Talanta 111 (2013) 111–118

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A comparative study between different alternatives to prepare gaseous standards for calibrating UV-Ion Mobility Spectrometers

Laura Criado-García, Rocío Garrido-Delgado, Lourdes Arce, Miguel Valcárcel *

Department of Analytical Chemistry, Annex C-3 Building, Campus of Rabanales, Institute of Fine Chemistry and Nanochemistry, University of Córdoba, 14071 Córdoba, Spain

ARTICLE INFO

Article history:
Received 7 November 2012
Received in revised form
18 February 2013
Accepted 21 February 2013
Available online 15 March 2013

Keywords:
Gaseous standards
Head-space
Exponential dilution
Gas generator
Calibration
UV-IMS

ABSTRACT

An UV-Ion Mobility Spectrometer is a simple, rapid, inexpensive instrument widely used in environmental analysis among other fields. The advantageous features of its underlying technology can be of great help towards developing reliable, economical methods for determining gaseous compounds from gaseous, liquid and solid samples. Developing an effective method using UV-Ion Mobility Spectrometry (UV-IMS) to determine volatile analytes entails using appropriate gaseous standards for calibrating the spectrometer. In this work, two home-made sample introduction systems (SISs) and a commercial gas generator were used to obtain such gaseous standards. The first home-made SIS used was a static headspace to measure compounds present in liquid samples and the other home-made system was an exponential dilution setup to measure compounds present in gaseous samples. Gaseous compounds generated by each method were determined on-line by UV-IMS. Target analytes chosen for this comparative study were ethanol, acetone, benzene, toluene, ethylbenzene and xylene isomers. The different alternatives were acceptable in terms of sensitivity, precision and selectivity.

1. Introduction

Ion Mobility Spectrometry (IMS) is a useful technique for on-field analysis [1]. In fact, the expeditiousness, trace-level sensitivity and operational simplicity of IMS have aroused increasing interest in its use in a variety of areas including pharmaceutical, forensic, biomedical and environmental sciences. For example, the IMS technique has been successfully used for the environmental monitoring of hazardous compounds. Among other advantages, IMS uses an inexpensive equipment running under atmospheric pressure [2], which makes it highly portable and suitable for the on-line monitoring of volatile organic compounds (VOCs) such as benzene, toluene and xylene isomers [3,4].

The operational principle behind IMS is very simple [5–10]. Thus, ions generated by an ionization source are driven to a Faraday plate (the detector) held in the end of the drift tube under a constant, uniform electric field, providing the number of ions detected a measure of the analyte concentration. The time each ion takes to travel the distance from the shutter grid to the detector, which is called the "drift time", depends on the ion mass, charge, shape and size. From the drift time and the instrumental parameters the reduced ion mobility, K_0 ($\mathrm{cm^2\,V^{-1}\,s^{-1}}$), can be calculated considering the influence of ambient pressure (P) and temperature (T) as is showing in the following equation:

$$K_0 = \left(\frac{1}{tE}\right)\left(\frac{PT_0}{P_0T}\right) \tag{1}$$

being l (cm) the length of the drift region, E ($\mathrm{V\,cm^{-1}}$) the electric field strength, t (s) the drift time, P the atmospheric pressure (P_0=101,325 Pa) and T the temperature of the drift gas (T_0=273 K).

The high operational flexibility of IMS facilitates the measurement of a variety of analytes in liquid, solid and gaseous samples; however, only gaseous samples can be directly introduced into an ion mobility spectrometer, so analytes present in liquid and solid samples must be volatilized prior to introduction into the instrument. An efficient sample introduction system (SIS) is therefore essential for accurate measurements by IMS [11]. If the target analytes are inefficiently extracted or transferred to an IMS instrument, their measurements will hardly be representative of the analytical problem at hand. This shortcoming led us to develop efficient types of SISs according to the type of sample allowing preparing calibration gas standards and introducing real samples to be measured. Measuring gaseous analytes (e.g. ethanol, acetone, benzene, toluene, ethylbenzene and xylene isomers) in air or liquid samples by UV-IMS requires calibrating the instrument with an appropriate method. Some commercial gas generators can produce traceable, precise, repeatable and accurate concentrations of chemicals and calibration gas standards [12–14]. Otherwise, this type of generation of gaseous standards is usually highly time-consuming and expensive. These two features are the

---

* Corresponding author. Tel./fax: +34 957 21 86 16.
E-mail addresses: qa1vacam@uco.es, qa1meobj@uco.es (M. Valcárcel).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.054

opposite of the main advantages of the UV-IMS (rapid and cheap technique). For this reason, two fast and inexpensive SISs as reliable as commercial gas generators were coupled to UV-IMS equipment to study their potential to produce standard gaseous compounds. The operational simplicity and relatively low cost make these alternatives very promising for calibrating IMS instruments. The aim of this work was to characterize the qualitative and quantitative response in the determination of VOCs gaseous standards by UV-IMS. The ion mobility spectra, reduced mobilities and analytical figures of merits of each analyte studied are also discussed.

2. Experimental

2.1. *UV-ion mobility spectrometer*

The UV-IMS instrument used, supplied by Gesellschaft für Analytische Sensorsysteme (GAS, Dortmund, Germany), is depicted in Fig. 1. The instrument is 350 × 350 × 150 mm in size, has a tube length of 12 cm, a weight of 5 kg, and uses a current supply of 230 V/50–60 Hz and a constant voltage supply of 333 V cm^{-1}. All spectra were recorded in the positive ion mode and acquired under the conditions listed in Table 1. The temperature and pressure in the drift tube were at 297 K and 101 kPa, respectively.

2.2. *Generation of gaseous standards*

Obtaining gaseous standards is a much more difficult task than producing liquid standards. In fact, the production of gaseous standards is subject to some problems including the wall memory effect and instrument noise [15,16]. This led us to study two home-made systems for obtaining gaseous standards to determine analytes present in liquid and gaseous samples which are shown in Fig. 2A and 2B. The results obtained with the exponential dilution method were compared with the gaseous standards generated by a commercial system which is illustrated in Fig. 2C. The operating conditions used are shown in Table 2. VOCs employed included ethanol, acetone, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene, all supplied by SIGMA (St Louis, MO, USA). Their physical and chemical properties are summarized in Table 3. These analytes were selected on the grounds of their belonging to representative families of VOCs.

2.2.1. *Generation of gaseous standards by static head-space system*

Gaseous standards were prepared from liquid standards when performing the home-made head-space system shown in Fig. 2A. This system could be suitable to determine analytes present in liquid samples (e.g. VOCs present in water samples). In each analysis, 100 μL of liquid standard was placed in a 1.5 mL glass vial which was in turn inserted into a 10 mL vial and tightly closed with a Teflon septum.

Samples were heated in an Eco 1G Thermoreator (Velp Scientific) for 1 min (volatilization step) while a stream of synthetic air 2.2 from Carburos Metálicos (Barcelona, Spain) was passed through the UV-IMS equipment. The flow rates (80 mL min^{-1} for the sample gas and

Table 1
UV-IMS operational parameters used in this work.

Parameter	Value selected
Number of spectra	25 and 250
Average	64
Trigger delay (ms)	0.4
Spectra length (points)	1024
Grid pulse width (μs)	500
Repetition rate (ms)	50
Sampling frequency (Hz)	30000

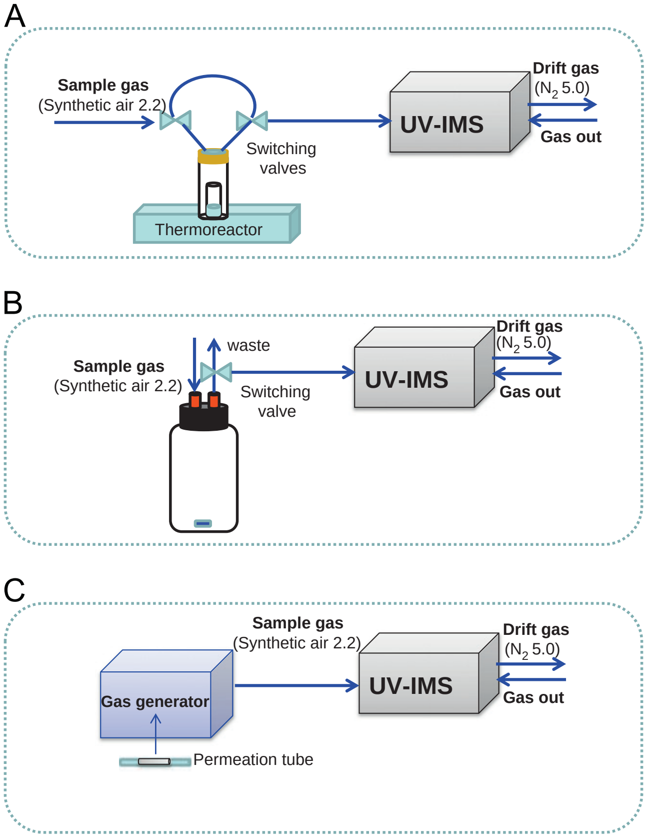

Fig. 2. Sample introduction system used to obtain gaseous standards from a head-space vial (A), an exponential dilution flask (B) or a calibration gas generator (C).

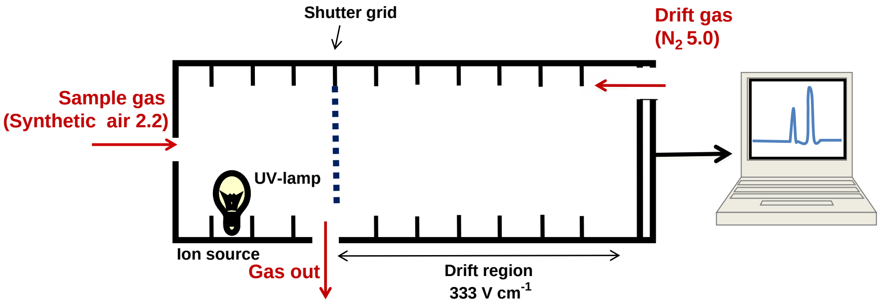

Fig. 1. Scheme of the UV-IMS instrument used.

Table 2
Operational conditions used to obtain gaseous standards by using the three proposed procedures.

Experimental conditions	Head-space method	Exponential dilution method	Gas generator
Volume of sample (μL)	100	1	[c]
Head-space volume (mL)	10	1000	–
Heating time (min)	5	1	–
Temperature (°C)	60, 80 and 90 [a]	Room temperature [b]	35
Sample gas (mL min^{-1}) Synthetic air 2.2	80	100	100
Drift gas (mL min^{-1}) N_2 5.0	140	150	150

[a] Different temperatures were chosen to generate the head-space vapors for each analyte: 60 °C for benzene, toluene, ethylbenzene and xylene isomers, 80 °C for acetone and 90 °C for ethanol.

[b] Although the analytes were evaporated using a dryer, the flask was not heated during the measurement.

[c] Permeation tubes of 4 cm were filled with each liquid analyte and its weight was measured to calculate the permeation rate.

Table 3
Physical and chemical properties of VOCs measured by UV-IMS.

Family	IUPAC name	Molecular weight (g mol^{-1})	Density (g mL^{-1})	Boiling point (°C)	Polarity	Ionization energy (eV)	Drift time obtained by exponential dilution (ms)
Ketones	Acetone	58.04	0.79	56.3	5.1	9.70	18.93
Alcohols	Ethanol	46.07	0.78	78	–	9.99	18.20
Aromatics	Benzene	78.11	0.87	80.05	2.4	9.24	15.83
	Ethylbenzene	106.17	0.86	136	–	8.77	17.63
	Toluene	92.14	0.86	110.8	2.4	8.83	16.69
	Xylene (*m*-, *o*-, *p*-)	106.16	0.86	138	2.5	8.44	17.43,17.38,17.47

140 mL min^{-1} for the drift gas) were controlled by an Altech Digital Flow Check HR™ device from Chromatographic Service GmbH. After 5 min heating, two stainless-steel switching valves (Selectomite®-7177G2Y, HOKE Incorporated, Spartanburg, SC) were actuated to have the head-space vapors formed in the vial swept out by the synthetic air stream and transferred to the UV-IMS system for measurement (injection step). Connections were made with 1/8-inch Teflon tubes obtained from Varian (Harbor City, Los Angeles, CA, USA) [17].

The calibration curves were obtained by preparing individual stock solutions of 100 mg L^{-1} for each analyte. Dilutions were made by placing 10, 50, 100, 200, 300, 400 or 500 μL of stock solutions in a 10 mL volumetric flask and making to volume with distilled water purified by passage through a Milli-Q system from Millipore (Bedford, MA, USA). These standard solutions were prepared on a daily basis and stored at ambient temperature until analysis.

2.2.2. *Generation of gaseous standards by exponential dilution flask*

Exponential dilution is a commonly used method for accurately delivering a range of concentrations to an IM spectrometer. This system could be used to determine analytes present in gaseous samples (e.g. VOCs in air samples). The home-made exponential dilution set-up of Fig. 2B was used here to prepare gaseous standards. Concentrations are given in parts-per-million in gas, $ppm_{(g)}$, which express the number of analyte molecules present in a million of molecules of air. Based on the ideal gas law ($PV=nRT$), the number of molecules of a gas is proportional to its volume; therefore, $ppm_{(g)}$ was calculated from this equation, using the volume, density and concentration of the analyte, the flask volume, atmospheric pressure and room temperature. The exponential dilution procedure involves placing a pure liquid standard with an initial volume of 1 μL in a 1000 mL (V_f) volumetric flask. Then, hot air is applied locally to the flask with a hot air gun to evaporate the little drop of 1 μL of analyte approximately at 300 °C only during 1 min. It results in an initial concentration (C_o) of gaseous standard [e.g. 2064 $ppm_{(g)}$ for ethanol], usually in synthetic air. In order to reduce such a high initial concentration, synthetic air 2.2 is passed through the volumetric flask during a specific time depending on the initial concentration of analyte [e.g. 20 min for ethanol] at a high flow rate (250 mL min^{-1}). A magnetic stir bar is placed inside the flask to stir the gas at 900 rpm. The resulting final concentration, C_t ($ppm_{(g)}$), is calculated as follows:

$$C_t = C_o e^{(-Ft/V_f)} \tag{2}$$

Being C_o ($ppm_{(g)}$) the initial concentration, F (mL min^{-1}) the flow rate of the gas, t (min) time, V_f (mL) the volume of the dilution flask.

The analyte concentration in the dilution flask is thus efficiently reduced [e.g. to 14 $ppm_{(g)}$ for ethanol] and the gaseous standard made ready for IMS measurement. The synthetic air 2.2 at a flow rate ($F=100$ mL min^{-1}) allowed to achieve decreasing concentrations of analytes (C_t) by diluting the initial concentration (C_o) of analyte in the gaseous sample. Therefore, the analyte signal and concentration decreases during the measurement.

2.2.3. *Generation of gaseous standards by a calibration gas generator*

Finally, a calibration gas generator called OVG-4® from Owlstone® (Cambridge, UK) shown in Fig. 2C was used to generate gaseous standards of acetone, benzene, ethylbenzene, toluene and *p*-xylene. Individual permeation tubes already filled with each analyte were provided by Owlstone® (Cambridge, UK). Before starting the measurement of gaseous standards by UV-IMS, it was necessary to condition each permeation tube during two days heating at 35 °C and passing a constant flow of 100 mL min^{-1} of synthetic air. Concentrations of gaseous standards provided by the gas calibration generator at each time were calculated taking into account the furnace temperature, permeation rate and the flow rate selected, using the software supplied by Owlstone®.

3. Results and discussion

Calibration standards must be prepared in a similar matrix or environment to that of the target analytes. This led us to propose different strategies to generate gaseous standards depending on whether the target analyte is present (in a liquid or gaseous sample). One home-made system based on head-space could be suitable to analyze VOCs present in liquid samples and another in which exponential dilution was performed to measure analytes present in gaseous samples. The results obtained from the gaseous home-made system performing exponential dilution method were also compared with the results provided by the commercial gas generator.

3.1. Evaluation of alternatives proposed to generate gaseous standards

3.1.1. Generation of gaseous standards by a static head-space system

The SIS previously reported by our research group [17], and others for the same purpose [5,15], cannot be used to determine analytes present in aqueous samples (e.g. waste water from a petrol station) because the liquid sample tends to condensate in the Teflon tube connecting the SIS to the UV-IMS instrument, which can seriously damage the equipment. Additionally, placing liquid standards directly in the vial present another problem; thus, the synthetic air stream drags the gaseous compounds formed in the vial, which leads to exceedingly strong signals and, occasionally, delays subsequent measurements owing to the need to clean the equipment. These problems were not initially observed by the authors [17] since the initial intended use of this SIS was to measure compounds present in non-aqueous, solid or even viscous samples (e.g. fat from pig or olive oil), these shortcomings led us to introduce a slightly modification in the SIS. In this work, the liquid standard was introduced in a little vial and it was placed in a bigger vial tightly closed. Such a simple modification prevented that the flow of gas fell on the standard liquid, allowing liquid standards to be measured without overload the IMS signal. In Fig. 3, different systems tested to perform head-space method are shown, namely: placing a 1.5 mL vial inside a 10 mL vial (A); a 250 μL Eppendorf tube inside a 10 mL vial (B) and a 1.5 mL vial inside a 20 mL vial (C). In all systems, 100 μL of acetone was placed inside an opened vial which was in turn placed in a tightly closed vial. These vials were heated at 50 °C during times from 1 to 30 min. During these times, a loss weight of the liquid standard was observed due to the fact that liquid molecules of acetone passed to the gas phase in the head-space inside the bigger vials. As can be seen in Fig. 3, an almost identical amount of gaseous acetone was produced in all systems used during the different heating times tested. For this reason, any of these devices could be used to measure VOCs present in liquid samples. In this work, the system A was selected.

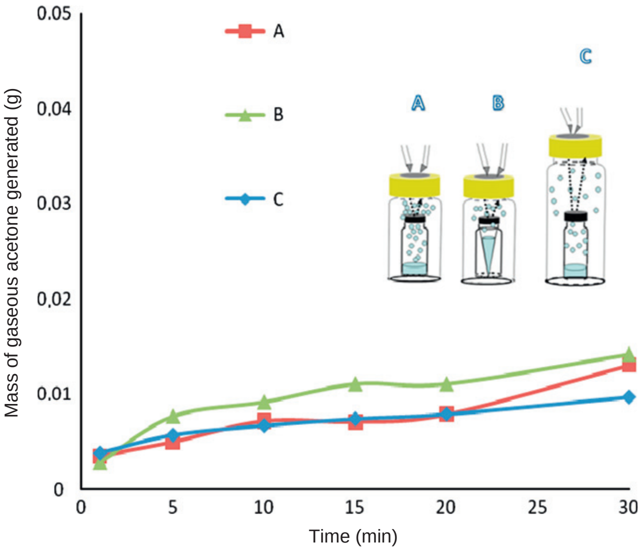

Fig. 3. SISs tested to perform head-space method.

Once the best SIS to perform the head-space method was chosen, sample volume, heating time, head-space volume, temperature, sample gas and drift gas were optimized with a view to maximizing repeatability and peak height of the ion mobility signal. The optimum values selected are summarized in Table 2.

3.1.2. Generation of gaseous standards by exponential dilution

Exponential dilution was carried out in a flask of 1 L using the experimental set-up shown in Fig. 2B. The entire liquid standard (1 μL) deposited inside the flask was quickly evaporated with a hot air gun. Heating and stirring were assessed in this experimental set-up. Stirring was found to improve the analytical signals. Also, using two flasks in the sequence led to a slightly increased signal as seen in previous work [18]; however, it was obtained a worse reproducibility in the measurements. Heating the flask at 30 °C under stirring also detracted from signal intensity. Finally, as recommended in a previous study [19] to enhance sensitivity, a single 1000 mL flask containing a magnetic stir bar was used in this work.

Therefore, exponential dilution is an effective choice for calibrating UV-IMS device instruments for analytes present in air samples. This SIS affords a simple, inexpensive method suitable for on-site analysis.

3.2. Analytical features

Analytical features of each method proposed in this work are shown in this section. Different analytes were used for each method depending on their availability.

3.2.1. Calibration curves, Limits of Detection (LODs) and Limits of quantification (LOQs)

The calibration curve, LODs and LOQs obtained for the head-space set-up are shown in Table 4. When the head-space method was used, the minimum concentration detected was much higher than the minimum concentration detected with exponential dilution set-up. The reason of this fact could be that when head-space method was performed, the liquid sample was heated to generate volatiles compounds which represent only a fraction of the total compounds present in liquid sample place inside the vial. Therefore, only the fraction of compounds passing to the gas phase was measured by UV-IMS. Moreover, the effect of moisture should be taken into account when the gaseous fraction is measured from a liquid sample since it might reduce the signal intensity. Notice that the UV-IMS device used in this work has not any membrane in the inlet port.

On the other hand, the results obtained (LODs, LOQs and precision values) using the exponential dilution set-up proposed to calibrate the UV-IMS device when analytes are present in air samples have been compared with the values obtained with the calibration gas generator. The results are illustrated in Table 5. LODs obtained with exponential dilution set-up were low [below 1 ppm$_{(g)}$] for ethanol and acetone, but slightly higher for aromatics such as *p*-xylene and toluene [1.8 and 1.6 ppm$_{(g)}$] respectively. Obviously, LODs and LOQs were lower using the commercial gas generator due to the fact that major inaccuracies in the preparation of gaseous standards were avoided. This comparison was vital to assess the suitability of each methodology proposed in this work. While the exponential dilution method was a cheap and quick alternative to calibrate IMS device, the calibration gas generator was successfully used to prepare lower concentrations of analyte in a more precise way, but unavoidably investing more money and time.

The main difference between the methods proposed in this work is that head-space is used for measuring analytes present in

Table 4
Calibration curve, LOD and LOQ obtained with the head-space set-up.

Analyte	Regression equation			LOD [a] (ppm)	LOQ [a] (ppm)
	Intercept ± S_a	Slope ± S_b	Regression coefficient (R^2)		
Acetone	0.0018 ± 0.0043	0.0043 ± 0.0002	0.977	3.0	10.0
Ethylbenzene	0.011 ± 0.002	0.00174 ± 0.00008	0.983	3.4	11.5
Benzene	0.005 ± 0.004	0.0026 ± 0.0002	0.933	4.6	15.4
Toluene	0.014 ± 0.003	0.0025 ± 0.0001	0.963	3.6	11.8
m−Xylene	0.011 ± 0.003	0.0032 ± 0.0002	0.959	2.8	9.4
o−Xylene	0.012 ± 0.002	0.0026 ± 0.0001	0.969	2.3	7.7
p−Xylene	0.011 ± 0.003	0.0017 ± 0.0001	0.944	5.3	17.6

[a] LODs and LOQs were calculated as 3 and 10 times, respectively, the standard deviation of the intercept of the calibration curve divided by its slope.

Table 5
Values of LOD and LOQ obtained with the exponential dilution method and calibrator gas generator.

Analyte	Regression equation				LOD [a] (ppm$_{(g)}$)	LOQ [a] (ppm$_{(g)}$)
	Procedure	Intercept ± S_a	Slope ± S_b	Regression coefficient (R^2)		
Ethanol	Exponential dilution	0.041 ± 0.002	0.0079 ± 0.0002	0.989	0.8	2.5
Acetone	Exponential dilution	0.012 ± 0.003	0.0109 ± 0.0004	0.981	0.8	2.8
	Gas generator	0.160 ± 0.003	0.0245 ± 0.0005	0.967	0.4	1.2
Ethylbenzene	Exponential dilution	0.04 ± 0.01	0.027 ± 0.001	0.968	1.1	4.1
	Gas generator	0.049 ± 0.005	0.140 ± 0.005	0.955	0.1	0.4
Benzene	Exponential dilution	0.054 ± 0.010	0.027 ± 0.001	0.973	1.1	3.7
	Gas generator	0.010 ± 0.001	0.0094 ± 0.0004	0.984	0.3	1.1
Toluene	Exponential dilution	0.03 ± 0.02	0.035 ± 0.002	0.923	1.6	5.4
	Gas generator	0.083 ± 0.001	0.032 ± 0.001	0.992	0.1	0.3
m−Xylene	Exponential dilution	0.11 ± 0.02	0.041 ± 0.002	0.971	1.5	4.9
o−Xylene	Exponential dilution	0.11 ± 0.02	0.041 ± 0.002	0.964	1.5	4.9
p−Xylene	Exponential dilution	0.013 ± 0.002	0.0033 ± 0.0002	0.939	1.8	6.1
	Gas generator	0.118 ± 0.002	0.078 ± 0.003	0.993	0.1	0.3

[a] LODs and LOQs were calculated as 3 and 10 times, respectively, the standard deviation of the intercept of the calibration curve divided by its slope.

liquid samples in a cheap and rapid way. On the other hand, exponential dilution set-up and generator gas calibrator device are used when analytes are present in gaseous samples. As a result, it is essential that these two methods: head-space and exponential dilution set-ups be used appropriately depending on the matrix in which is present the analyte.

3.2.2. *Precision*

Precision expressed as RSD (%), was assessed for target analytes performing head-space set-up, exponential dilution system and using the calibrator gas generator described in Fig. 2. Intraday RSD values were lower for drift time in all cases studied. Average values of RSD for head-space (3.57% for peak height and 0.40% for drift time) were slightly lower than the values obtained for exponential dilution set-up (10.46% for peak height and 0.54% for drift time). A reason of this fact could be the irreproducibility of preparing the gaseous samples in the dilution flask. On the other hand, the precision using the commercial gas generator have been also evaluated in a same day (0.30% for peak height and 0.22% for drift time). Therefore, RSD values obtained using the calibration gas generator were lower than the values obtained with both home-made methods. These values demonstrated the high precision of this commercial device to prepare individual standard solutions. With this study, it may seem that there is evidence of IMS repeatability when good practices are followed.

3.2.3. *Selectivity*

Selectivity was assessed by measuring 5, 10, 20 ppm$_{(g)}$ of a gaseous mixture containing five BTX (benzene, toluene, *m*-xylene, *o*-xylene and *p*-xylene) and measuring the head-space generated by heating at 60 °C a liquid mixture containing 5, 10 and 20 ppm of the same analytes in water under the experimental conditions described in Table 2 and in Fig. 2A and 2B, respectively.

Only one intense peak at 17.78 ms which could correspond to a monomer (M$^+$) and a little peak shoulder at 17.98 ms were obtained from a gaseous mixture of the analytes which is illustrated in Fig. 4A; the peak increased from 5 to 20 ppm$_{(g)}$ keeping the same shape and decreasing slightly the little shoulder when the concentration was increased. The global signal of all analytes from a gaseous mixture appeared at a slightly longer drift time (17.78 ms) compare to the signal obtained for the individual analytes (benzene at 15.83 ms, toluene at 16.69 ms, *m*-xylene at 17.43 ms, *o*-xylene at 17.38 ms and *p*-xylene at 17.47 ms). These differences in drift times can be ascribed to ion-molecules reactions produced inside the UV-IMS device. So, when a gas mixture of different analytes is introduced in the UV-IMS device a cluster of higher molecular weight might be formed. Therefore, more time is needed for this new ion to reach the end of the drift tube and be detected by the Faraday plate. In addition, this bigger ion cannot be resolved in the drift tube due to the structural similarities of the target analytes.

On the other hand, when vapors from the liquid sample from 5 to 20 ppm were measured, which is shown in Fig. 4B, it could be assumed that the first peak obtained in the IMS spectrum correspond to a monomer ion (M$^+$ at 16.65 ms) and the second peak correspond to a dimmer ion (M$_2^+$ which appear later in the IMS spectrum at 17.61 ms). The reason of the emergence of monomer and dimmer peaks in the IMS spectra could be associated with the fact that when the concentration of analyte molecules is increased further, the monomer may be clustered with an additional molecule, forming a dimmer [5]. This phenomenon is clearly distinguished in this case due to the small amount of volatile compounds produce after heating (during 5 min) 100 μL

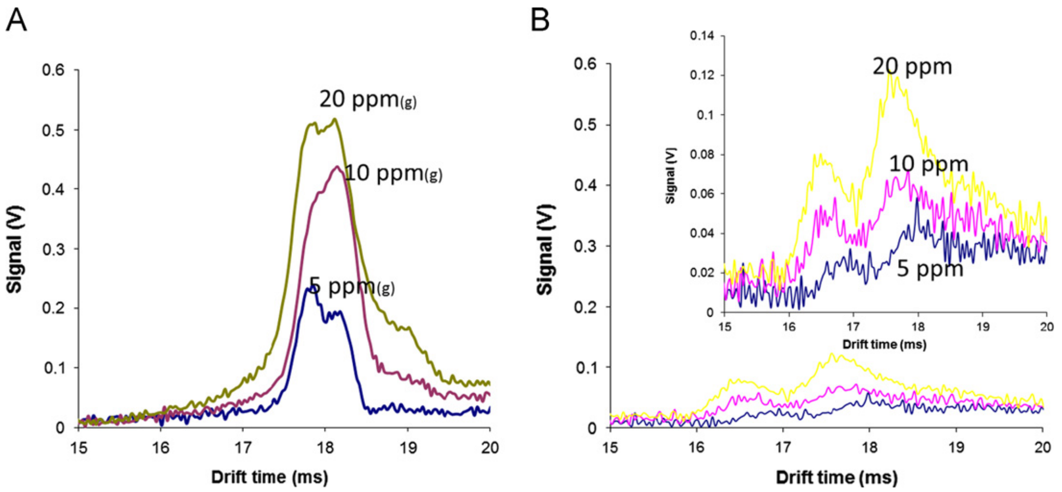

Fig. 4. UV-IMS spectrum for (A) a blended gaseous sample containing 5, 10 and 20 ppm$_{(g)}$ of benzene, toluene, *m*-xylene, *o*-xylene and *p*-xylene in a 1 L flask and (B) the vapors from the head-space generated by heating at 60 °C a liquid mixture containing 5, 10 and 20 ppm of benzene, toluene, *m*-xylene, *o*-xylene and *p*-xylene in water.

Table 6
Comparison of the three methods proposed in this work to prepare gaseous standards.

Analytical properties		Head-space method	Exponential dilution method	Gas generator
Sensitivity	LOD	2.3–4.6 ppm	0.8–1.8 ppm$_{(g)}$	0.1–0.4 ppm$_{(g)}$
	LOQ	7.7–17.6 ppm	2.5–6.1 ppm$_{(g)}$	0.3–1.2 ppm$_{(g)}$
Robustness		Medium	Medium	High
Time [a]		< 10 min	< 45 min	> 48 h
Cost		Low	Low	High
Operation		Easy	Easy	Medium
Possibility to prepare blended gas mixtures		Yes	Yes	No

[a] Time needed for performing a complete set of concentrations to calibrate the UV-IMS device for each analyte.

of liquid standard using the head-space method. Furthermore, when this method is used, humidity could be other fact to be considerated in the apparition of monomer and dimmer in the IMS spectra. More molecules of water reach the IMS device when we are heating a liquid standard to produce volatiles analytes than when gaseous standards are introduced directly in the IMS by using the exponential dilution method.

From these results it can be concluded that, due to the similar molecular weights of compounds measured in this work prevent its separation by using only UV-IMS. Therefore, we recommend using a pre-column in order to accurately separate and identify each analyte present in the sample prior to its IM analysis. Furthermore, a membrane placed before the entrance of volatiles to the UV-IMS device would be highly recommended to avoid the humidity influence on the ion mobility signals.

Finally, some analytical properties of the three systems tested were compared in Table 6. The attractiveness of the home-made methods proposed for liquid and gaseous samples are mainly the speediness, low cost, simplicity and acceptable sensitivity values. The different optimized methods shown in this work will be used in the future to measure analytes present in different samples from workplaces environment by using UV-IMS technology.

3.3. *Reduced mobilities of compounds studied*

Once studied the analytical features of the different experimental set-up to produce gaseous standards, the reduced mobility, K_0, has been calculated for each target analyte by using the different methods proposed in order to accurately identify analytes from the IM spectra. K_0 corrects operational and environmental deviations. K_0 values, which were calculated from Eq. (1), are compared with previously reported values in Table 7. In practice, K_0 does not always match reported values; the differences usually are ascribed to differences in the preparation of standards and the ionization source used. As can be seen from Table 7, the K_0 values obtained by other authors with an identical ionization source (a UV-lamp) were very similar, whereas those obtained by using a different (radioactive) source to measure ethanol, acetone, toluene, *m*-xylene and *p*-xylene were markedly different [4,5,20–24]. Variations in K_0 values have been also observed associated to the different methods used to generate gaseous standards. Fig. 5 shows the spectra for the individual analytes from a gaseous sample containing 50 ppm$_{(g)}$ measuring by using the exponential set-up already described. As can be seen in Table 3, despite benzene and toluene have a higher molecular weight than acetone and ethanol appeared first, at lower drift time in the IMS spectra. After them, the rest of BTX appeared and finally ethanol and acetone which have a lower molecular weight. The reason why it is easier for aromatics compounds to appear sooner in the IMS spectra could be attributed to the presence of delocalized electrons and the molecule conformation [25–27]. So, under constant electric field, aromatics compounds must move more easily along the IMS drift tube than other family of compounds. Therefore, they appear before in the IMS spectra than linear molecules such as acetone and ethanol.

Notice that lower signal intensity was obtained when ethanol was measured by UV-IMS compared with the signal intensity obtained with the others analytes analyzed. A possible reason of this fact could be related to tendency of this molecule to be affected by the water molecules (5% RH approx.) present in the sample gas (synthetic air). Humidity could act as an interferent and consequently it might reduce the IMS signal as it has been studied for other authors [28,29].

On the other hand, the spectra for toluene, ethylbenzene and benzene were quite similar (an intense peak with different

Table 7
Reduced mobility of the target VOCs studied.

Compound	Method	Drift time (ms)	K_0 calculated	IMS type	Method	K_0 reported	Ref
Acetone	Head-space	18.23 ± 0.04	1.830 ± 0.004	UV-IMS	Head-space	1.75	[20]
	Exponential dilution	18.93 ± 0.12	1.76 ± 0.01	Tritium (^{3}H) TOF-IMS	Exponential dilution	1.44	[23]
				HSCC-UV-IMS	Exponential dilution	1.74	[21]
	Gas generator	17.69 ± 0.03	1.880 ± 0.003	^{63}Ni-CF-IMS	Gas generator	2.32	[24]
Ethanol	Exponential dilution	18.20 ± 0.04	1.830 ± 0.004	UV-IMS	Exponential dilution	1.91	[5]
				Tritium (^{3}H) TOF-IMS	Exponential dilution	1.58	[23]
Ethylbenzene	Head-space	17.15 ± 0.02	1.94 ± 0.02	–			
	Exponential dilution	17.63 ± 0.04	1.89 ± 0.04	–			
	Gas generator	17.07 ± 0.02	1.950 ± 0.003	–			
Benzene	Head-space	17.10 ± 0.08	1.95 ± 0.01	–			
	Exponential dilution	15.83 ± 0.03	2.110 ± 0.005	MCC-UV-IMS	Exponential dilution	2.27	[4]
				HSCC-UV-IMS	Exponential dilution	2.01	[21]
	Gas generator	16.84 ± 0.03	1.980 ± 0.004	^{63}Ni-CF-IMS	Gas generator	2.31	[24]
Toluene	Head-space	17.13 ± 0.05	1.94 ± 0.01	–			
	Exponential dilution	16.69 ± 0.09	2.00 ± 0.01	MCC-UV-IMS	Exponential dilution	2.13	[4]
				HSCC-UV-IMS	Exponential dilution	1.91	[21]
	Gas generator	16.66 ± 0.03	2.00 ± 0.04				
m-Xylene	Head-space	15.98 ± 0.05	2.09 ± 0.01				
	Exponential dilution	17.43 ± 0.04	1.910 ± 0.004	MCC-UV-IMS	Exponential dilution	2.05	[4]
				HSCC-UV-IMS	Exponential dilution	1.83	[21]
o-Xylene	Head-space	15.69 ± 0.02	2.120 ± 0.003	–			
	Exponential dilution	17.38 ± 0.04	1.920 ± 0.005	–			
p-Xylene	Head-space	17.17 ± 0.02	1.940 ± 0.003	–			
	Exponential dilution	17.47 ± 0.06	1.910 ± 0.007	–			
	Gas generator	16.91 ± 0.02	1.970 ± 0.003	UV-hydrogen discharge lamp-IMS	Gas generator	1.83	[22]

(–) No reported values available. (TOF=Time of flight; HSCC=high speed capillary column; CF=cross flow; MCC=multicapillary column).

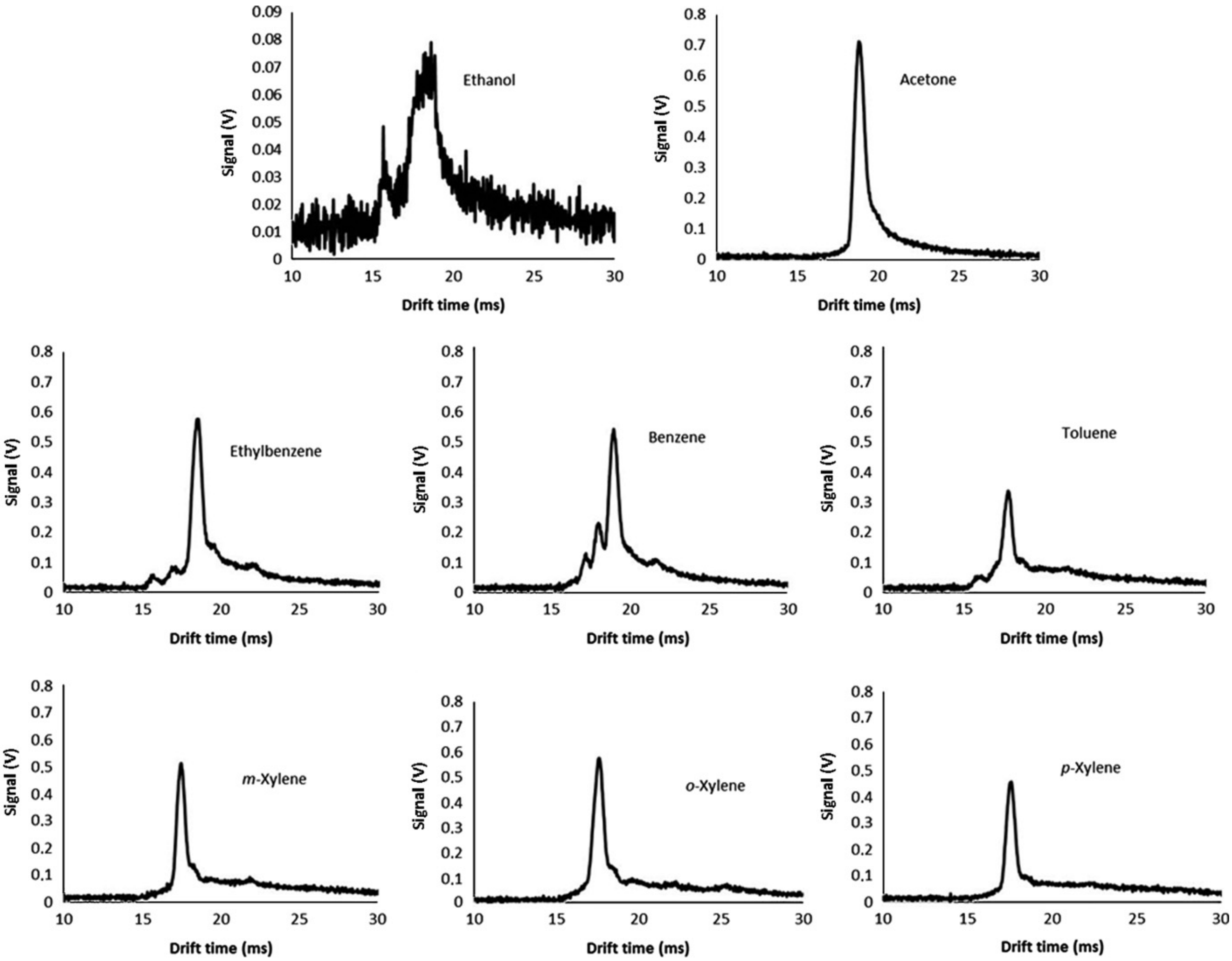

Fig. 5. UV-IMS spectra for 50 ppm$_{(g)}$ VOC gaseous standards obtained by exponential dilution as shown in Fig. 2B.

shoulders can be appreciated), signals appearing at about 17 ms. Xylene isomers, which belongs to the same compound family as benzene and toluene, exhibited a slightly different spectrum (only one intense peak without shoulders), however. The spectra for the three isomers of xylene were quite similar, which made distinguishing their reduced mobilities rather difficult. The difficulty in identifying these compounds by direct UV-IMS (i.e. without a pre-separation column) arises from the similarities between the target analytes. Based on the foregoing, one can expect determining the studied analytes individually in a single sample to be rather a difficult task. However, the proposed method can be used effectively to screen air samples and determine these analytes by using a sorbent tramp column coupled to the UV-IMS in order to improve sensitivity and selectivity. It should be noted that the K_0 values calculated in this work for some of the analytes tested are for the first time reported in the literature. These values are crucial towards their identification in air samples analyzed by UV-IMS.

4. Conclusions

Based on the results of this work, using the proposed home-made SISs as well as the calibration gas generator for UV-IMS allows the reliable production of gaseous standards and calibration of IM equipment. The proposed home-made headspace SIS provided acceptable values of LOD and LOQ throughout the operational range studied for all compounds studied. The exponential dilution setup used affords quick and sensitive measurements of the different concentrations of gaseous VOCs tested. All these results were comparable with the ones obtained with the calibration gas generator. The proposed calibration methods will be used in future work to determine the studied pollutants in liquid and air samples from workplaces such as gas stations and industries.

The IMS was not intended to replace traditional analytical instruments such as GC/MS, but rather to provide a rapid, inexpensive quantitative and qualitative method as a complement to other well-established methods. Its portability and rapid response make IMS a useful tool for online and in situ environmental analyses. The simplicity of use and relatively low cost of the equipment and the methods proposed makes IMS quite attractive and promising for general use in analytical practice in air quality control. Before using this device for field monitoring, a robust and reliable calibration method should be performed. In this work, UV-IMS equipment has been demonstrated to be able to be calibrated in a simpler manner by using different home-made systems depending if the analytical problem to be resolved is in aqueous or gaseous samples.

Acknowledgments

Funding from Spain's DGICyT (Grant CTQ2011-23790) is gratefully acknowledged. LRCG wishes to thank the Spanish Ministry of Education, Culture and Sport for award of a pre-doctoral grant (AP2009-3528) as well as the Institute of Physics CSIC (Madrid, Spain) for the concession of calibration gas generator during the experimental work.

References

[1] J.I. Baumbach, Int. J. Ion Mobil. Spectrom. 11 (2008) 3–11.
[2] L. Arce, in: R.A Meyers (Ed.), Encyclopedia of Analytical Chemistry, 2011, pp. 333–350.
[3] G. Allison, J. Autom. Chem. 20 (1998) 1–7.
[4] St. Sielemann, J.I. Baumbach, H. Schmidt, P. Pilzecker, Field Anal. Chem. Technol. 4 (2000) 157–169.
[5] G.A. Eiceman, Z. Karpas, Ion Mobility Spectrometry, Boca Raton, Fl 33487-2742, 2005.
[6] J.E. Roehl, Appl. Spectrosc. Rev. 26 (1991) 1–57.
[7] G. Walendzik, Anal. Bioanal. Chem. 382 (2005) 1842–1847.
[8] A.B. Kanu, H.H. Hill Jr., J. Chromatogr. A 1177 (2008) 12–27.
[9] D.C. Collins, M.L Lee, Anal. Bioanal. Chem. 372 (2002) 66–73.
[10] G.A. Eiceman, L.G. Gonzalez, Y.F. Wang, B. Pittman, G.E. Burroughs, Talanta 39 (1992) 459–467.
[11] L. Arce, M. Menéndez, R. Garrido-Delgado, M. Valcárcel, Trac-Trends Anal. Chem. 27 (2008) 139–150.
[12] ⟨www.hovacal.de⟩, 2012 (accessed 30.10.12).
[13] ⟨www.owlstonenanotech.com⟩, 2012 (accessed 30.10.12).
[14] ⟨www.vici.com⟩, 2012 (accessed 30.10.12).
[15] A. Neganowska-Nowak, Crit. Rev. Anal. Chem. 35 (2005) 31–55.
[16] P. Konieczka, Trac-Trends Anal. Chem. 26 (2007) 744–751.
[17] R. Alonso, V. Rodríguez-Estevez, A. Domínguez-Vidal, M.J Ayora-Cañada, L. Arce, M. Valcarcel, Talanta 76 (2008) 591–596.
[18] S. Greenhouse, Anal. Chim. Acta 236 (1990) 221–226.
[19] B. Borderie, D. Lavabre, G. Levy, J. Photochem. Photobiol. A: Chem. 56 (1991) 13–23.
[20] R. Garrido-Delgado, L. Arce, C.C. Pérez-Marín, M. Valcárcel, Talanta 78 (2009) 863–868.
[21] Z. Xie, S. Sielemann, H. Schmidt, F. Li, J.I. Baumbach, Anal. Bioanal. Chem. 372 (2002) 606–610.
[22] C.S. Leasure, M.E Fleischer, G.K. Anderson, G.A. Eicemann, Anal. Chem. 58 (1986) 2142–2147.
[23] C. Tiebe, Anal. Bioanal. Chem. 395 (2009) 2313–2323.
[24] M. Zhang, S. Wexler, Int. J. Mass Spectrom. 258 (2006) 13–20.
[25] K.E. Peters, C.C. Walters, J.M. Moldowan, The Biomarker Guide: Biomarkers and Isotopes in the Environment and Human History, Cambridge University Press, 5 A.D.
[26] M. Meot-Ner, P. Hamlet, E.P. Hunter, F.H. Field, J. Am. Chem. Soc. 100 (1978) 5466–5471.
[27] E. Matito, M. Durán, M. Solà, J. Chem. Phys. 122 (2005) 14109–14117.
[28] W. Vautz, S. Sielemann, J.I. Baumbach, Anal. Chim. Acta 513 (2004) 393–399.
[29] M. Mäkinen, Talanta 84 (2011) 116–121.