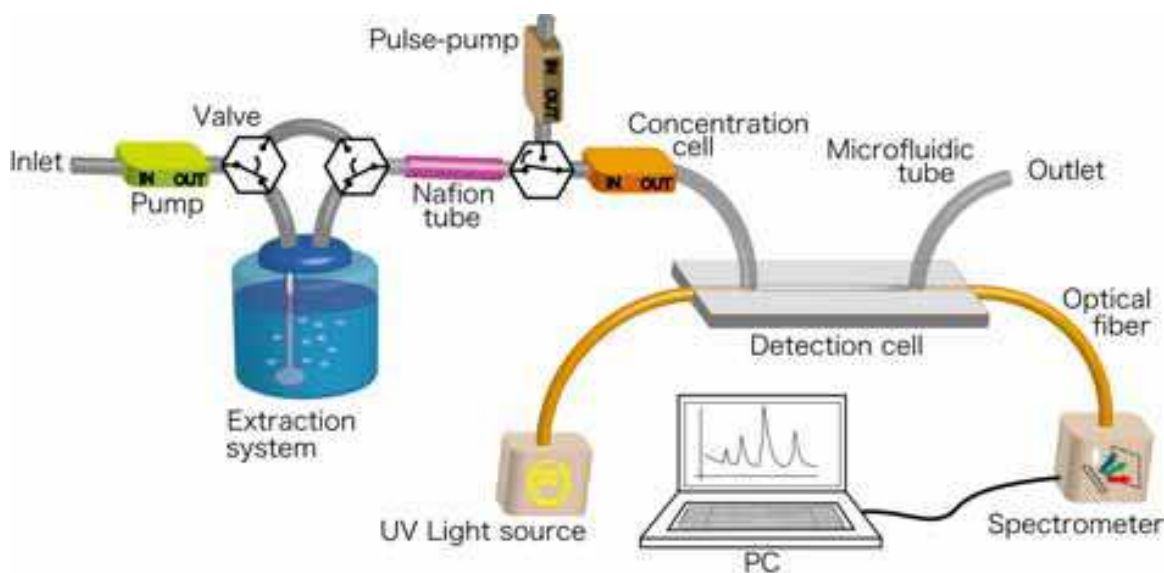

Fig. 8. Schematic view of the high-sensitivity aqueous benzene sensor with an extraction, concentration, and detection stages.

Adsorbent

Over the past few years, several compounds have been investigated as potential adsorbents for air monitoring system: MCM-41, SBA-15, and SBA-16 as mesoporous silicates, and ZSM5

as zeolite. Mesoporous silicates offer huge surface areas, large pore sizes, and regular and well-ordered structures. Regarding the benzene adsorption, several papers dealing with the optimization of pore sizes via the synthesis process have pointed to SBA-16 as the best alternative (Ueno *et al.*, 2005). Meanwhile, the ZSM5 zeolite has been widely used for gas separation, including for that of volatile organic compounds, which makes it a potential adsorbent.

With benzene/ dry nitrogen calibrated gas samples, the performance of SBA-16 and ZSM5 materials as benzene adsorbent were measured under similar experimental conditions (Fig. 9). SBA-16 exhibit saturation after few minutes, while ZSM5, despite a gradual slope decrease with time, does not within the first 70 minutes. This indicates that concentration efficiency with SBA-16 is better at short concentration time, but the tendency reverses as the concentration time increases (Fig. 9).

Thus, despite a lower efficiency within the first 10 minutes of concentration time, both SBA-16 and ZSM5 remain potential candidates as adsorbents. However, SBA-16 exhibits stronger affinity to water molecules than ZSM5. Thereafter, we then exclusively used ZSM5 as adsorbing material.

Drying system

Prior to the concentration cell, we tested two passive methods based on Nafion tube technology to get rid of some of the RH content of the carrier gas. Explanations about the basic concept can be found in the product datasheet:

"When gas containing water vapor passes through Nafion tubing, the water is absorbed by and moves though the walls of the tubing, evaporating into the surrounding air in a process called pervaporation. The reaction is driven by the humidity gradient until equilibrium is reached".
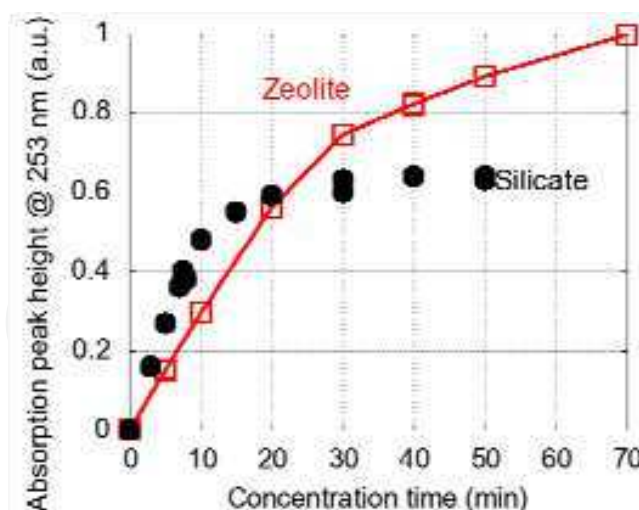

Fig. 9. Concentration efficiency at 10 ppbV calibrated gas with SBA and ZSM5 adsorbing materials versus concentration time.

The other components, such as BTX gases, are totally retained, and the benzene concentration of the carrier gas remains unaffected despite the gas's flowing through the Nafion tube. This reaction is quite fast, and a 30-cm long tube operating at flow rates of about a few ten standard cubic centimeter per minute (sccm) provides sufficient space for

reaching equilibrium at the outlet. Moreover, the Nafion tube requires no maintenance or source of energy and is resistant to most chemicals. Its robustness and maintenance-free characteristic then makes it particularly suitable for on-site experiments.

Nevertheless, this system doesn't provide any active control of the sample gas RH, and the carrier gas humidity level depends directly on the ambient RH level. All the experiments were performed in a clean-room environment, with the RH parameter effectively monitored and controlled at levels within the 45% +/ - 15% range. As a consequence, the Nafion tube leads to a decrease of the carrier gas RH from 90 to a mean value of 45% in our experiments (Fig. 10).

If more precise control of the RH is needed (such as when operating in a very humid environment, such as summer in Tokyo, Japan), similar technology, which we call a "Nafion box", enables drying of sample gas down to the dew point of -30/ -40 degree C whatever the ambient air RH is. The Nafion tube is encapsulated inside a closed container filled with desiccant (millimeter-sized spheres) that provides a dry local environment by absorbing almost all the water molecules within the container volume. Then, after reaching equilibrium, the carrier gas also exhibits a very low RH level at the tube outlet. However, this device requires regular maintenance to replace or refresh the spheres (re-activation of the used spheres by thermal desorption), which remains a significant drawback.

The two drying systems were tested and their performance compared using the same pre-concentration cell filled with zeolite adsorbent and using equivalent benzene/ water sample solution. The results did show some measurable differences, given that all the experiments were performed in a clean-room environment (RH: 45% +/ - 15%). However, the configuration with just the Nafion tube enables sensitivity levels far below the requirements, making any further improvement unnecessary. In order to get a maintenance-free set-up, we then used exclusively that set-up for the next experiments.
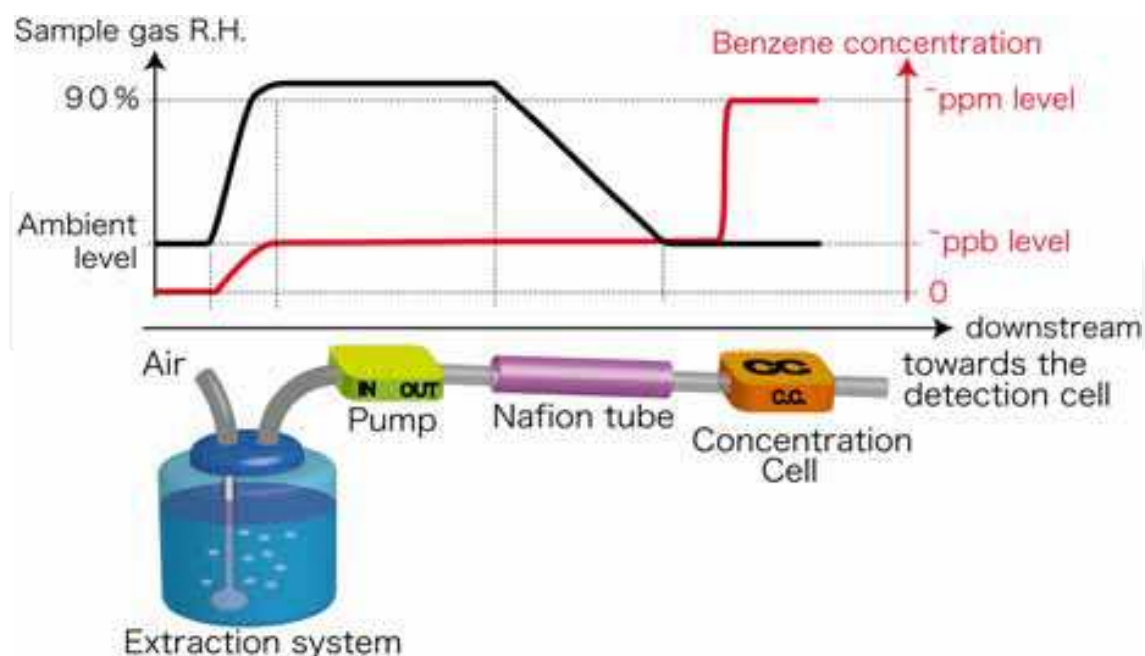

Fig. 10. Evolution of carrier gas content in terms of RH and benzene concentration along the microfluidic channel.

4. Portable aqueous benzene characterization

4.1 Sensitivity

Experiments were first performed with a 5-min concentration time and aqueous benzene concentration varying within the low ppbV range. To assess the improvement in terms of sensitivity, we plot in Fig. 11 the benzene peak absorption amplitude as function of aqueous benzene concentration for the two experimental set-ups, *i.e.*, with and without the concentration stage.

First, the concentration stage doesn't deteriorate the sensor's response, which remains linear in both cases with a comparable slope. For both set-ups, the linear range may extend for concentrations higher than those shown in Fig. 11. However, the lack of experimental data at higher concentration levels does not allow us to assess the linear range upper limit with certainty.

Furthermore, the use of the concentration stage leads to an overall shift of the response of about more than 2 orders of magnitude towards the low concentration levels. This huge improvement yields a detection limit of about 300 pptV, which is five hundred times below the previously reported LOD and more than ten times below the regulatory levels in both Japan and America (11 and 5 ppbV respectively).

In summary, the concentration cell leads to subsequent sensitivity improvement that enables us to clear the drinking water regulatory levels, while the response remains linear over more than two orders of magnitude. Furthermore, due to the 5-min concentration time, one measurement takes less than ten minutes, including all the steps required to calibrate the spectrophotometer.
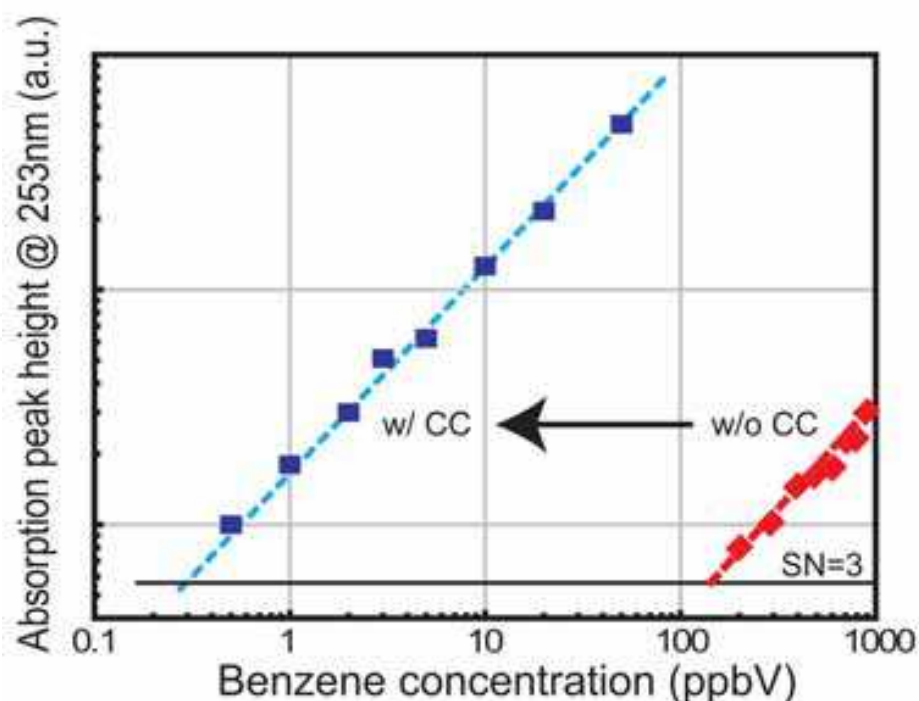

Fig. 11. Aqueous benzene sensor response around the ppbV benzene concentration range with (blue squares) and without (red diamonds) the concentration stage.

4.2 Concentration time

The previous results were all otained with a 5-min concentration time, which provides enough sensitivity improvement to clear the regulatory levels without increasing the measurement time too much. However, the concentration time directly influences the sensitivity. From a theoretical point of view, there should be a linear relationship between concentration enhancement and concentration time. However, depending on the adsorbing material, we already demonstrated saturation or a decrease of the slope as the concentration time increases (Fig. 9). A series of experiments with 4-ppbV benzene solution and bubbling extraction were then carried out to evaluate the concentration efficiency profile of zeolite adsorbent versus concentration time (Fig. 12).

As shown in Fig. 12, from 0 to 20 min., the absorption peak amplitude due to benzene compound linearly increases, pointing to a linear increase of the accumulated benzene molecule versus time. However, with concentration time exceeding 20 minutes, the signal saturates. The blue square is from the results at 4-ppbV concentration shown in Fig. 11, and demonstrates consistency between the two sets of experiments, and that increasing the concentration time within the linear range will result in linear improvement of the LOD reported earlier. We can therefore expect a further improvement of sensitivity by a factor of three, leading to a LOD down to less than 100 pptV.

In terms of the response profile, the results in Fig. 12 are quite different from those in Fig. 9. Nevertheless, the benzene concentration profile of carrier gas differs in the two cases.

Figure 13 summarizes the tendencies: with the air monitoring system, a steady carrier gas concentration leads to a gradual decrease of the concentration efficiency, while for aqueous sample, the time-dependent carrier gas benzene concentration results in saturation of the corresponding concentration efficiency. Actually, with the air monitoring system, we used
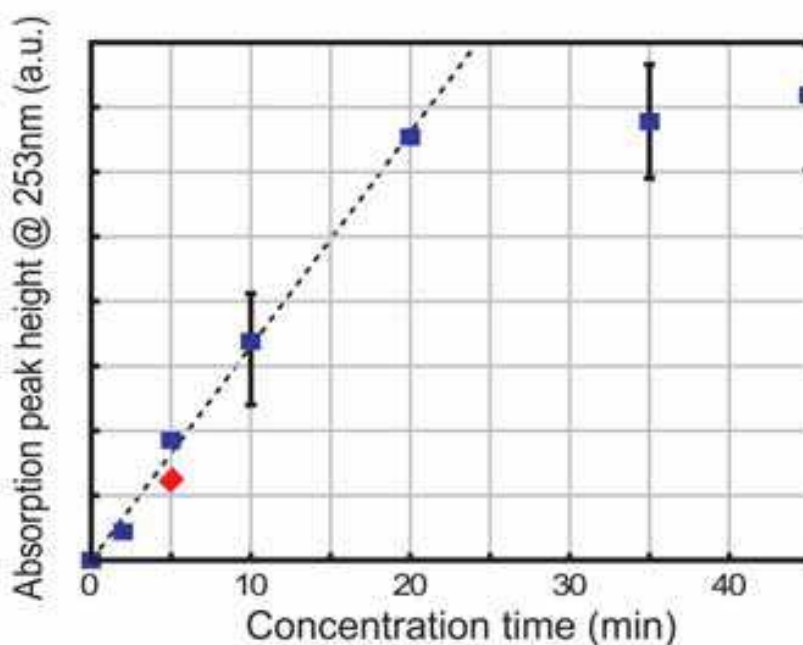

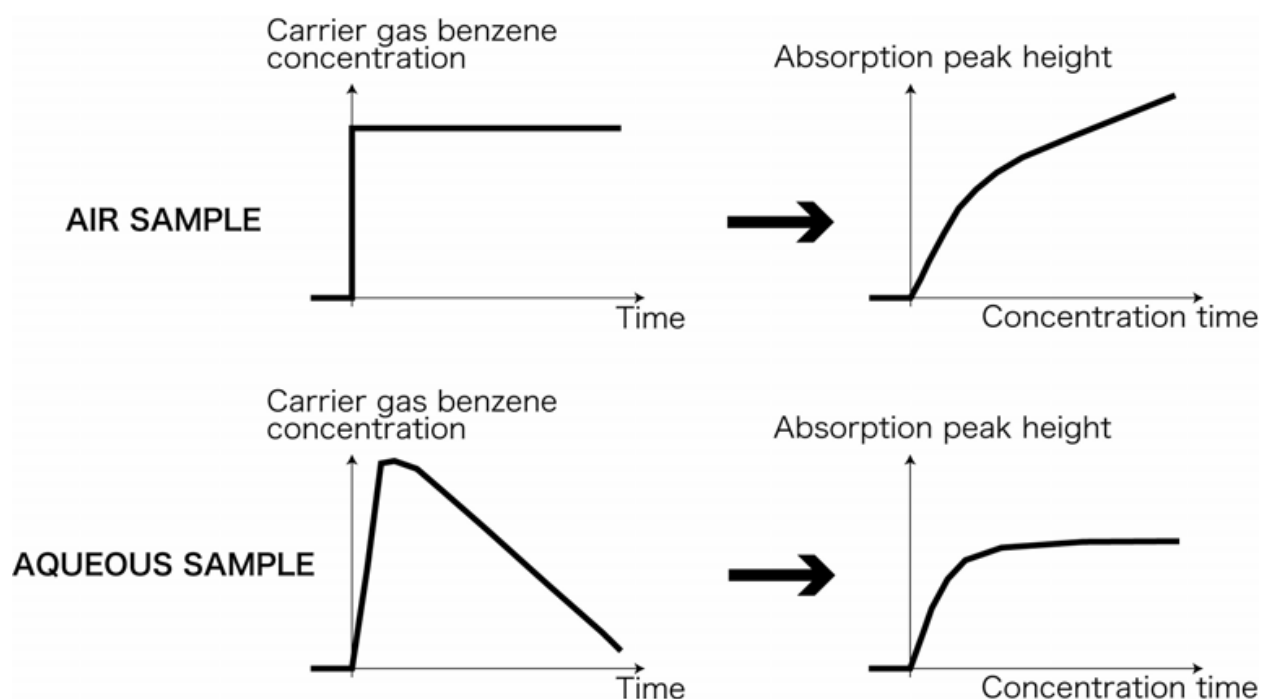Fig. 12. Concentration efficiency of a cell filled with zeolite adsorbent versus concentration time.

Fig. 13. Comparison of response of concentration cell filled with zeolite (right) for two carrier gas concentration profiles (left).

calibrated benzene sample gas mixed with dry nitrogen as the carrier gas. As a result, the RH remained very low, and the benzene concentration stayed constant during the entire measurement process. In comparison, the carrier gas RH after extraction/ passive drying tube exhibits RH levels of about 45% and the benzene concentration exhibits a time-dependent profile.

However, as explained earlier in section 3-4, drying the carrier gas after extraction to very low RH levels leads to noticeable improvement of about 20%, but it doesn't change the overall tendency. Independantly of the RH difference, the saturation with aqueous measurements then may be seen as a more drastic decrease of the slope as the carrier gas concentration also decreases with time.

4.3 Selectivity

All the results presented earlier were obtained with pure benzene solutions we prepared at desired concentrations. However, the main source of environmental contamination has been identified as gasoline pollution, where benzene toluene and xylene are mixed with other compounds. Figure 14 shows the absorption spectra of benzene, toluene, and o-xylene, as three compounds diluted in commercially available gasoline. Due to the severe toxicity of benzene, drastic regulations have been set for the benzene concentration in gasoline. Nowadays, gasoline is composed of about 5% benzene, 35% toluene, and other compounds that may include o-xylene at lower concentration levels. Therefore, the main contamination source has a toluene concentration about seven-fold higher than that of benzene on average, though toluene absorption spectrum exhibits peaks in the same area as benzene (areas in grey in Fig. 14). Nevertheless, benzene is the only compound subject to mandatory regulation and thus the only one requiring a direct measurement procedure. Theoretically, if the analysis takes into account all the reference spectra of compounds in
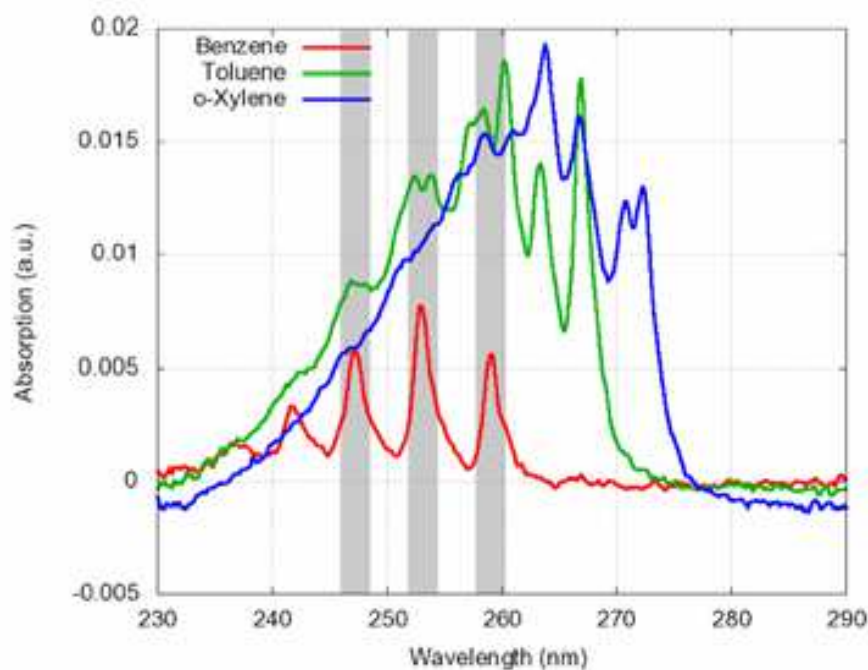
Fig. 14. Reference absorption spectra of benzene, toluene and o-xylene in the 230-290-nm wavelength range.

solution that aborb in the studied wavelength range, accurate and simultaneous quantitative measurements of several compounds from one spectrum should be possible. However, in practice, such a database of reference spectra including all potential contaminants remains an ideal, making the separation efficiency a valuable characteristic. By analogy with, for example, the gas chromatographic column prior to mass-spectrometer, efficient separation should bring to the detecting area all compounds successively, one by one, preventing overlap and interference between two or more solutes. Thus, unidentified compounds should be separated from the compounds of interest and detection of each compound done at maximum sensitivity, despite huge variation in concentrations among all the solutes.

Our sensor is composed of extraction and concentration stages, which may both result in selectivity. Nevertheless, the selectivity coming from the concentration cell remains negligible due to our thermal cycle characteristic. In our experiments, we quickly heated the adsorbent to temperatures far above the level at which benzene desorption occurs. This procedure then guaranties the best sensitivity because all of the adsorbed molecules are released simultaneously, within as small a carrier gas volume as possible. However, the three BTX compounds exhibit quite close desorption temperature. As a result, despite a chromatographic desorption process for adsorbed molecules, the fast increase of temperature yields the almost simultaneous release of adsorbed BTX compounds, cancelling the chromatographic effect. In what follows, we therefore focus exclusively on the bubbling extraction method.

Measurement of a benzene/ toluene/ o-xylene solution in water at 0.45/ 3/ 3 ppmV concentrations, respectively, was then performed without any concentration stage (Fig. 6).

Figure 15 shows the first eight consecutive output raw spectra. The response exhibits the typical "bubbling-like" profile as mentioned previously (Fig. 7), with an initial rapid increase followed by a constant and slow decrease of the absorption amplitude.
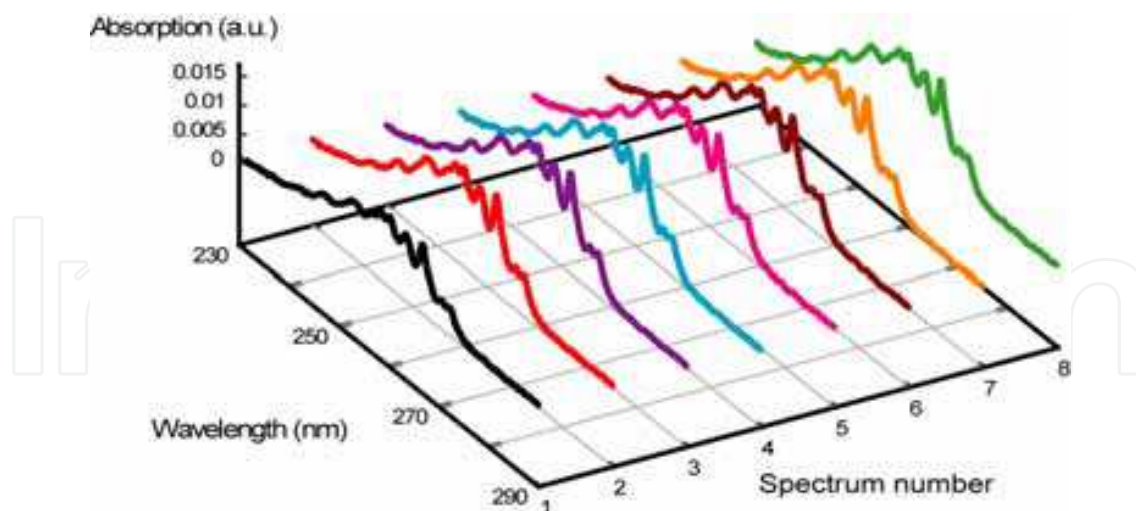
Fig. 15. Raw absorption spectra versus time with bubbling extraction.

In order to evaluate the contribution of each compounds independently, we then performed manually a fit of the experimental data from the reference spectra shown in Fig. 14 weighted by coefficients. Thus,

$$RawSpec = a.BenzRS + b.TolRS + c.oXylRS \qquad (1)$$

where *RawSpec* stands for the raw output spectrum, *BenzRS*, *TolRS,* and *oXylRS* for reference spectra of benzene, toluene, and o-xylene, respectively, and *a,b,* and *c* are linear coefficients determined manually.

Results corresponding to the third spectrum are summarized in Fig. 16, which includes three different graphs: the experimental data and the spectrum built from the fitting process (top); the experimental raw data and the three BTX contributions pondered by fitted coefficients and plotted separately (middle); the experimental data and the spectrum built from the fitting process without the benzene contribution (bottom).

As shown in top graph of Fig. 16, we could reach a good correlation between the experimental spectrum and the reconstructed one obtained from the manual fitting procedure. Despite the noise background slightly diverging at higher wavelenght, the two curves are almost perfectly super-imposed in the peak area.

When the three contributions from the reconstructed spectrum are plotted separately (middle, Fig. 16), the benzene contribution remains comparatively low, with a ponderation coefficient approximately six times lower that those of toluene and o-xylene. This ratio is similar to the concentration differences between the three compounds at which the sample solution was prepared. Furthermore, the same procedure has been utilized with later output spectra (not shown). It was found that despite an overall decrease of the absorption peak amplitudes as the spectrum rank increases, the ratio between the three compounds from the manual fit remains constant. With the exact same extraction profile for the three compounds (tendancy similar to Fig. 7 and amplitude proportional to the compound concentration in the feed solution), this extraction method provides no specificity and operates with the same efficiency on the three BTX compounds.
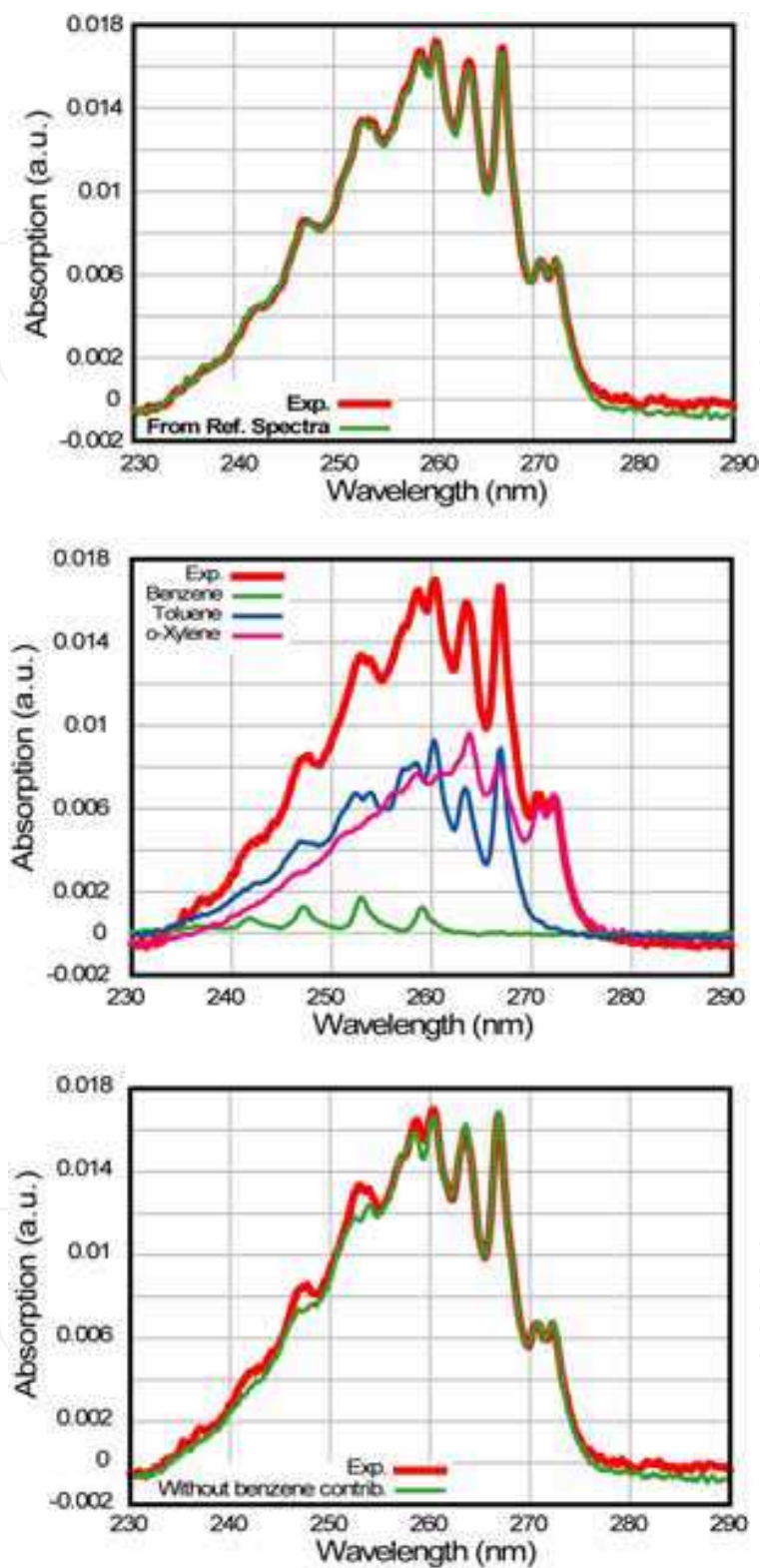
Fig. 16. Estimation of the respective contributions of benzene, toluene, and o-xylene for the third spectrum with bubbling extraction.

When removing the benzene contribution from the reconstructed spectrum (bottom, Fig. 16), the two curves slightly and locally diverge, but the difference remains quite small

compared to the overall signal amplitude and shape. The overlap of absorption bands, especially between benzene and toluene, leads to interference that can potentially disturb the precise estimation of benzene contribution. In practice, determination of benzene still remains possible, but the task may be quite difficult due to the background level (background including toluene at a concentration seven-times higher) and potential interference from unknown compounds dissolved in the feed solution.

5. Summary and future work

We described in this chapter a portable aqueous benzene sensor that combines bubbling extraction and concentration and detection stages. The bubbling module extracts several compounds simultaneously from the liquid to the vapor phase, while the performance of the concentration stage prior to detection cell leads to high sensitivity. We then demonstrated a LOD about 300 pptV, far below the requirements with a ten minutes measurement time. Furthermore, the sensor response remains linear over more than two orders of magnitude. Systematic studies of concentration time also demonstrated that this sensor allows some flexibility for finding the appropriate compromise between sensitivity/ measurement time depending on the application requirements. All the measurements were performed in a controlled atmosphere with RH levels of around 45%. When the RH of ambient air may become ploblematic, the moisture exchanger tube should be replaced with the drying box, which provides active and efficient control over the carrier gas RH. Though a system with the drying box requires more often maintenance, it provides a sensor unit the proper on-site conditions without any limitation in terms of ambient air RH. The sensor then represents a potential alternative to bulky standard equipment as an on-site early alert system.

However, some issues remain for future development of our sensor. As discussed earlier, considering the main contamination source to be a gasoline spill, the sensor should exhibit specificity in order to separate benzene and toluene at the detection stage. Thanks to the concentration stage, we have achieved LOD levels far below the requirement. The margin we got about the sensitivity allows some degree of freedom for improving the selectivity. As a consequence, another chromatographic extraction method may represent a good compromise by providing better selectivity despite worsened sensitivity, but still in the pptV range.

Regarding the final application of this sensor, we will also focus our efforts on the development of an in-line and continuous aqueous benzene extraction system. Right now, the portable sensor enables one to perform on-site high-sensitivity measurements. However, an operator must still take a sample of the liquid and transfer it to the extraction tank, as is the case for measurements based on standard techniques. Due to the limited number of skilled operators and the huge number of sites to be monitored, the frequency of benzene monitoring is calculated from previous measurement campain results and the potential risk/ impact of a benzene contamination. As a consequence, the time between two consecutive measurements at a specific site may vary from days to months. In order to detect benzene contamination at a very early stage, a drastic reduction of this delay is a real need that only continuous and operator-free measuring devices can fulfil. A sensor combining high-sensitivity with continuous measuring sequence may then result in significant advances towards the supply of safe drinking water.

7. Acknowledgments

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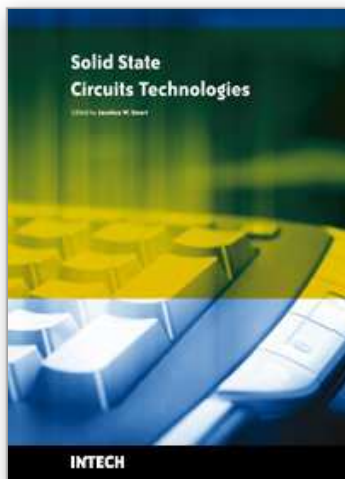
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The evolution of solid-state circuit technology has a long history within a relatively short period of time. This technology has lead to the modern information society that connects us and tools, a large market, and many types of products and applications. The solid-state circuit technology continuously evolves via breakthroughs and improvements every year. This book is devoted to review and present novel approaches for some of the main issues involved in this exciting and vigorous technology. The book is composed of 22 chapters, written by authors coming from 30 different institutions located in 12 different countries throughout the Americas, Asia and Europe. Thus, reflecting the wide international contribution to the book. The broad range of subjects presented in the book offers a general overview of the main issues in modern solid-state circuit technology. Furthermore, the book offers an in depth analysis on specific subjects for specialists. We believe the book is of great scientific and educational value for many readers. I am profoundly indebted to the support provided by all of those involved in the work. First and foremost I would like to acknowledge and thank the authors who worked hard and generously agreed to share their results and knowledge. Second I would like to express my gratitude to the Intech team that invited me to edit the book and give me their full support and a fruitful experience while working together to combine this book.

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