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Using corona discharge-ion mobility spectrometry for detection of 2,4,6-Trichloroanisole

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ABSTRACT

In this work possible application of the corona discharge-ion mobility spectrometer (CD-IMS) for detection of 2,4,6-Trichloroanisole (TCA) has been investigated. We applied CD-IMS interfaced with orthogonal acceleration time of flight mass spectrometer (CD-IMS-oaTOF) to study the ion processes within the CD-IMS technique. The CD-IMS instrument was operated in two modes, (i) standard and (ii) reverse flow modes resulting in different chemical ionisation schemes by $NO_3^-(HNO_3)_n$ (n=0,1,2) and $O_2^-(H_2O)_n$ (n=0,1,2), respectively. The $O_2^-(H_2O)_n$ ionisation was associated with formation of Cl^- and $(TCA–CH_3)^-$ ions from TCA. The $NO_3^-(HNO_3)_n$ ionisation, resulted in formation of $NO_3^-(HNO_3)(TCA–Cl)$ adduct ions. Limit of detection (LOD) for TCA was determined in gas (100 ppb) and solid phases (150 ng).

1. Introduction

The wine industry and consumers themselves deem that wine aroma is an important attribute of product quality. The presence of halo-anisoles is an oenological problem in wine industry because of their low sensory threshold. Trichloroanisole (TCA), particularly the 2,4,6-TCA isomer, is considered as the main substance causing the unpleasant odour of wine also known as “cork taint”, mentioned in some researches [1,2]. This musty, mouldy odour of tainted wine originating from the cork material is directly detected by consumers of wine and is defined as similar to wet cardboard, mushrooms, earthy smell, etc. [1]. The dominant mechanism for generation of 2,4,6-TCA, not a naturally creating compound, is process of O-methylation of 2,4,6-trichlorophenol (2,4,6-TCP) by filamentous fungi [3]. The concentration considered as an appreciable defect in wine ranges from 10–40 ng L^{-1} [4]. TCA is presumed as the major culprit for tainted wine that influences directly wine producers. Their financial losses due to this unacceptable flavour are calculated to be in billion US dollars range [5].

Serious detection problem of this semi-volatile compound lies in low concentration at which this analyte could be present in wine. Hence it is substantial for determination of 2,4,6-TCA to retrieve suitable pre-concentration, pre-separation and sensitive analytical device for measuring signal intensity. The conventional sample preparation techniques for estimating 2,4,6-TCA involve liquid–liquid extraction (LLE) [6], solid phase micro-extraction (SPME) [7], stirbarsorptive extraction (SBSE) [3], solid phase extraction (SPE) [8] and head-space solid-phase micro-extraction (HS-SPME) [9]. All these techniques suffer different restrictions including protracted and multistep procedures, high analysis price, poor sensitivity, low selectivity and high degree of matrix effect. Although the HS-SPME method has been availed in research dealt with water and wines [10], it disposes of inadequate selectivity and sensitivity.

Several analytical methods have been proposed for the proper concentration determination of the compounds responsible for tainted wine flavour [1,11,12]. Considering the physico-chemical properties of semi-volatile compound 2,4,6-TCA, a novel gas chromatography–mass spectrometry (GC–MS) method, focused on this compound residues in white and red wine was reported by Patil [11]. The efficiency of 2,4,6-TCA analysis was affected by few factors, including extraction solvent type chosen (toluene in this case) and particularly its volume. The detection limit of this compound reached value of 0.0083 ng mL^{-1}. This technique offers distinct advantages, but it still does not dispose of such sensitivity and selectivity as ion mobility spectrometry.

Ion mobility spectrometry (IMS) is an analytical technique that characterises molecules by their gas phase mobility and is frequently used for detection of various kinds of explosives, drugs

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and narcotics. IMS provides fast and high sensitive response to presence of not only explosives, but also toxic chemicals. In addition, ion mobility spectrometers are comparatively inexpensive and provide spectra in milliseconds range. These advantages make IMS device suitable for investigation of volatiles compounds in different fields [13]. Several studies have been focused on detection of presence of 2,4,6-TCA in wine with IMS [1,12].

Headspace-multicapillary column coupled with IMS (HS-MCC) has been used for the direct detection of 2,4,6-TCA sample contaminating wine and cork stoppers. The sample was added to a headspace vial and it was processed without any additional treatment in fully automated modules (headspace, multicapillary column and IMS). The limits of detection obtained in this work were 0.012 ng L^{-1} for wine and 0.28 ng g^{-1} for the cork stopper [12].

Karpas et al. has applied IMS to investigate 2,4,6-TCA compound in wine. In positive ion mode, the dominant peaks observed corresponded to a monomer ion and a lower intensity dimer species, with values of reduced mobility (K_0) of 1.58 and 1.2 $cm^2\,V^{-1}\,s^{-1}$. In negative mode three peaks as a response on TCA were detected with reduced mobilities of 1.64, 1.48 and 1.13 $cm^2\,V^{-1}\,s^{-1}$, respectively. The first observed peak was attributed to a trichlorophenoxide species and another two peaks were ascribed to chloride attachment adducts of a TCA monomer and dimer. In addition, this scientific group has reached detection limits of 1.7 ppm in the gas phase and 2.1 μg in the solid phase [1] Table.1.

The main goal of this work was to study atmospheric pressure gas-phase ion chemistry of 2,4,6-TCA in CD-IMS coupled with orthogonal accelerated time of flight mass spectrometer (CD-IMS-oaTOF). The IMS ion source was based on negative corona discharge. The CD was operated in two modes; the standard gas flow mode which generated $NO_3^-(HNO_3)$ and $NO_3^-(HNO_3)_2$ reactant ions [14] and the reverse gas flow mode with the main reactant ions $O_2^- \cdot (H_2O)_n$ [15]. Research also included determination of detection limit for 2,4,6-TCA, in gas phase as well as in solid phase, by CD-IMS.

Table 1
Operation parameters of the CD-IMS instrument.

Drift tube length	12.1 cm
Electric field intensity	495 V/cm
SG pulse	15 μs
Drift gas flow	1.2 L/min
Sample gas flow	0.4 L/min
Drift tube temperature	380 K
Used resolution	30

2. Experiment

The TCA detection was studied using two different instruments, (i) standalone single flow CD-IMS instrument and (ii) CD-IMS-oaTOF instrument. The CD-IMS instrument was used for LOD determination in reverse flow regime and the CD-IMS-oaTOF instrument was used for the ion chemistry study in standard and reverse flow regimes.

2.1. IMS instrument

We used home built single flow CD-IMS (Fig. 1) in this study. The gas outlet was placed behind the corona ion source thus the CD was operated at reverse flow regime [15]. The opening time of the Shutter Grid (SG) in present experiment was 15 μs with repetition rate 17 ms. Sixteen IMS spectra were used for signal averaging resulting in duty cycle of 0.272 s. The IMS instrument is capable of working with resolution up to 90. However, in this study the resolving power of the IMS instrument was set to 30 full width half maximum (FWHM) in order to achieve better sensitivity. The IMS was operated at sub atmospheric pressure and was heated to 380 K. The atmospheric air, additionally purified by molecular sieve traps (Agilent), was used as a drift gas. The drift gas flow was 1.2 L min^{-1}. The sample gas was guided through a 5 cm stainless steel capillary of 0.5 mm inner diameter, heated at the 356 K. The work of our instrument at sub atmospheric pressure allowed us to suction of atmospheric air (without any purification), to the reaction region of IMS, through the capillary [16]. The sample gas flow was 0.4 L min^{-1}.

2.2. IMS-oaTOF instrument

In addition to the standalone IMS instrument, we have performed IMS-oaTOF studies of the negative ions formed from TCA. The functionality of IMS-oaTOF instrument has been described by Sabo et al. [14,17]. The CD reactor was in point-to-plane geometry. The IMS was operated with drift field 543 V cm^{-1}, the SG gate was opened for 110 μs with period of 20 ms. The IMS-oaTOF instrument was operated in two different gas flow regimes. In the reverse flow regime the gas outlet was located behind the CD gap with a drift gas flow of 1 L min^{-1} and the sample gas flow of

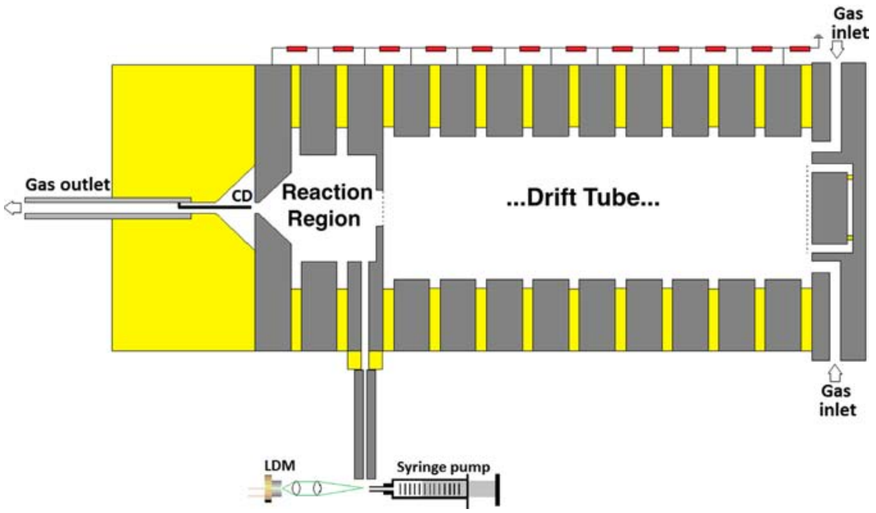

Fig. 1. Schematic view of the CD-IMS instrument.

40 mL min^{-1} [14,15]. In this configuration the gas flow was opposite to ions movement in the CD gap that resulted in the removal of neutral product of CD from CD gap. In the standard flow regime the gas outlet was located in the reaction region of IMS with a drift gas flow of 0.8 L min^{-1}, a sample gas flow of 0.2 L min^{-1} and a CD gas flow of 0.1 L min^{-1} [14]. In this gas flow mode the gas flows through the CD gap in the same direction as the ions.

The IMS instruments were calibrated on the base of the known value of the reduced ion mobility of $N_2O_2^-$ in O_2 drift gas. The reduced mobility of this ion has value of 2.52 cm^2 V^{-1} s^{-1} [15] and is used as a calibration standard in our laboratory.

2.3. Gases and chemicals

The N_2/O_2 mixture of purity 5.0 (LindeGas) in ratio 4:1 was used as a zero air for CD-IMS-oaTOF instrument. The atmospheric air purified by the molecular sieve traps (Agilent) was used as drift gas in the CD-IMS instrument. The 2,4,6-Trichloroanisole (TCA) was purchased from Sigma Aldrich (purity 99%). The TCA was used without additional purification. Methanol used as solvent for TCA and preparation of solutions was of analytical grade purity.

2.4. Sample preparation

For the gas phase sample, we used 30 mg of TCA inserted into 10 mL syringe filled with atmospheric air, placed into a syringe pump (Kent Scientific). The syringe needle tip was interfaced in front of the stainless steel capillary injection port of the CD-IMS instrument. We waited for 15 min in order to achieve equilibrium vapour pressure of TCA in the syringe. After that time the volume of the syringe was pumped at different flow velocities. The concentration of TCA in the volume of the syringe was calculated on the basis of the known value of the vapour pressure 2.065 Pa at 25 °C [18].

For the solid phase, six stock solutions were prepared by weighing TCA samples and dissolving in methanol, yielding concentrations of 10 mg mL^{-1}, 5 mg mL^{-1}, 2.5 mg mL^{-1}, 1.25 mg mL^{-1}, 0.625 mg mL^{-1} and 0.31 mg mL^{-1}, respectively. Subsequently, 0.5 μL of each solution was expelled from the volume of 1 μL syringe (Hamilton) to the syringe needle tip. After evaporation of methanol, the needle tip was placed in front of the capillary inlet. A laser beam generated by Laser Diode Module (LDM), was focused on the syringe tip in the front of the stainless steel capillary of IMS instrument as depicted in Fig. 1. The sample desorbed by the laser from the syringe tip was transported to the reaction region of IMS via the heated capillary. We used LDM of 532 nm wavelength (Power Laser s.r.o.) and power 300 mW.

In the case of the CD-IMS-oaTOF instrument, in order to get higher concentration of the TCA gas sample, 5 mg TCA was evaporated from a small aluminium pot using a heater made of nicrom wire and mica plates. The temperature for evaporation of the sample was set to 433 K. The zero air with flow rate of 40 mL min^{-1} in reverse gas flow mode and 200 mL min^{-1} in standard gas flow mode, transported the TCA sample into the reaction region of the CD-IMS-oaTOF instrument.

3. Results and discussion

3.1. IMS spectra

The IMS spectrum of TCA measured by the CD-IMS-oaTOF instrument at 360 K in the reverse flow regime is depicted in the Fig. 2a and related MS spectrum is available in the Fig. 2b. The 4.86 ms and 5.16 ms peaks (reduced ion mobilities of 2.37 and 2.23 cm^2 V^{-1} s^{-1}) correspond with reactant ion peaks (RIP). As seen from the corresponding mass spectrum, the 2.37 cm^2 V^{-1} s^{-1} peak is composed of $N_2O_2^-$ ions ($m/z=60$) while the 2.23 cm^2 V^{-1} s^{-1} IMS peak is composed of O_2^-, $O_2^-(H_2O)$, CO_4^-, $CO_4^-(H_2O)$, $N_2O_3^-$, $N_2O_3^-.(H_2O)$ ($m/z=32$, 50, 76 and 94) [15]. The response of the CD-IMS-oaTOF instrument on TCA sample resulted in formation of two new IMS peaks at drift times of 4.46 ms and 7.2 ms (reduced ion mobilities 2.58 and 1.6 cm^2 V^{-1} s^{-1} respectively). The mass spectrum (MS) shows two species as a response on TCA, the Cl^- ($m/z=35$ and 37) and $[TCA–CH_3]^-$ (de-methylated TCA anion) composed of MS peaks m/z 195, 196, 197,198 and 199 Da [1]. The reduced mobility 2.58 cm^2 V^{-1} s^{-1} of Cl^- ions is slightly different from the mobility value 2.69 cm^2 V^{-1} s^{-1} reported by Karpas et.al [1]. As main reason for this inaccuracy we see in different drift gas humidity as well like IMS drift tube temperature conditions in both experiments. These conditions should significantly affect the abundance of water molecules attached to Cl^- ions what affects the reduced mobility of Cl^- clusters. On the other hand the reduce mobility 1.6 cm^2 V^{-1} s^{-1} for the $[TCA–CH_3]^-$ ions is in fairly good agreement with the value 1.64 cm^2 V^{-1} s^{-1} reported in previous study [1]. We assume that these ions are formed via charge transfer reactions:

$$O_2{}^-(H_2O) \text{ or } CO_4{}^-(H_2O)+\text{TCA}\rightarrow Cl^- +(\text{TCA–Cl}) \tag{1}$$

$$O_2{}^-(H_2O) \text{ or } CO_4{}^-(H_2O)+\text{TCA}\rightarrow[\text{TCA}-CH_3]^- +CH_3 \tag{2}$$

We were not able to find neither kinetic nor thermochemical data (enthalpy of formation of TCA, electron affinity of $[TCA–CH_3]$, enthalpies of formation of fragments and radicals) for these dissociative charge transfer reactions. However, the observation of these ions in IMS experiments indicates that these reactions are

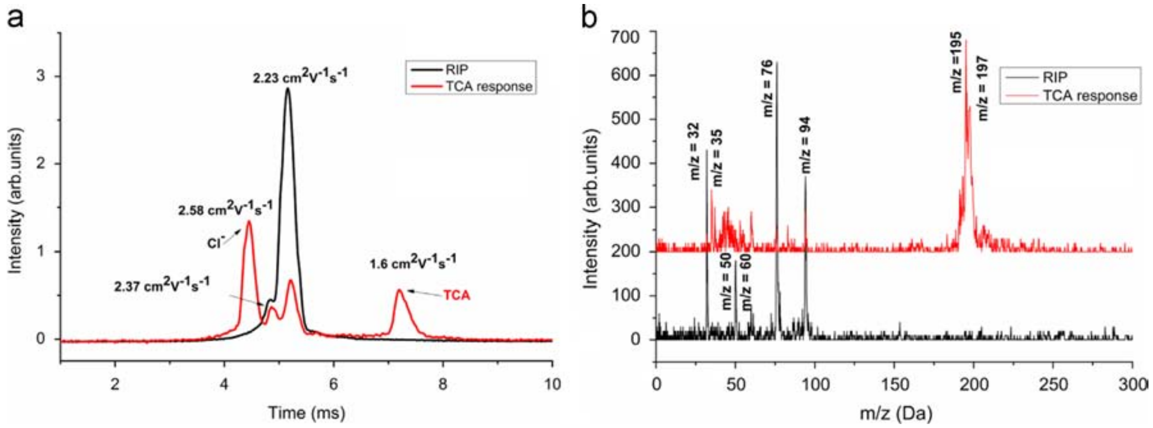

Fig. 2. (a) IMS spectrum of TCA in the reverse gas flow mode and (b) corresponding mass spectrum of TCA in the reverse gas flow mode.

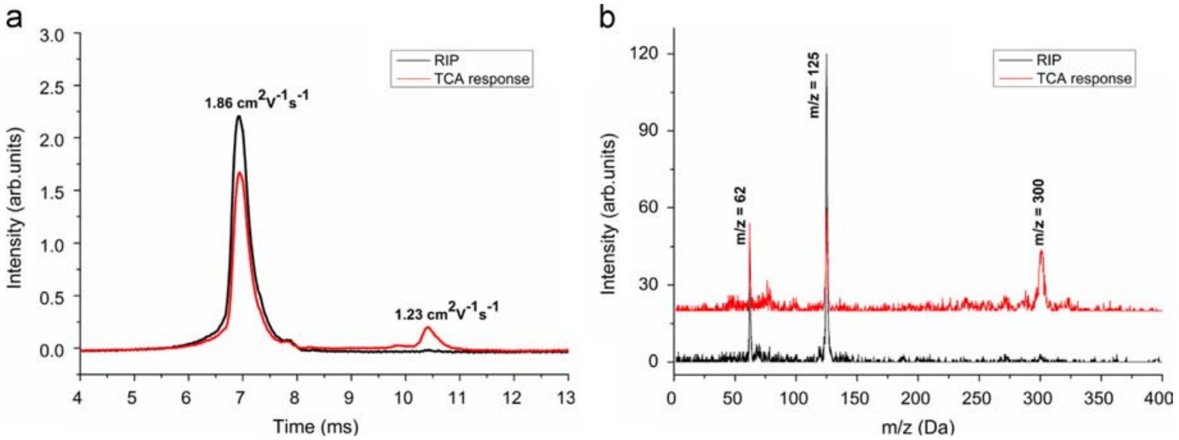

Fig. 3. (a) IMS spectrum of TCA in standard gas flow mode and (b) corresponding mass spectrum of TCA in standard gas flow mode.

exothermic. In the reverse gas flow mode, the reactant ion peaks (RIP) are similar to those generated from the radioactive ^{63}Ni [15] ($O_2^-(H_2O)_n$, 0,1,2). In the standard gas flow mode, the major reactant ions are $NO_3^-(HNO_3)_n$ ($n=0,1,2$) [14]. The RIP measured by the CD-IMS-oaTOF instrument operated in the standard gas flow mode at temperature of 318 K are shown in Fig. 3. As we can see from this picture the RIP at the drift time of 6.92 ms (reduced mobility of 1.86 $cm^2 V^{-1} s^{-1}$) (Fig. 3a) is composed of the ion $m/z=125$ (Fig. 3b) and was assigned to $NO_3^-(HNO_3)$ ion. The NO_3^- ions ($m/z=62$) are present in the MS spectrum due to fragmentation of the $NO_3^-(HNO_3)$ in the vacuum interface of the CD-IMS-oaTOF instrument [14]. The response of $NO_3^-(HNO_3)$ RIP on 2,4,6-TCA results in appearance of one peak in IMS spectrum at the drift time of 10.42 ms (reduced mobility of 1.23 $cm^2 V^{-1} s^{-1}$) (Fig. 3a). This peak is composed of ions with $m/z=300$ (Fig. 3b). We were not able to find any information concerning interaction of 2,4,6-TCA with $NO_3^-(HNO_3)$ we tentatively assign this peak to $NO_3^-(HNO_3)(TCA–Cl)$ ions. Unlike in the case of reverse flow mode, the separated chlorine is not observed in the normal flow mode since chlorine electron affinity is less than that of the reactant ions, mainly NO_3^-.

3.2. Temperature effect

Since the m/z 300 is assigned to cluster ion of $NO_3^-(HNO_3)(TCA–Cl)$, we were interested in stability of this ion with increasing temperature of IMS. The investigated range of temperature was from 303 K to 363 K. The response of the CD-IMS-oaTOF instrument in this temperature range on 2,4,6-TCA, operated in the standard gas flow mode, is shown in Fig. 4. The intensity of the heavier cluster $NO_3^-(HNO_3)_2$ decreases in favour of the lighter cluster due to increasing temperature. Generally, large clusters brake to small clusters as temperature increases. However, the intensity of $NO_3^-(HNO_3)(TCA–Cl)$ peak was first increasing with increasing IMS temperature (until 323 K) and then started to decrease. This behaviour could be explained by considering the two parallel reactions.

$$RI + HNO_3 \leftrightarrow NO_3{}^-(HNO_3)_2 \tag{3}$$

$$RI + TCA \leftrightarrow NO_3{}^-(HNO_3)(TCA–Cl) + Cl \tag{4}$$

In these reactions, RI stands for the reactant ion, $NO_3^-(HNO_3)$. As temperature increases, Reaction 3 moves backward, producing more RI's which push Reaction 4 forward, hence more TCA response. On the other hand, temperature causes reaction 4 to pull backward. These two opposite effects determine the number density of TCA related ions. The increasing trend continues to 323 K where the concentration of the RI becomes almost constant, as seen in Fig. 4. As temperature increases further the TCA ions decomposition dominants so that there is no response on presence of TCA after reaching IMS temperature to 363 K. The intensity of ion $NO_3^-(HNO_3)_2$ is significant at lower IMS temperature, particularly at 303 K [14]. As we can see from this figure, the disappearance of cluster $NO_3^-.(HNO_3)_2$ ion was observed already at temperature of 318 K [14].

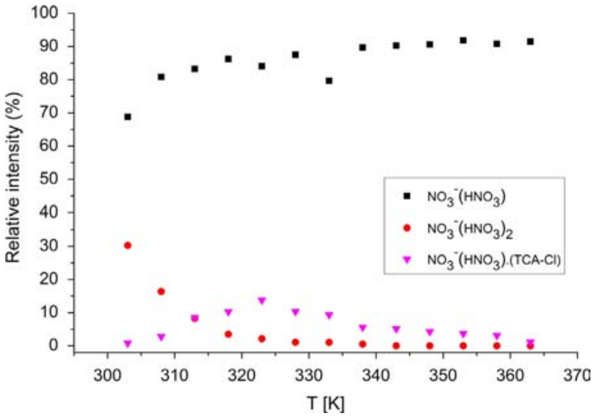

Fig. 4. Relative intensities of $NO_3^-(HNO_3)$, $NO_3^-(HNO_3)_2$ and $NO_3^-(HNO_3)(TCA–Cl)$ ions measured under different IMS temperatures.

3.3. Limit of detection

The solid phase and gas phase LOD were determined using CD-IMS. As the $NO_3^-(HNO_3)$ reactant ion chemistry was shown not to be effective for determination of LOD of 2,4,6-TCA, we decided to operate the CD-IMS instrument only in the reverse gas flow mode with Cl^- ion for determination of LOD.

The solid phase LOD was measured in the range from 2.5 µg to 150 ng (Fig. 5a). The specific amount of TCA was spread on the needle tip of 1 µL syringe. The needle tip was in the next step placed in front of heated capillary of the CD-IMS instrument and the sample was desorbed from the surface by the laser diode module. The LOD of 150 ng was determined in this case. The linear calibration curve for this concentration range is shown in Fig. 5a. The calibration curve was obtained from amplitude of the peaks and calculated via the univariant technique.

The gas phase LOD was determined on the following way, 30 mg of TCA was placed into a 10 ml syringe. The vapour inside

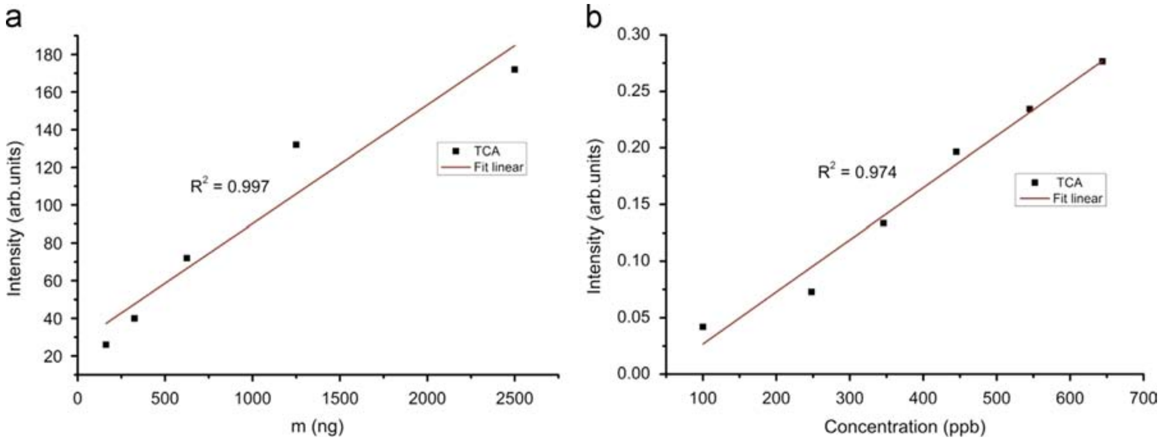

Fig. 5. Calibration curves for TCA measured from (a) solid; and (b) gas phases.

the syringe was pumped in the front of the heated capillary of the CD-IMS instrument, the air flow through the capillary was 400 mL min^{-1}. The gas flow from the syringe was controlled by the syringe pump in the range from 15 mL min^{-1} to 2 mL min^{-1} that represents TCA concentration from 650 ppb to 100 ppb. The linear calibration curve for this concentration range is shown in Fig. 5b. The calibration curve was obtained from amplitude of the peaks and calculated via the univariant technique. As we can see from this figure the LOD of TCA measured in the gas phase was 100 ppb.

4. Conclusion

The potential of the CD-IMS and CD-IMS-oaTOF instrument for detection of TCA was demonstrated in this research. IMS and MS spectra of TCA were investigated. Dominant ions detected in the reverse mode were Cl^- and $(TCA–CH_3)^-$. However, in the standard mode, the detected IMS peak was attributed to $NO_3^-(HNO_3)(TCA–Cl)$ ions with reduced mobility of 1.23 cm^2 V^{-1} s^{-1}and $m/z = 300$ Da. The experiment confirmed the possible application of the CD-IMS technique for TCA detection in both operation modes in the negative polarity. The solid phase LOD for TCA was determined to be 150 ng for a sample desorbed to IMS by simple LDM of 532 nm wavelength with 300 mW power. In the gas phase we achieved a 100 ppb LOD for the TCA. This LOD is significantly better then in IMS studies where the conventional radioactive ionisation source was used [1,19]. Thus the CD-IMS has better potential to be used for the detection of TCA in gas or solid phase.

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