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Rapid and reversible adsorption of BTX on mesoporous silica thin films for their real time spectrophotometric detection in air at ppm levels

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Abstract

Benzene, toluene and xylenes (BTX) are among the most toxic volatile organic compounds that can be emitted into the environment of different workplaces. Regulations to protect workers continue to strengthen permissible exposure limit (PEL), and short-term exposure limit (STEL) for any 15-minutes period are defined for BTX that should be controlled with rapid, selective and sensitive on-site sensors. For that purpose, a real-time analysis of BTX is described here, using the UV spectrometric determination of instantaneously concentrated pollutants in a thin film of mesoporous and transparent silica deposited onto quartz plates. A new optical cell has been designed to achieve the lowest detection limits, up to the ppm level in air for benzene, toluene and p-xylene. The sensor was equipped with an air dryer to detect BTX in the presence of humidity and major interfering volatile organic compounds (acetone, ethanol, butanone and cyclohexane). The sensor has detection limits below defined PEL and STEL for benzene, toluene and xylenes. The adsorption properties of BTX on the sensor surface were quantitatively analyzed using the Freundlich equation, showing the singular behavior of benzene adsorption on the surface of silica relative to toluene and p-xylene.

Keywords

VOC, benzene, toluene, xylene, BTX, mesoporous silica, UV absorption

Introduction

Benzene, toluene and xylenes (BTX) are among the most toxic volatile organic compounds (VOCs) that are widely found in industrial environments. A large number of manufacturing processes and uses involving petrol and fuels, varnishes, paints, rubber, solvents, chemicals can be sources of these volatile compounds. The first regulation dealing with work places air quality appeared more than three decades ago. Nowadays, the legislation defined permissible exposure limit (PEL) and short-term exposure limit (STEL) for benzene, toluene and xylenes (see Table S1, the limits defined by the Occupational Safety & Health Administration – USA and European Union).

STEL imposes a rapid detection whereas the low permissive levels at long time exposure impose a sensitive detection (down to 1 part per million of air for benzene). Methods and techniques allowing detection at very low levels are described in the literature, most of them are based on active or passive adsorption/pre-concentration on sorbent material followed by thermal or solvent desorption and chromatographic analysis [1–3]. In most cases, the analysis is not taking place in situ and the delays necessary to deliver the results are typically ranging from a couple of hours to days, even when short sampling times are used.

The development of portable devices allowing on-site detection is thus the subject of many studies. Sensors based on metal oxides semiconductor properties variation during adsorption of BTX gave rise to recent works [4,5]. Semiconductor sensor based on Cr-doped NiO hierarchical nanostructures [6] allowed to detect 5 ppm xylenes or toluene without significant cross response of 5ppm benzene, formaldehyde, ethanol, hydrogen, and carbon monoxide, respectively. However, the detection of benzene in the presence of other aromatic molecules is not shown. Quartz crystal microbalance (QCM) sensors based on adsorption on pentacene was recently proposed to reach the sensitivity criteria and to allow to distinguish the responses of the separated analytes [7]. Functionalized SBA-15 mesoporous silica functionalized with

4,4'-diaminodiphenyl sulfone-based was deposited on a QCM sensor, allowing the detection of toluene down to 20 ppb [8]. Cavitand molecules were also designed as selective adsorbent and were implemented in a micro-electro-mechanical system (MEMS) coupled to a photoionization detector (PID) detection. It allowed very sensitive detection in a short time but no selectivity was experimentally demonstrated [9]. Differential ion mobility spectrometry (DMS) is also capable of detecting very low amounts of BTX, pattern recognition for benzene, toluene or xylene in filtered air containing various amount of water vapor have been recently published [10,11]. Excellent sensitivities are often demonstrated, but the efficiency in the presence of humid air is often diminished and the selectivity of the detection of BTX in the presence of other pollutants is not always demonstrated. Moreover the ability to determine one of the BTX in the presence of another BTX is not reported.

The experimental strategy we adopted to reach sensitivity, selectivity and reversibility is to concentrate the pollutant by adsorption on a transparent solid and to detect it simultaneously by in situ UV spectrometric determination (i.e., there is no desorption step). The principle of such experiment has been described before [12] and was initially developed for BTX detection using a transparent mesoporous silica monolith (~2 mm thick) as sorbent. This approach allowed the detection of very low BTX concentrations, however, the pollutant adsorption was found to be non-reversible over a short time scale (less than 3 minutes), making this approach unsuitable for real time sensing [13]. A reversible detection of BTX was later reported, using mesoporous silica thin disks displaying bigger pores [14]. In a previous study, we considered films made of mesoporous silica nanoparticles [15]. The low thickness, less than 4 μm , and the high inter and intra-particle porosities of the film allowed to obtain rapid responses and the sensor was regenerated in less than 30 s. Cyclohexane had no effect on the BTX detection while polar organic molecules (ethanol, butanone, and acetone)

increased the signal. Removing humidity using an air drier was shown to allow the detection of toluene in air initially humid.

The aim of the present report is to demonstrate that real time analysis can be achieved with this approach (preconcentration in porous silica and UV spectrometric determination), even in the presence of interfering pollutants, and to estimate the detection limits that can be achieved. We have considered mesoporous silica thin film (150-250 nm thickness) deposited on quartz plates to concentrate instantaneously and reversibly the BTX molecules. A new optical cell was designed and built in order to improve the sensitivity of the sensor. Adsorption properties of BTX in the mesoporous silica were analyzed quantitatively.

Experimental section

Chemicals

Tetraethoxysilane (TEOS, 98%), cetyltrimethylammonium bromide (CTAB $\geq 98\%$), hydrogen chloride (37%), anhydrous pure toluene (99.8%), benzene (99.8%), p-xylene(99%), cyclohexane (99.5%), butanone ($\geq 99\%$), anhydrous ethanol ($\geq 99.8\%$) and acetone ($\geq 99.9\%$) have been used as received from Sigma Aldrich-France.

Thin film elaboration

The experimental protocol to obtain the thin films is based on a previously reported protocol from Grosso et al [16]. Briefly a sol is prepared by mixing TEOS:CTAB:ETOH:H₂O:HCl (mol to mol ratio 1:0.14:20:5:0.004, respectively) and allowed to age for 4 days under stirring. The resulting sol has been dip-coated on 8x9x1 mm quartz plates with 2 mm s⁻¹ withdrawal speed maintaining the relative ambient humidity at 50%. Quartz plates have been cleaned with ethanol and treated with sodium hydroxide and dried at 130°C prior the deposition. Curing for 2 days at 130°C is followed by a calcination for 4 hours at 450°C. The film was characterized by TEM (Figure S1) which revealed a well-defined mesostructure. The film

thickness determined by profilometry was between 150-250 nm. 78-90% of transmittance was observed for one modified plate (i.e., two films, one on each side, Figure S2, curve b) in the wavelength range 190-400 nm and more than 15% in the same wavelength range for 5 plates (i.e. 10 films, Figure S2, curve c).

BTX detection

The setup allowing BTX detection is illustrated in Figure 1 (left). The films were continuously exposed to UV light emitted from the D2000 Oceanoptics source. The signal intensity was followed by the Oceanoptics QE65000 spectrometer every 25 ms and an average spectrum was saved every 5 s. Two chambers (42.5 L and 5.8 L) were used for the generation of the synthetic air with controlled amount of BTX. The flow circuit was built with Teflon® tubes. During the analysis, the pump was delivering a flow rate of 0.1 L min⁻¹, and the flow was adjusted to 4.7 L min⁻¹ for the regeneration of the adsorbent with a second circuit.

Two measuring cells have been used. The first one, which had already been described in a preceding paper [15] was composed of two brass blocks in which a slot was incised in order to introduce the quartz plate, the second one, designed and built for this study holds at the same time 5 plates spaced by 1 mm (Figure 1B). In both cases, the zero absorbance value is the one obtained with the plate(s) coated with the thin film before any exposure to BTX.

Calibrated SnO₂ detectors at the input and output of the measuring cell allow to control the accuracy of the amounts of pollutant flowing in the measurement cell and to ensure that it was the same as the one generated (controlled by a PID detector in the generation chamber).

A portable air dryer (PDseries-50 tubing- and 30 cm length, Perma Pure LLC, USA) has been added in the setup between the generation chamber and the measurement cell in

order to remove the humidity from the air to be analyzed before it enters the measurement cell.

Results and discussion

Validation of the sensor for toluene detection in humid air

The BTX sensor is described with a simplified scheme in Figure 1A. A quartz plate modified with mesoporous silica allowing BTX adsorption was introduced in a cell that was designed for allowing at the same time the flow of the air to be analyzed and the measurement of UV light absorption by chemical species adsorbed in the mesoporous silica. First, experimental evaluation was done with a cell allowing analysis with a single quartz plate modified with mesoporous silica. Another cell allowing the use of five plates (Figure 1B) was later used for improving the analytical performances of the sensor.

Due to its low toxicity and its simplicity (no isomers) toluene was considered all along this work as a BTX model. Once optimized, the experimental setup and methods were tested for their ability to determine benzene and xylene.

Detection of BTX at ppm level is not that difficult in the absence of any interfering molecule, and this can be achieved with SnO₂ sensors that were introduced in the setup for controlling the accuracy of the concentrations of pollutants. However, in the working environments where BTX are potentially present, water is always present in a relatively large amount compared to the BTX. Indeed, 50% of relative humidity under atmospheric pressure corresponds to 11700 ppm of water at 20°C, *i.e.* four to five order of magnitude higher than the concentration of BTX. Thus, a great attention was first paid on the effect of water on toluene detection.

The principle of the sensor that is evaluated here is to concentrate rapidly the pollutant by reversible adsorption on the mesoporous silica surface and, simultaneously, to detect it by absorption spectroscopy. Figure S3A shows the typical spectrum that can be obtained by the

sensor in the presence of 20 ppm toluene, in dry air. An absorption signal is observed between 230 and 280 nm when toluene molecules are adsorbed on the mesoporous silica layer. The signal to noise ratio may appear poor as shown in Figure S3A. Indeed, the complete spectrum was acquired for the need of the demonstration, but this is not necessary for the application of the sensor for which the acquisition can be limited to several wavelengths with a longer spectrophotometric acquisition time, that allows reducing the noise. The influence of water on toluene detection is shown in Figure S3B. The sensor was exposed to 20 ppm toluene in a synthetic air with 50 % relative humidity. A signal is still discernable, but its intensity was decreased dramatically, at a level that makes impossible the quantification of toluene. A strategy that has been successfully used before implies the removal of water by an air dryer before it comes in contact with the sensor [15]. Figure S3C shows the application of the air dryer on the toluene detection. Air with toluene and water was flowing through the air dryer before to enter the detection cell of the sensor (as it is shown in Figure 1A). An absorption peak is observed between 230 and 280 nm, which indicates that the detection of toluene is well recovered when air is pretreated with the air dryer. In the next steps of this study, air dryer is always applied for pre-treating the air that is analyzed. We compared the repeatability of the sensor response to 20 ppm toluene by preparing two batches of sensors and testing them 1) in dry air and 2) in humid air with an air dryer. The standard deviation is found similar, close to 10 % of the sensor response, for the two batches of sensors and no significant difference is observed between the two conditions of measurement (Figure S4).

Validation of the sensor for toluene detection in the presence of other VOCs

Other volatile species may also be found in the workplace, that can interfere with the detection of BTX [17,18]. In this work we limited the interference study to the VOC likely found together with BTX in real situations, i.e. ethanol, acetone, butanone and cyclohexane. First, we evaluated the influence of the air dryer on the removal of polar (ethanol, acetone and

butanone) and non-polar molecules (cyclohexane). The sensor response to successive exposure of the to 20 ppm toluene, and 40 ppm of ethanol, acetone, butanone and cyclohexane is shown Figure 2. The setup was also equipped with SnO₂ sensors that are very sensitive sensors but lack selectivity. When UV and SnO₂ sensors are exposed three times to toluene, this BTX is detected on both sensors, with an absorbance increasing from 0 to 0.01 with UV detection at 267 nm, and the response of SnO₂ sensor increasing by 0.9 V in the presence of toluene. On the contrary, no signal was detected when the sensors were exposed to air containing 40 ppm of ethanol, acetone and butanone. These three molecules give a signal with SnO₂ or UV detection (see Figure S5 for an illustration of their UV detection). In fact, the air-dryer used to eliminate water, is also eliminating very efficiently these polar molecules from the air while toluene is kept at the same concentration. Cyclohexane is a non-polar molecule that cannot be eliminated by the air-dryer. For this reason, it is easily detected at 40 ppm by the SnO₂ sensor. This molecule is thus a major interfering species of SnO₂ detection. At the opposite, since cyclohexane does not absorb light in the UV range, it does not interfere with the detection of toluene.

To finalize this evaluation, the spectroscopic detection of 20 ppm toluene was performed in the presence of 40 ppm of ethanol, acetone, butanone and cyclohexane using the air dryer. Figure S6 depicts the relative sensor response to toluene and toluene with other VOC. The variability observed between the different experiments is included in the experimental error observed for each experiment, demonstrating that toluene detection is not significantly affected by the presence of ethanol, acetone, butanone and cyclohexane, when the air dryer is used to pre-treat the air before it is analyzed.

Sensor LOD and LOQ

Initial attempts to detect BTX were performed with a single quartz plate led to limit of detection of 2 ppm, 10 ppm and 1 ppm for toluene, benzene and p-xylene, respectively. While

these values are sufficient for reaching PEL and STEL reported in Table S1 for toluene (50 to 300 ppm) and p-xylene (50 to 100 ppm), it is still far from the benzene concentrations that have to be monitored (1 ppm for PEL and 5 ppm for STEL). In order to increase the sensitivity of the sensor, we built a detection cell with 5 quartz plates, covered on both sides by mesoporous silica. Figure 3 reports the continuous detection of toluene from 1.1 to 196 ppm. The spectra show clearly the presence of toluene (Figure 3A) and continuous measurement of absorbance allows to build a calibration curve over a wide range of concentration (Figure 3B). The same experiment was performed with p-xylene (Figure S7) and benzene (Figure S8 and S9). The detection limits were evaluated using 267 nm for toluene detection, 274 nm for p-xylene detection and 252 or 190 nm for the detection of benzene. In these conditions, the detection limits reached 1 ppm for all three molecules (Figure S9).

Time response of the sensor

The sensor response is very rapid. Figure S10 shows the comparison in time response of a SnO₂ sensor and the spectroscopic sensor developed here, when the concentration of toluene was changed from 0 to 1.3 ppm, from 16 to 22 ppm and from 187 to 237 ppm. For these three ranges of concentrations, the time response of the SnO₂ sensor and of the spectroscopic sensor is comparable. These series of experiments show that the response of the spectroscopic sensor is not limited by adsorption phenomenon in the mesoporous layer, and that the temporal dynamic of the sensor is mainly governed by the mass transport of the pollutant in the fluidic from the source of pollution (that is here generated by us) to the sensor. 90 % of the response is reached in 40 s, whatever the concentration range (Figure S11) and should be easily reduced by reduction of the tubing length between the pint of air collection and the measurement cell. The sensor allows thus a continuous monitoring of BTX in complex environments.

Non-linearity of the sensor

We further analyzed the sensor response. Each plateau of the incremental curves given in the Figures 3, S7 and S8 gives the absorbance value at a given concentration. These values are plotted in Figure 4 as a function of the concentration. The molar extinction coefficient of the adsorbed species are not known, which means that the adsorption isotherms cannot be rigorously established. Nevertheless, we can assume that the Beer-Lambert law is valid, and that the reported values are proportional to the number of mole adsorbed. We can see that the sensor does not give a linear response as a function of the BTX concentration. Fitting these curves is not possible with a straight line or a Langmuir equation, and the equation derived from the Freundlich model must be considered. Only the α may be discussed since, in this equation, K is a function of the molar absorption coefficient which is depending on the species.

$$A = \frac{K(P/P_0)^\alpha}{1+K(P/P_0)^\alpha} \quad (\text{equation 1})$$

α value coming out from the nonlinear least square analysis is higher than 1 for benzene, indicating a cooperative adsorption, and lower than 1 for toluene and p-xylene (isotherms shown in Figure 6). Thus, the adsorption of benzene differs from the adsorption of toluene or p-xylene. In a previous report, in which the adsorbing layer was a self-assembled film of mesoporous nanoparticles displaying both intra-particle and inter-particle porosities, this phenomenon was attributed to a heterogeneity in the adsorption sites energy. Here, the adsorbing material is very well defined and its porosity is unique, so this interpretation must be discarded. In fact, adsorption of benzene is very limited on silica surface, and the observed heterogeneity comes from a higher interaction of benzene with benzene than with silica.

Conclusion

The selective and sensitive detection of BTX in air was investigated. The use of thin transparent films of mesoporous silica supported on quartz as adsorbing material, together with an online air drier and a multi-plate detection cell allowed to determine BTX in real time at levels as low as 1 ppm, suitable for STEL monitoring according to the existing legislation. No significant interference of polar (water, acetone, ethanol, butanone) and non-polar (cyclohexane) molecules was observed. The next steps in this development is a miniaturization of the all device and a detailed study of complex mixture of BTX with chemometric approaches before field application.

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Figure captions

Figure 1. (A) Schematic representation of the setup for detection of BTX in air and (B) drawing of the 5 plates cell containing the sensing material.

Figure 2. (Top) Absorbance and (Bottom) SnO₂ sensor response measured in the presence of (A&B) 20 ppm toluene, (C&D) 40 ppm ethanol, (E&F) 40 ppm acetone, (G&H) 40 ppm butanone and (I&J) 40 ppm hexane.

Figure 3. (A) UV spectra recorded in the presence of toluene at 1.1 ; 2.2 ;3.3 ; 4.4 ; 5.5 ; 6.6; 7.7; 13.2 and 18.7 ppm from bottom to top and (B) Absorbance at 267 nm measured with time in the presence of toluene from 1.1 to 196 ppm.

Figure 4. Influence of the concentration of (a) benzene, (b) toluene and (c) p-xylene on the absorbance measured at (a) 252 nm, (b) 267 nm and (c) 274 nm. The line is representative of the best fit with equation 1 (adjusted parameter in Table S2). All measurements have been performed with the same multi-plate sensor.

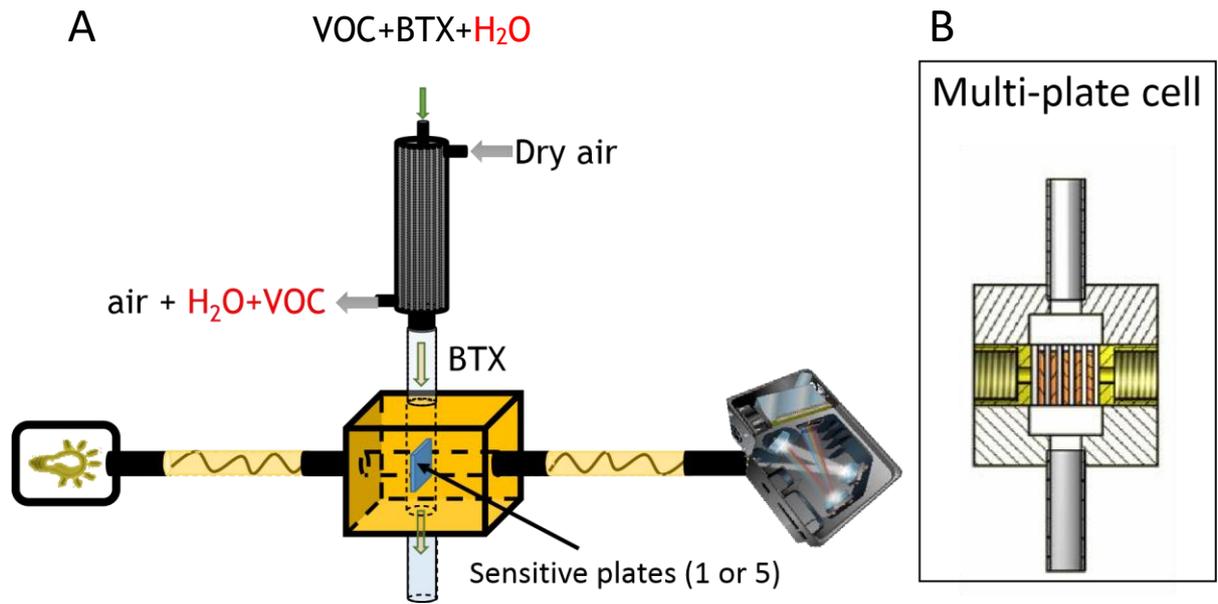


Figure 1

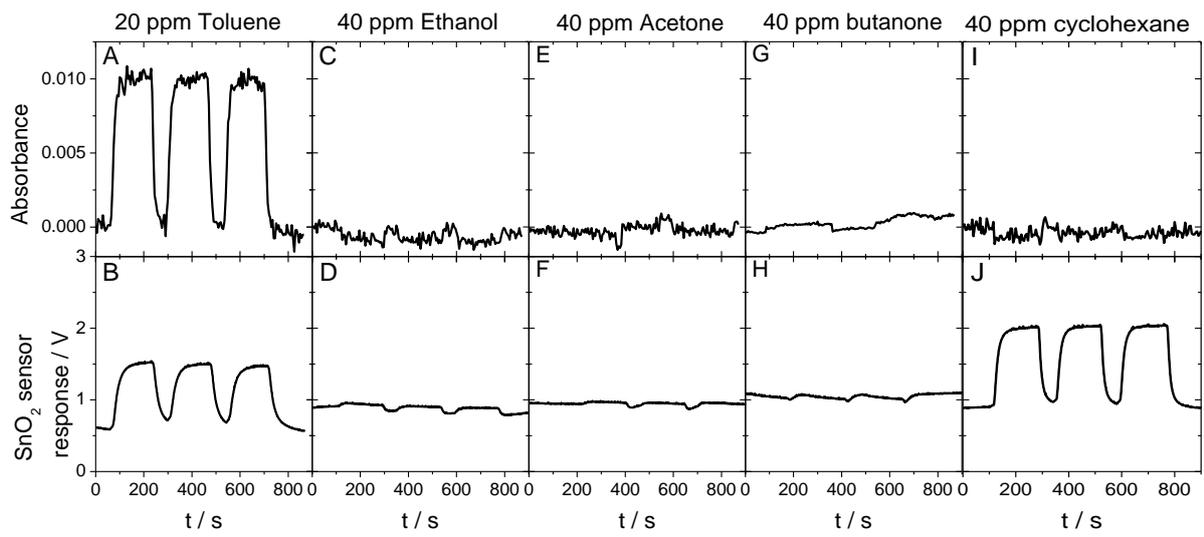


Figure 2

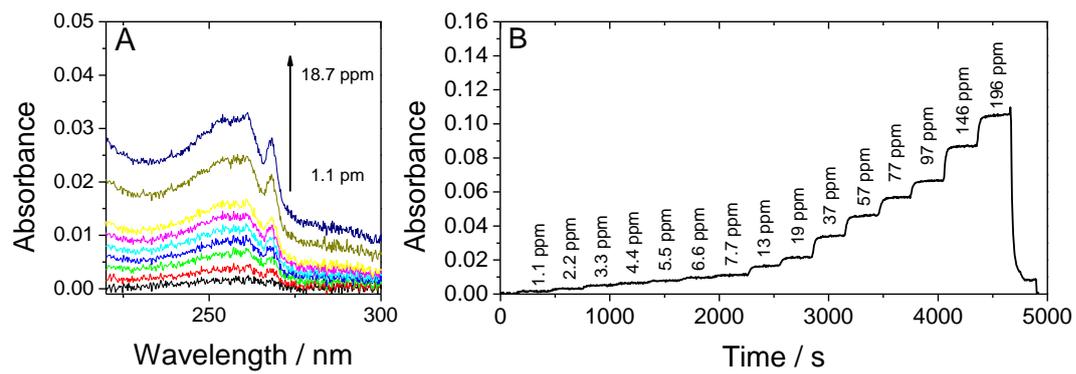


Figure 3

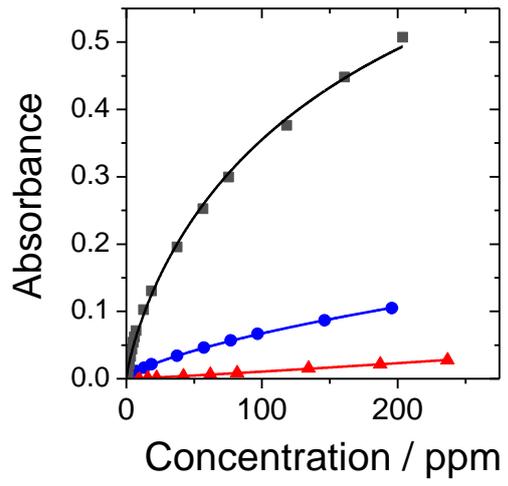


Figure 4

