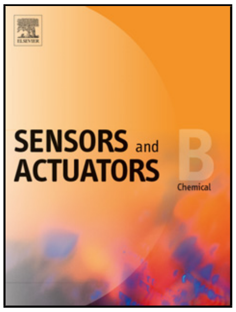

Title: Photoionization-ion mobility spectrometer for non-targeted screening analysis or for targeted analysis coupling a Tenax TA column

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Photoionization-ion mobility spectrometer for non-targeted screening analysis or for targeted analysis coupling a Tenax TA column

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Abstract

Photoionization-ion mobility spectrometer (UV-IMS) can be used as a screening instrument to distinguish gasoline vapors from other similar samples, obtaining characteristic fingerprints in a quick and simple analysis. A non-targeted approach can be used to resolve many problems, moreover, this device can also be used for targeted analysis. In this case a Tenax TA trap was connected to the UV-IMS as a pre-separation step in order to identify compounds present in the gasoline gaseous sample, such as benzene and toluene. Firstly, target analytes were trapped in a Tenax TA column at ambient temperature and then they were desorbed thermally in an oven and connected to the UV-IMS for their analysis. Instrumental parameters such as temperature ramp, sample gas flow rate, drift gas flow rate, adsorption time and adsorption flow rate were optimized to obtain high sensitivity, selectivity and precision to determine benzene and toluene in vapour gaseous samples. The UV-IMS was calibrated with standard gases generated in an exponential dilution flask, obtaining a limit of quantification of 1.8 and 1.9 mg m^{-3} for benzene and toluene, respectively. The method developed was successfully applied to identify these analytes in air samples close to a gasoline spillage.

Keywords: gaseous samples, screening, ion mobility spectrometry, Tenax TA trap.

1. Introduction

Indoor and outdoor air monitoring and measurement of air pollutants are vital for evaluating people's health and maintaining a healthy environment [1]. The development of a selective and sensitive analytical method to monitor volatile organic compounds (VOCs) in vulnerable areas with high level of VOCs is needed [2]. Benzene, toluene, ethylbenzene and xylene; known as BTEX, belong to the aromatic carbonyl group of volatile organic compounds [3]. BTEX compounds are concentrated in outdoor environments near industrial areas, next to petrochemical facilities [4] and in gas stations or parking areas [5]. BTEX are toxic compounds that even with exposure to small quantities may result in damage to human health [6]; diseases such as cancer and chronic respiratory disorders are reported [7] due to exposure to these compounds. Benzene and toluene are the two main analytes in this group, since benzene is classified in group 1 (human carcinogen) according to the International Agency on Research and Cancer (IARC) classification. Method 1501 of the National Institute for Occupational Safety and Health (NIOSH) states that gas chromatography-flame ionization detector (GC-FID) is the official instrument to measure BTEX compounds from air samples, hence most recent works use this technique [8] and also GC-MS [9] for the determination of BTEX in air.

The main disadvantage of using GC-FID is that measuring cannot be performed in-field and in some situations the possibility of obtaining measurements in real time is necessary. For this reason, the use of a sensor which can set off an alarm in the event of a high concentration of BTEX is needed and this device could prevent some catastrophes. Ion Mobility Spectrometry (IMS) has already been used as a sensor to assess air quality. Moreover, it is a powerful tool for measuring BTEX in air samples [10] both quantitatively and qualitatively. IMS, with its advantages in operating under atmospheric pressure, its portability and detecting analytes presented in low concentration [11] along with performing relatively fast analysis, make it a promising technique in the field of environmental analysis. By contrast, the main drawback of IMS is the low resolution [12] for identifying individual signals for each component of a mixture. Selectivity can be enhanced by using a pre-separation step based on thermal desorption in order to resolve different components prior to IMS analysis [13].

In this work, Tenax TA, a widely used adsorbent for air analysis, was selected as a suitable alternative for improving the selectivity of the UV-IMS method. Target analytes in gaseous samples were retained in this sorbent and then thermal desorption was performed prior to its analysis by UV-IMS. The main advantage of this sorbent is that it has no chemical reaction with ozone, thus it is considered as inert to any sample compounds [23]. Tenax TA has been used previously as an adsorbent trap, combined with IMS, to retain pentan-2-one from liquid standards [14], aldehydes from olive oil [13], tert-butyl ether from water samples [15] and microbial biomarkers from air samples [16]. Also Tenax TA was used with Carbotrap in a sorbent mixture to determine cadaverine and putrescine from permeation tubes [17]. However, as far as we know, it is the first time this material has been used *in situ* to retain benzene and toluene present in air samples, and determined them by UV-IMS.

For all of these reasons, the aim of this work is to show the potential of UV-IMS as a portable instrument to be used as a sensor which can give a quick and a global signal of BTEX present in gaseous samples. Furthermore, when needed, the selectivity of the method can be improved by including a pre-separation step with Tenax TA to identify and quantify benzene and toluene in air samples.

2. Experimental

2.1. Chemicals and materials

Benzene, toluene, ethylbenzene and (*m*-, *p*- and *o*-) xylene were obtained from Sigma Aldrich (St Louis, MO, USA) with a purity of 99%. In Table 1 the main physical and chemical properties of the target analytes are summarized. Methanol was used for cleaning the syringe. All BTEX standards were stored in a fridge at low temperature (4 ˚C). The Tenax TA solid sorbent (2,6-diphenylene oxide) was purchased from Scientific Instrument Services (Ringoes, New Jersey, USA). An empty stainless steel column (25 cm x 0.6 cm) was filled with 1 g of solid Tenax TA. Before being used, the Tenax TA column was activated in an oven by passing N_2 gas at a flow rate of 20 mL min^{-1} at 250 ˚C for 4 hours. Blanks (flushing nitrogen through an empty vial) were carried out before each measurement. Gasoline and diesel samples were purchased from a local petrol station and heat transfer fluid (HTF) was supplied by DOW® (Edegem, Belgium).

2.2. Ion Mobility Spectrometer

The UV-IMS instrument used was supplied by Gesellschaft für Analytische Sensorsysteme (GAS, Dortmund, Germany). The instrument is 350 mm x 350 mm x 150 mm in size, with a drift tube length of 12 cm. The total weight of the instrument is 5 kg, and it uses a current supply of 230 V/50–60 Hz. The voltage applied is a constant voltage supply of 333 V cm^{-1}. The instrument is operated at ambient temperature and pressure. Purified nitrogen (N_2, 5.0) supplied by Abelló Linde (Barcelona, Spain) was used as sample and drift gas in this work. The heat unit was 5892A Chromatographic oven supplied by HP Hewlett Packard. Flow rates were controlled by using an Alltech Digital Flow Check HR™ instrument, supplied by the Chromatographie Service GmbH. Spectra were acquired in the positive ion mode. Data obtained was stored and treated with GASpector® software (Version 3.9.9.DSP from G.A.S.-Gesellschaft für Analytische Sensorsysteme, Dortmund, Germany). The length for each spectrum was 1024 points (each spectrum being formed with an average of 64 scans), the grid pulse width was 100 µs, the repetition rate was 50 ms and the sampling frequency was 30 kHz. UV-IMS conditions are summarized in Table 2.

2.3. Experimental-set up

The system used to prepare the gaseous standards was an exponential dilution flask (EDF) coupled to the UV-IMS as shown in Figure 1. 1 µL of each pure liquid standard was placed in a 1000 mL volumetric flask (V_f) using a glass syringe. Then, volatilization of liquid standards drops was achieved by heating the flask for 1 min at approximately 300 ºC using a hot air gun PHG 600-3 from Bosch, obtaining an initial concentration (C_0) (i.e. 855.7 mg m^{-3} of benzene). A heater mantle from J.P. Selecta (Barcelona, Spain) was used to maintain the temperature of EDF and ensure the homogeneity of the gases during the exponential step. In order to decrease the initial concentration, a flow of N_2 (i.e. 300 mL min^{-1}) was passed through the EDF for a specific time (i.e. 20 min), obtaining a lower concentration (C_t) in the EDF (i.e. 2.1 mg m^{-3} of benzene) by using the equation (1)

$$C_t = C_o e^{(-Ft/V_f)} \tag{1}$$

being C_o and C_t (mg L^{-1}$_{(g)}$) the initial and final concentration, F (mL min^{-1}) the flow rate of the gas, t (min) time, V_f (mL) the volume of the dilution flask.

Once the required initial concentration was reached, the switching valve was directed towards the IMS for direct analysis of the gaseous sample. It can also be directed to the Tenax TA column to start the adsorption step, as illustrated in Figure 1. Then, the retained compounds on the Tenax TA were thermally desorbed and transferred to the UV-IMS to start the measurement as illustrated in Figure 1B. The direction of the analyte desorption was the same as the direction in which they have been adsorbed on the Tenax TA. The temperature program was as follows: initial temperature 60 ˚C for 1 min, a temperature ramp of 15 ˚C min^{-1} up to 220 ˚C held for 2 min. The sample gas flow rate was 20 mL min^{-1} and the drift gas was 100 mL min^{-1}. Blanks for the UV-IMS and blank analysis to test the column were processed prior to each measurement in order to avoid carry over between samples.

2.4. Real measurements

Firstly, the proposed method was tested for measuring gaseous samples by placing 2 µL of gasoline directly into the EDF. The signal obtained in this case was compared with other similar samples, such as diesel and HTF, to check the correct selectivity of the method.

Besides this, real air samples collected from Campus of Rabanales (University of Córdoba, Spain) car parking area, in which a gasoline spillage was reproduced, were measured using the method proposed. Sampling started at midday by pouring 5 mL of gasoline 95 on the pavement in a shaded area. Meteorological conditions were recorded at the sampling site for each sample. Five air samples were collected at different time intervals by using a Tenax TA column connected to a pump & flow controller PFC-6020 supplied by Ion Explorer by Ramem IONER (Madrid, Spain), operated at 100 mL min^{-1} for 30 min. Immediately, after the sampling collection, the Tenax TA trap was placed in the oven to start the desorption of the analytes retained in the column. In this step, the Tenax TA trap was connected to the UV-IMS for its analysis at the optimized conditions.

3. Results and discussion

In this study, firstly the UV-IMS was used as a sensor for a rapid screening of air samples close to a gasoline spillage. The second step was to couple a Tenax TA column to the UV-IMS instrument to determine benzene and toluene in gaseous samples also close to a gasoline spillage. This combination resulted in an improvement of the sensitivity and selectivity of the method proposed by using UV-IMS. Ethylbenzene and xylene isomers were included during the optimization study of the proposed method.

3.1. UV-IMS as a sensor to differentiate gaseous samples

IMS can be used as a sensor for a quick analysis. 2 µL of gasoline and other similar samples, such as diesel and HTF, were placed inside the EDF to measure the volatile components of each sample. This method provides us with specific fingerprints of each type of sample which allow us to differentiate gasoline from other similar samples, as can be seen in Figure 2. Gasoline produced two peaks which appeared at 18.3 ms and another less intense at 19.31 ms. These signals were different to the spectra obtained for diesel and HTF samples, in which 4 peaks were obtained in the range of 18.15-20.78 ms. Based on this simple analysis, it can be confirmed that UV-IMS may be used as a tool for non-targeted analysis to differentiate gasoline samples from other samples, such as diesel and HTF, with a quick analysis of less than 7.5 min (150 spectra). Notice that in case of spillage, these samples cannot be distinguished in an easy way, so UV-IMS can be a useful tool in a forensic context.

3.2. Tenax TA trap as a pre-separation step coupled to UV-IMS

BTEX compounds can be released from gasoline and, in order to demonstrate the need to couple a Tenax trap TA to the UV-IMS, the following experiment was carried out first. Six individual BTEX at 2 mg m^{-3} were placed in the EDF and measured by the UV-IMS. Figure 3A shows the topographic plot when the gaseous sample was measured directly by UV-IMS. As can be seen, only a single peak was detected, tailing along the IMS topographic plot which most probably correspond to the sum of individual signals from the components in the mixture. The reason why this peak appeared at a longer drift time (16.51 ms), if we compared it with the individual signal of benzene (14.68 ms) and toluene (15.38 ms), is related to the formation of a bigger cluster when all compounds are together. Therefore, it took more time to reach the Faraday plate of the IMS compared with the drift times of individual analytes from the mixture, which were lower for all cases (<16 ms). Figure 3B shows the topographic obtained when the same gaseous sample was measured by using Tenax TA trap-UV-IMS. As can be observed, benzene (spectrum 142) and toluene (spectrum 168) signals can be separated from the rest of the compounds present in the gaseous sample mixture due to the differences in their boiling points. No separation was achieved for ethylbenzene and xylene isomers present in the gaseous sample attending at their similar chemical properties (close boiling point and molecular weight values).

3.3. Parameters optimization of the proposed method by using Tenax TA trap coupled to the UV-IMS

Tenax TA was chosen to improve the selectivity of the UV-IMS method due to its low cost, prolonged use and reduced reactivity with ozone, and thus its suitability for air monitoring.

Temperature program

Ramp temperature was firstly optimized. A gaseous sample mixture, containing 2.1 mg m^{-3} of each analyte (benzene, toluene, ethylbenzene and xylene isomers) was used. Three temperature ramp levels (5, 15 and 20 ˚C min^{-1}) were tested. The adsorption on Tenax TA column was performed at 30 ˚C, recommended by the manufacturer of the Tenax TA. The desorption temperature range was set from 60 to 220 ˚C with an initial time of 2 min at 60 ºC and a final time of 5 min at 220 ºC. Finally 15 ºC min^{-1} was chosen for further experiments according to the high intensity of peaks and the good resolution assessed in terms of eluting time, benzene peak eluted in 33 s and toluene in 27 s and the difference in time between them was 42 s. The same behavior in terms of sensitivity and selectivity was also observed at a higher concentration (42 mg m^{-3}) of the mixture.

Factorial design optimization for parameters that affect the adsorption and desorption steps in the Tenax TA column

Two multilevel factorial designs were prepared to optimize parameters of the adsorption (adsorption time and adsorption flow rate) and desorption step (temperature ramp, sample and drift gas flow rate) when using Tenax TA column coupled to the UV-IMS. These parameters were chosen attending to their higher influence they had on the two steps aforementioned. The objective of the optimization was to maximize intensity of the peaks heights and resolution between the analytes peaks. Each design consisted of a total of 18 experiments making it up 36 experiments for the whole optimization process. The two factors were studied in three different levels. Each experiment was done by duplicate and the intensity for each peak appearing on topographic maps was recorded along with the drift time and spectra number. In Table 3 the conditions studied and the value selected for each parameter is summarized. A gaseous sample containing initial concentrations of 5.8 mg m^{-3} for benzene, 5.7 mg m^{-3} for toluene, 5.7 mg m^{-3} for ethylbenzene and 5.7 mg m^{-3} for xylene isomers was used for optimization study. The exponential dilution flow rate selected was 200 mL min^{-1} and dilution time was 25 min. The optimum values were chosen according to the highest signal obtained in the IMS spectra.

In the adsorption step, adsorption time and adsorption flow rate were optimized. The influence of the adsorption time was examined at three different levels 5, 15 and 30 min. Adsorption of target compounds on the trap increased with time during the first 30 min. The effect of the adsorption flow rate was studied from 100 to 300 mL min^{-1}. Peak height increased when flow rate was at 100 mL min^{-1}, above which it decreases slightly.

For the desorption step, the sample gas and drift gas flow rates were also studied. It can be concluded that the maximum intensity for benzene and toluene was achieved by using sample gas flow rate of 20 mL min^{-1} and drift gas of 100 mL min^{-1}. Figure 4A and 4B show, as an example, the surface plots obtained for benzene obtained with Minitab 17 for adsorption time and flow rate, and for sample and drift gas flow rates used in the desorption step; respectively.

3.4. Analytical features

The proposed analytical method was validated in order to assess its suitability to identify and quantify benzene and toluene in gaseous air samples. The validation was performed by calculating the limit of detection (LOD) and limit of quantification (LOQ). LOD and LOQ were calculated by dividing three or ten times, respectively, the intercept standard error by the linear coefficients of the calibration curves (slope). Each measurement was performed by triplicate. Table 4 shows the values obtained for LOD and LOQ of benzene and toluene obtained with the Tenax TA trap-UV-IMS method and a comparison with the values obtained when measuring benzene and toluene individually with the EDF coupled to the UV-IMS. The concentration range used for the calibration curve was 0.76-9.50 mg m^{-3}. As can be observed, the LOD and LOQ values obtained for Tenax TA trap-UV-IMS method were much lower compared with direct measurements performed with the UV-IMS due to the preconcentration achieved with the sorbent material. Pre-concentration and better separation was achieved thanks to the use of Tenax TA column that allowed resolving some peaks from the BTEX mixture since they are eluted one by one by thermal desorption and can be detected in the UV-IMS device.

The precision study was assessed by using a standard gaseous of benzene and toluene at 3.8 mg m^{-3}. The measurements were taken under the same experimental conditions. A precision study was carried out by performing repeatability and reproducibility studies as seen in Table 5. Repeatability was assessed by analyzing 6 replicates during one day in which the precision was lower than 1.3% for drift time and 0.8% for retention time. RSD values were higher for peak intensities (<19.9%). These values indicate that the experiment is repeatable and precise enough for in-field analysis. Reproducibility was also evaluated by analyzing 9 replicates over 3 consecutive days. The high values of %RSD found in some cases can be attributed to the fact that the sample introduction system is basically home-made and it is not operated in an automated manner, which in turn slightly increases the influence of personal errors in the preparation of standards.

3.5. Real samples analysis

The proposed method was tested to monitor real air samples of a gasoline spillage in a parking area following the methodology exposed in this work. Benzene and toluene was quantified in these air samples. As was expected the concentration of benzene and toluene decreased with time. As shown in Table 6, toluene was the compound which showed a higher concentration (15.08 mg m^{-3}) in the analyzed samples. This value could be attributed to the fact that toluene level in gasoline is double the amount of benzene, according to the EPA. In all cases concentrations for benzene and toluene found in the air at the point of the spillage on the pavement amounted to the short term exposure limit (STEL). Toluene was the only analyte that can be quantified in the five samples taken from the spillage. Also, the first measurement of benzene was above the LOQ and can be calculated using the calibration curve.

4. Conclusion

This work has demonstrated the potential of the UV-IMS as a sensor providing characteristic fingerprints of gaseous samples. This enables us to differentiate gasoline vapors from other possible oily vapors that can be released into the environment in case of spillage.

The Tenax TA column was proposed as a pre-separation step to improve low resolution offers by UV-IMS. As has been demonstrated, the method proposed enabled the separation of benzene and toluene signals from the rest of the compounds presented in the BTEX gaseous sample mixture due to the differences in their boiling points. After validation, it can be concluded that not only selectivity was enhanced but also sensitivity of the proposed methodology was highly improved due to the preconcentration achieved with Tenax TA trap. One limitation of the proposed methodology is that separation obtained with Tenax TA and UV-IMS was not enough to differentiate compounds with similar chemical properties such as xylene isomers and ethylbenzene that could be present in the gaseous mixture. But these signals did not interfere with the target compounds during the measurement. This methodology was implemented successfully to identify and quantify benzene and toluene in real air samples close to a gasoline spillage source above the LOQ of 1.8 and 1.9 mg m^{-3}, respectively. The Tenax-UV-IMS method offers a reliable, simple and inexpensive approach to enhance some basic analytical properties such as selectivity and sensitivity. This methodology could be used in the future in some gas stations and industrial working areas as an on-site air monitoring alarm for any sudden release of benzene and toluene or any other potential pollutant.

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The authors have declared no conflict of interest.

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Biographies

L. Criado-Garcia obtained her international PhD in Sciences with Cum Laude mention in 2016, entitled “New contributions of ion mobility techniques in environmental and clinical field” supervised by Dr. Arce and Prof. Valcárcel. She has already published 5 scientific articles and presented 12 oral and poster communications in national and international conferences related to the use of ion mobility spectrometer and other related ion mobility techniques in the analytical area.

N. Almofti got a bachelor degree in Pharmacy in 2010 from Arab International University (AIU). In 2013 he was awarded with the Erasmus Mundus Full Scholarship in Forensic Science offered by the Educational, Audiovisual and Culture Executive Agency (EACEA) of the European Commission for two years in Spain, Portugal and United Kingdom. In 2015 he finished his master project under the supervision of Dr. Arce at the University of Córdoba, Spain and he obtained his master degree in Forensic Science with Distinction.

L. Arce obtained her PhD in Sciences in 1999. Since 2007, she is an Associated Professor at the University of Córdoba, Spain. Her main research project is devoted to the **development of** *new metrology analytical strategies* **using Ion Mobility Spectrometry and Capillary Electrophoresis among other techniques** in the agro-food and environmental field. She is co-author of 73 scientific articles (h index: 22) and 5 books chapters. She has co-supervised 7 Doctoral Theses and 14 Master Degree. She is teaching Analytical Chemistry subjects in different degrees and in an ERASMUS MUNDUS Master (Forensic Science).

Figure captions

Figure 1. Experimental set up used for direct measurement with the exponential dilution flask coupled to the UV-IMS and including the pre-separation step with Tenax TA trap coupled to the UV-IMS including (A) adsorption step and (B) desorption step set-up.

Figure 2. Topographic plot obtained from volatiles of (A) gasoline, (B) diesel and (C) heat transfer fluid by direct UV-IMS. Extracted IMS spectrum for each sample.

Figure 3. (A) Topographic plot and spectrum 50 of a mixture of BTEX at 2 mg m^{-3} obtained by direct measurement with UV-IMS. (B) Topographic plot obtained from the same sample by using the proposed methodology Tenax-UV-IMS. Extracted IMS spectra for benzene (spectrum 142) and toluene (spectrum 168) are also plotted.

Figure 4. Surface plots obtained for benzene optimization for (A) gas flow rate and time for the adsorption step and (B) sample gas flow rate drift gas flow rate used for the desorption step.

Figure 1.

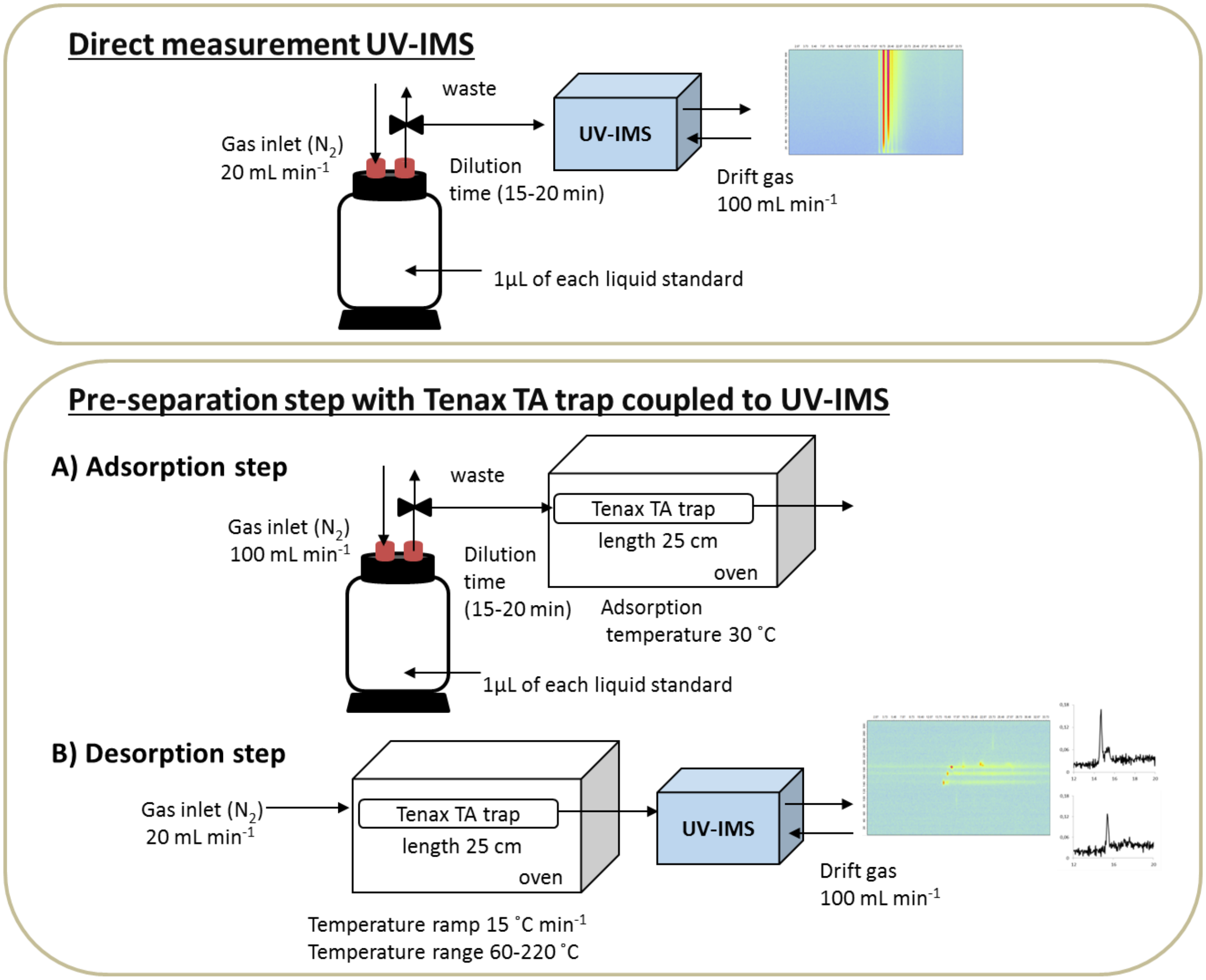
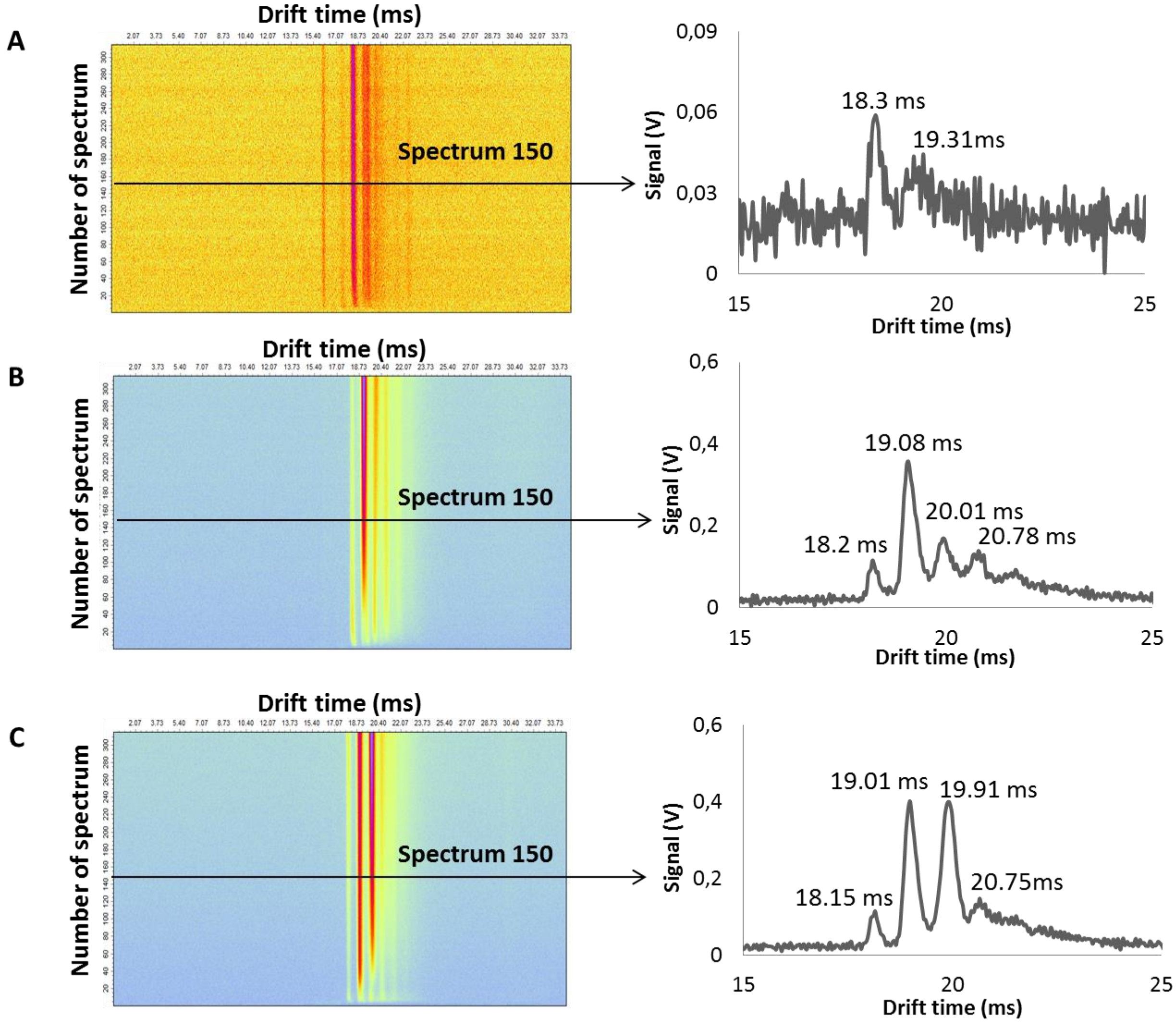

Direct measurement UV-IMS
waste
Gas inlet (N_2)
20 mL min^{-1}
Dilution
time (15-20 min)
UV-IMS
Drift gas
100 mL min^{-1}
1µL of each liquid standard
Pre-separation step with Tenax TA trap coupled to UV-IMS
A) Adsorption step
waste
Gas inlet (N_2)
100 mL min^{-1}
Dilution
time
(15-20 min)
Tenax TA trap
length 25 cm
oven
Adsorption
temperature 30 °C
1µL of each liquid standard
B) Desorption step
Gas inlet (N_2)
20 mL min^{-1}
Tenax TA trap
length 25 cm
oven
Temperature ramp 15 °C min^{-1}
Temperature range 60-220 °C
UV-IMS
Drift gas
100 mL min^{-1}

Figure 2.


A
Drift time (ms)
2.07 3.73 5.40 7.07 8.73 10.40 12.07 13.73 15.40 17.07 18.73 20.40 22.07 23.73 25.40 27.07 28.73 30.40 32.07 33.73
Number of spectrum
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Spectrum 150
Signal (V)
0,09
0,06
0,03
0
18.3 ms
19.31ms
15
20
25
Drift time (ms)
B
Drift time (ms)
Number of spectrum
Spectrum 150
Signal (V)
0,6
0,4
0,2
0
19.08 ms
20.01 ms
18.2 ms
20.78 ms
15
20
25
Drift time (ms)
C
Drift time (ms)
Number of spectrum
Spectrum 150
Signal (V)
0,6
0,4
0,2
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19.01 ms
19.91 ms
18.15 ms
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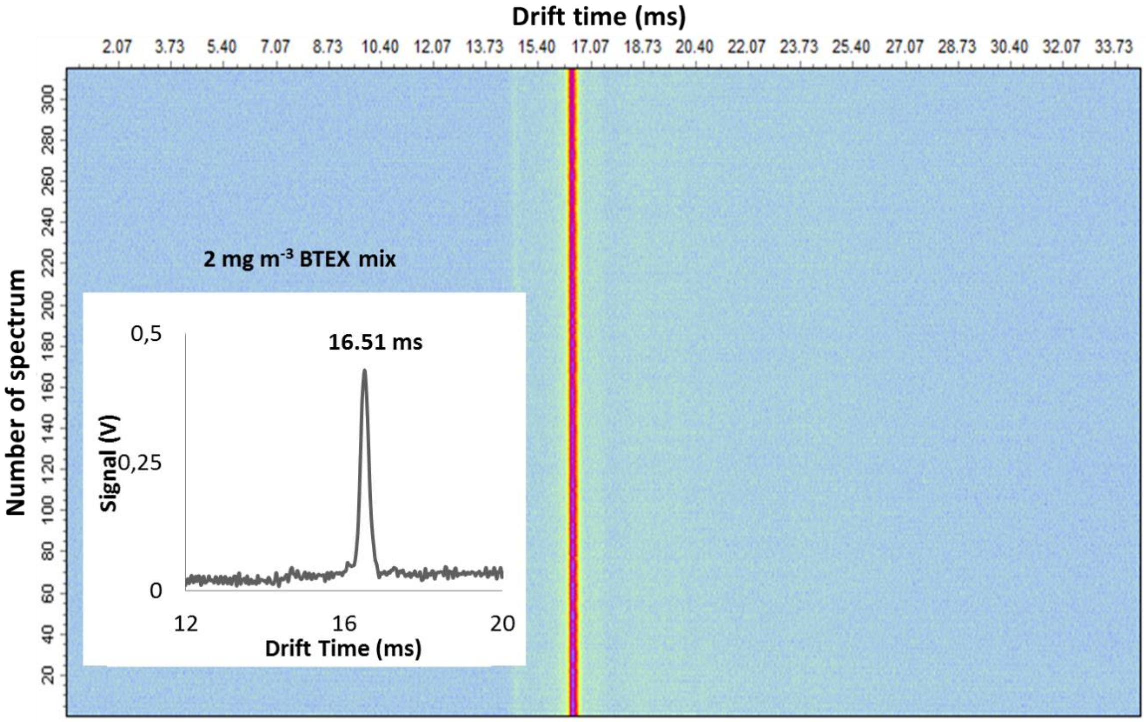
15
20
25
Drift time (ms)

Figure 3

(A)


Drift time (ms)
2.07 3.73 5.40 7.07 8.73 10.40 12.07 13.73 15.40 17.07 18.73 20.40 22.07 23.73 25.40 27.07 28.73 30.40 32.07 33.73
Number of spectrum
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
2 mg m-3 BTEX mix
16.51 ms
Signal (V)
0,5
0,25
0
12
16
20
Drift Time (ms)

(B)

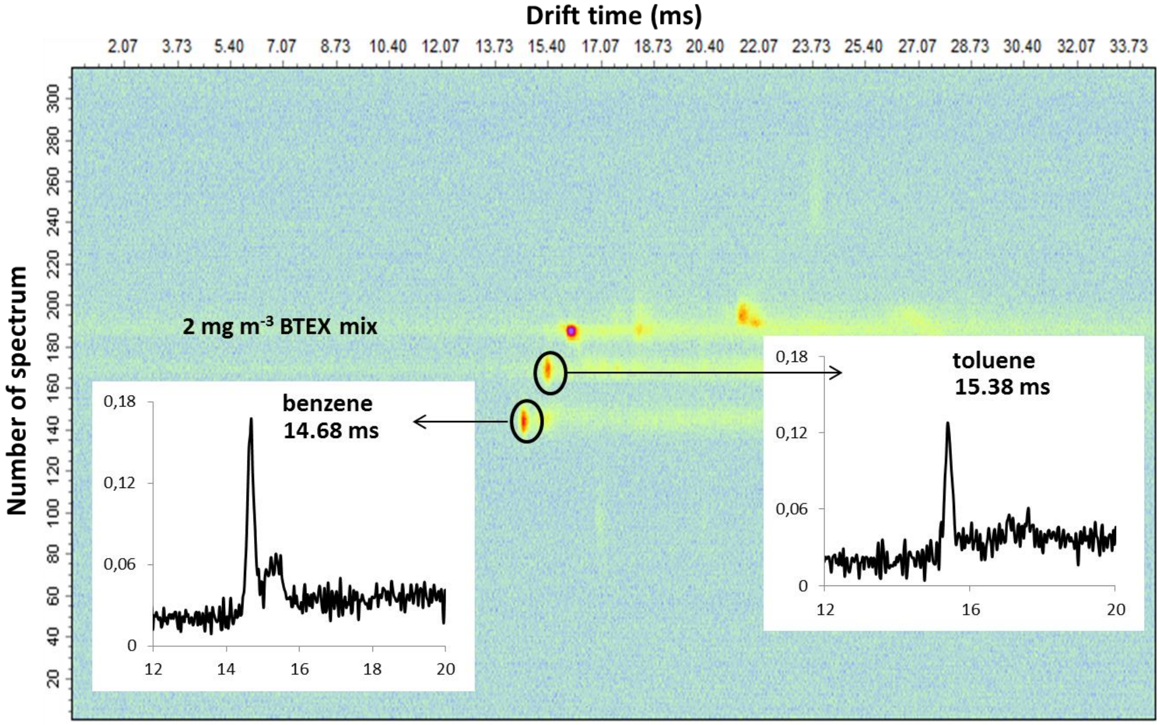

Drift time (ms)
2.07 3.73 5.40 7.07 8.73 10.40 12.07 13.73 15.40 17.07 18.73 20.40 22.07 23.73 25.40 27.07 28.73 30.40 32.07 33.73
Number of spectrum
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
2 mg m-3 BTEX mix
benzene
14.68 ms
0,18
0,12
0,06
0
12
14
16
18
20
toluene
15.38 ms
0,18
0,12
0,06
0
12
16
20

Figure 4.

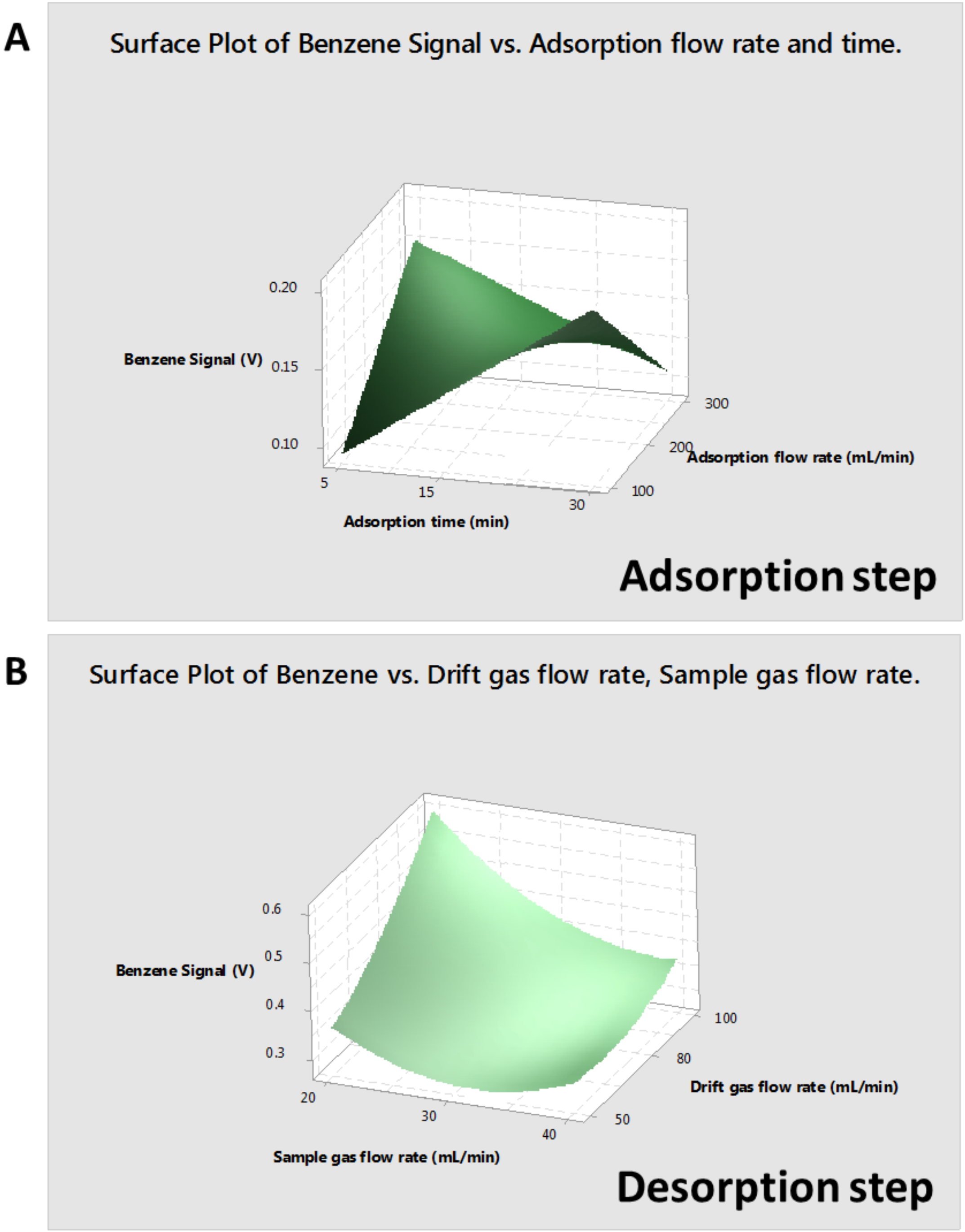

A
Surface Plot of Benzene Signal vs. Adsorption flow rate and time.
Benzene Signal (V)
0.20
0.15
0.10
5
15
30
Adsorption time (min)
100
200
300
Adsorption flow rate (mL/min)
Adsorption step
B
Surface Plot of Benzene vs. Drift gas flow rate, Sample gas flow rate.
Benzene Signal (V)
0.6
0.5
0.4
0.3
20
30
40
Sample gas flow rate (mL/min)
50
80
100
Drift gas flow rate (mL/min)
Desorption step

Table 1. Physical and chemical properties of BTEX compounds.

IUPAC name	**Molecular weight (g mol^{1})**	**Boiling point (ºC)**	**Ionization energy (eV)**
Benzene	78.11	80.05	9.24
Ethylbenzene	106.17	136	8.77
Toluene	92.14	110.8	8.83
m-Xylene	106.16	139	8.44
o-Xylene	106.16	144.5	8.56
p-Xylene	106.16	138.2	8.44

Table 2. The UV-IMS system conditions.

Parameter	**Value**
Pressure of drift tube	Atmospheric
Temperature of drift tube	ambient
Drift and sample gas	N_2 (5.0 = 99.999%)
Drift gas flow rate	100 mL min^{-1}
Sample gas flow rate	20 mL min^{-1}
Drift voltage polarity	Positive
Ionization source	UV lamp (10.6 eV)
Trigger delay	0.4 ms
Grid Pulse width	100 µs
Repetition rate	50 ms
Sampling frequency	30000 Hz
Electric field strength	333 V/cm
Length of the drift tube	12 cm

Table 3. Optimization of the operating condition of the proposed system.

Parameters	**Units**	**Levels**	**Level 1**	**Level 2**	**Level 3**	**Optimum value**
Adsorption step						
Adsorption time	min	3	5	15	30	30
Adsorption flow rate	mL min^{-1}	3	100	200	300	100
Desorption step						
Temperature ramp	˚C min^{-1}	3	5	15	20	15
Sample gas flow rate	mL min^{-1}	3	20	30	40	20
Drift gas flow rate	mL min^{-1}	3	100	200	300	100

Table 4. Regression coefficient, LOD and LOQ obtained.

Analyte	**Tenax-UV-IMS**						**Direct UV-IMS**	
	Calibration curve ***y = ax +b****	**R^2**	**Sa**	**Sb**	**LOD (mg m^{-3})**	**LOQ (mg m^{-3})**	**LOD (mg m^{-3})**	**LOQ (mg m^{-3})**
Benzene	y= 0.0438x +0.0544	0.958	0.008	0.003	0.54	1.79	1.54	5.14
Toluene	y= 0.0278x +0.0527	0.976	0.005	0.002	0.57	1.90	2.74	9.14

* The dependent variable (y) was peak height intensity in volts (V) and the independent variable (x) was the concentration of the analyte in the gaseous sample (mg m^{-3}).

Table 5. Precision study of the proposed method, values are presented as %RSD.

	Compounds	Intensity	Drift time	Retention time
Repeatability n=6	Benzene	13.11	1.24	0.81
	Toluene	19.95	0.98	0.74
Reproducibility n=9	Benzene	12.71	1.43	0.78
	Toluene	16.38	1.18	0.66

Table 6. Concentrations obtained for benzene and toluene from gasoline spillage on pavement over time.

5 mL gasoline spillage on pavement	Elapsed time (min)	Concentration (mg m^{-3})	
		Benzene	Toluene
Sampling 1	5	2.24	15.08
Sampling 2	90	<LOQ	13.89
Sampling 3	165	<LOQ	11.73
Sampling 4	240	<LOQ	8.96
Sampling 5	335	<LOQ	7.23