

Detection of Volatile Organic Compound with an Ion Mobility Spectrometry Cell Type Device with a Corona Discharge Ionization Source

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Using the cross flow ion mobility spectrometry (CFIMS) concept, together with a pulsed corona discharge ionization source, a prototype of IMS cell type device was constructed and tested. In this work, we report the experimental conditions to set up the instrument and the analytical results based on the principal components analysis (PCA) obtained in the detection of toluene, acetone, ethanol and isoamyl acetate on gas phase. The advantages of this new design are the high ions concentration obtained compared to the commonly used ⁶³Ni source, the simplicity of the CFIMS and the rapid response time.

Keywords: Ion Mobility Spectrometry (IMS), Corona Discharge, Principal Component Analysis (PCA), Gas Monitoring.

1. INTRODUCTION

Ion Mobility Spectrometry (IMS) is a technique to trace and characterize organic vapours in ambient air. This technique comprehends ionization of the molecules and their subsequent temporal flight through an electric field. The analysis and characterization of molecules are based on the analytical separation from different ionic mobilities.¹ The distribution of the charge collected at the detector assembly constitutes a fingerprint for each organic compound.

The IMS technique has a very rapid response time, which makes it attractive for high control demand situations. IMS for *in-situ* detection in military, safety and environmental applications has generated great interest in this area of research.^{2,3}

The pulsed corona discharge ionization (PCDI) source for ion mobility spectrometry has demonstrated high efficiency to produce ions and also, it is possible to eliminate the typical ion injection gate in the IMS cell.⁴ Moreover, the pulse of ions generated by such sources is quite stable despite the instabilities associated with the phenomenon

of electrical corona. These characteristics of the PCDI encourage us to use this technique as an ionization source in this work. The physics and mechanism of corona discharge are well described in the bibliography.^{5,6}

2. EXPERIMENTAL DETAILS

An experimental device was designed to generate and trace ions based on the model proposed by Solis and Sacristán:⁷ the electric field is transversal to the ion flow determined by the carrier gas. A scheme is shown in Figure 1. It consists of three principal parts: (A) the sample and carrier gas inlet, (B) the ionization source and (C) the detection cell.

A carrier gas passes through a trap dragging the vapor of the sample towards the ionization zone where it is ionized with a type of pulsed corona discharge (PCD). Due to the high intensity of the discharge the molecules are fragmented in different ions that constitute the fingerprint of the substances. The ions generated pass through a grounded metal grid and are finally dragged towards the detection cell. The detection cell is an array of 7 grounded copper electrodes of 2 mm × 2 mm with a separation between each one of them of 0.5 mm, mounted in

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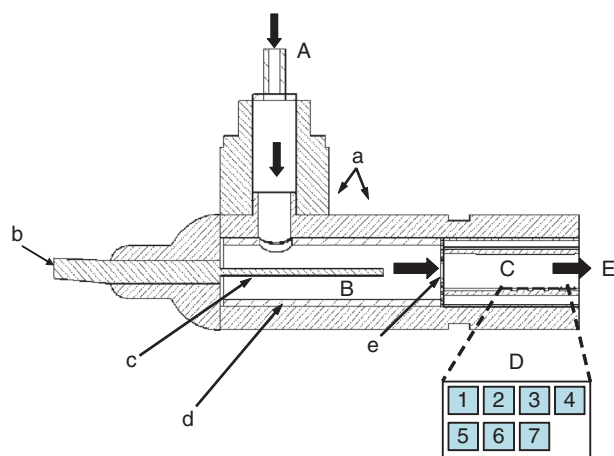


Fig. 1. Lateral section of the experimental device: (A) Sample and carrier gas flow inlet, (B) Ionization source (corona discharge), (C) Detection cell, (D) Detectors arrangement (upper view), (E) Sample and carrier gas flow outlet, (a) Teflon body (support), (b) High-voltage wire, (c) Steel needle (positive electrode), (d) Copper cylinder (grounded electrode), (e) Metallic grid. The wide arrows indicate the flow of carrier gas and sample.

a printed circuit board placed in a plane (indicated with D in Fig. 1), facing a reference electrode connected to a constant potential that can be varied in a range between 10 V and 100 V. The ion source plus detection cell is 5 cm long.

The electrical signal generated by the ions is measured in an oscilloscope synchronized with the discharge pulse, avoiding the use of ion gates. The experiments were carried out at atmospheric pressure and room temperature, and a controlled flux of N_2 (Indura 99.998%, $H_2O \leq 3 \text{ mg ml}^{-1}$) was used as carrier gas. The signals strongly depend on the carrier gas flux, the humidity of the sample, the input temperature and the electric field applied. These variables have been carefully measured in order to establish the best measurement conditions. The results obtained are modulated by the ionic mobilities of the substances. Four organic compounds were studied by this system: ethanol absolute (Merck, pro-analysis, 99.8%), toluene (Mallinckrodt, analytical reagent, 99.8%), acetone (Sintorgan, analytical reagent, 99.5%), and isoamyl acetate (Carlo Erba, analytical reagent, 99.8%), all of them were used without prior purification.

3. RESULTS AND DISCUSSION

3.1. Pulsed Corona Discharge (PCD) Ionization Source Characteristics

Corona discharge is a kind of electric discharge, generated by a strong non-uniform electric field at the edge of a conductor when the size of the electrode is much smaller than the interelectrode distance and prior to electrical breakdown. In our PCD system this ratio is equal to 0,1 and can be included in the corona regime.⁵ The PCD

Table I. Operational variables of pulsed corona discharge ionization source.

Electrical parameters	
Amplitude of pulse voltage	5 kV
Duration of pulse voltage	20 μs
Repetition rate	2 Hz
Estimated positive ions per pulse	10^8

system consists of a needle to cylinder plane geometry. The central electrode, shown in Figure 1, is a stainless steel needle of 0.4 mm of diameter fixed inside a Teflon cylinder. A grounded copper cylinder of 8 mm of diameter closes the discharge circuit of the pulse. The needle is concentric to the copper cylinder; hence, the distance between electrodes is approximately 4 mm. Also, for the characteristics of the discharge, no internal erosion of the device is observed. Table I indicates the electrical parameters used in this work. A stainless steel grid is placed between the ionization chamber and the detection cell in order to screen the high electric field produced during the ionization discharge.

3.2. Ion Detection Cell Performance

Typical signals (voltage vs. time) were obtained for toluene, acetone, ethanol and isoamyl acetate molecules (not shown).

In order to make the identification of each compound the numerical integration of each detector signal was made. This value represents the accumulated charges in each detector. The integrated signal was subsequently plotted as a function of the detectors, and the results are presented in Figure 2.

To improve the level of discrimination, the principal components analysis (PCA), commonly applied in chemical analysis, was used.⁸ The PCA algorithm is based on a linear transformation that projects the original space into one of lower (two in our case) dimensions.

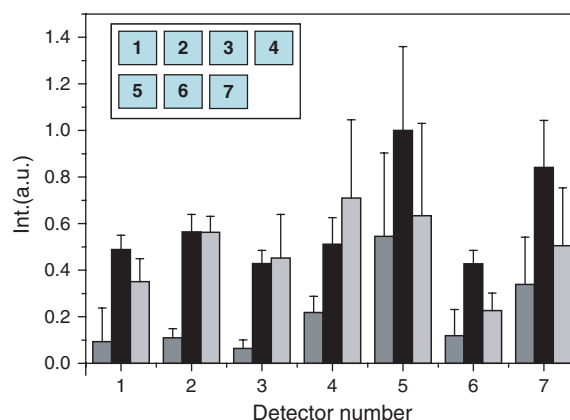


Fig. 2. Integrated electrode signal for toluene (□), acetone (■) and ethanol (■) as a function of the electrode position. At the upper left of the diagram, the location of each detector in the detection cell is shown.

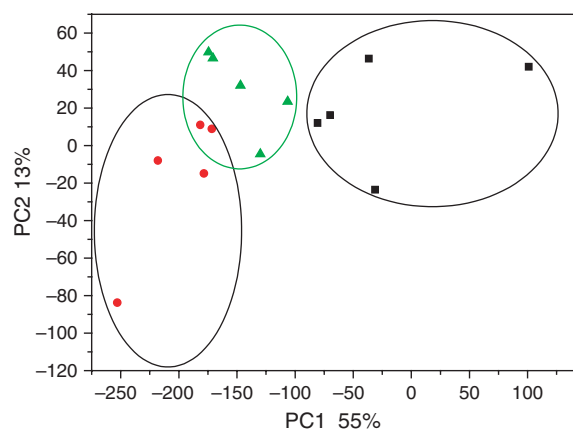


Fig. 3. Measurements of PCA of Acetone (■), Ethanol (●) and Toluene (▲).

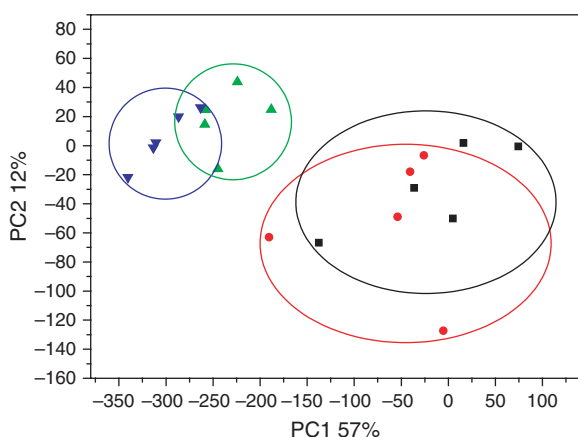


Fig. 4. Measurements of isoamyl acetate PCA at different concentrations: 10 $\mu\text{g ml}^{-1}$ (■); 100 $\mu\text{g ml}^{-1}$ (●); 1000 $\mu\text{g ml}^{-1}$ (▲) and 10000 $\mu\text{g ml}^{-1}$ (B).

The success of the discrimination of acetone, ethanol and toluene was analyzed. The PCA algorithm was performed using the covariant matrix and taking into account the first two principal components. For each compound, response data from the seven sensors corresponding to the integrated signal were reduced by PCA analysis to enable two dimensional score plots. Results are shown in Figure 3 with 55% the first principal component and 13% the second principal component. Three different regions can be established, which correspond to the different organic compounds. There is a slight overlap between ethanol and toluene. However, this problem can be overcome by increasing the number of accumulated data for each measurement.

The detection limit of the system was evaluated by means of isoamyl acetate diluted in toluene at four concentrations: 10, 100, 1000 and 10000 $\mu\text{g ml}^{-1}$ (Fig. 4). These two compounds were chosen because of their different values of mobility constant K_0 between each other, avoiding overlapped signals.⁹ The results show that this device allows measuring minimum detectable concentrations in the order of 1000 $\mu\text{g ml}^{-1}$.

4. CONCLUSIONS

An experimental prototype of IMS type device is proposed. According to the results, the system can discriminate different organic compounds depending on the ionic mobilities of the molecules. The advantage of the PCD system is the high ions concentration obtained compared with ^{63}Ni commonly used.

Although the analysis by PCA allows a correct discrimination of the compounds, further studies will be made with the aim to improve the identification of compounds and the limit of detection.

This device will be used as the first step in the development of a new type of sniffer.

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