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Simultaneous detection of benzene and toluene using a pulsed ion mobility spectrometer

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ABSTRACT

Ion mobility spectrometry (IMS) is a well known method for fast trace gas detection in air. Having simple instrumentation, IMS is especially suited when portability and highest sensitivity are required. However, due to competing chemical ionization processes in the reaction region of IMS, it can be difficult or even impossible to detect small amounts of certain substances in a complex mixture. A prominent example is the detection of low benzene concentrations in the presence of higher toluene concentrations. In this paper we present experimental results of simultaneous toluene and benzene detection by using a pulsed electron source for ionization and demonstrate how this can help to overcome the major issue of atmospheric pressure chemical ionization (APCI).

1. Introduction

Ion mobility spectrometry (IMS) is a well known method for detecting hazardous compounds in air. Typical applications are the detection of chemical warfare agents, explosives and drugs of abuse [1]. Combined with gas chromatography and/or mass spectrometry, IMS is also successfully used in many other applications, such as protein analysis [2]. Detection limits in the low parts per billion range, fast response and recovery times, and simple instrumentation have made this technique quite popular in the field of portable gas detectors [3]. Most commercial devices are normally equipped with radioactive electron sources, such as H-3, Ni-63 or Am-241 to ionize the sample molecules, but many other ionization principles have been successfully applied, e.g. corona discharge [4,5] or optical sources [6,7]. After ionization the ions are accelerated into a drift tube, where they collide with ambient air molecules leading to an average drift velocity. This velocity depends on numerous parameters, which include the ion mass and collision cross section. Thus different ions have different drift velocities, and consequently need a characteristic time of flight for passing the drift tube. IMS devices are limited in their resolving power which usually varies between 30 and 60; their distinctive advantage is ultra-high sensitivity combined with quite simple instrumentation [1].

The device in general consists of three regions: A reaction region, followed by a drift region and a collector region. The sample molecules are ionized in the reaction region, usually in ambient air under ambient conditions. Free electrons initiate a cascade of chemical gas phase reactions that generate positively and negatively charged reactant ions which can further ionize sample molecules to form product ions by either proton transfer reactions or adduct formation with $O_2{}^-(H_2O)_n$ or $H_3O^+(H_2O)_n$ reactant ion clusters. These reactant ion clusters form a signal in an IMS spectrum that is called reactant ion peak (RIP, which is always present unless all the reactant ions are consumed during the analyte ionization process). After a certain time of ionization the ions are injected into the drift tube by an electrical field in the reaction region, and depending on the polarity of the injection field the device detects either all negatively or positively charged ions; these two polarities are called negative and positive mode of the IMS device. Depending on the electron and proton affinity some analytes are better ionized by negative reactant ions and thus better detected in the negative mode, and vice versa [1]. In the drift region, the ions drift toward the detector and separate due to their different mobilities in ambient air. A stronger electric field in the collector region further accelerates the separated ions finally to the detector so that they produce a suitable signal.

Due to many different ion species present during the ionization process, additional ion–ion and ion–molecule reactions of analyte ions are possible. Therefore, it is extremely difficult if not impossible to obtain quantitative information from the IMS

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spectrum. Furthermore, masking or complete disappearance of certain analyte ions is possible. In the positive mode especially the proton affinity of the analytes in combination with their concentration affects the peak height in the spectrum. A good example is dimethyl methylphosphonate (DMMP) having high proton affinity of 898.4 kJ/mol that increasingly dominates the spectrum with an increasing concentration. Similarly, substances with a proton affinity lower than that of protonated water clusters (ca. 690 kJ/mol for water) cannot be ionized and thus do not form a signal in the IMS spectrum [1].

Due to its low proton affinity of 750 kJ/mol benzene belongs to the group of substances which are difficult to detect using IMS devices with standard radioactive electron sources [8]. Thus other techniques and ionization sources have been used in the past [9–11], with optical sources being most successful [12–15]. However, some of these sources suffer from low ionization efficiency and therefore less sensitivity. In addition, long term stability and complex instrumentation is disadvantageous. As mentioned above, the detection of benzene in the presence of toluene with a higher proton affinity of 784 kJ/mol is difficult since atmospheric pressure chemical ionization (APCI) leads to competing gas phase reactions in favor of toluene. Thus, with an increasing toluene concentration the benzene peak in the spectrum decreases [16]. This paper shows how the pulsed operation of a non-radioactive electron source can improve the detection of benzene in the presence of toluene.

2. Experimental

The experimental set up has been intensively described in previous publications [17–19], so that just a brief summary is given here. For all experiments we use a modified Draeger Ion Mobility Spectrometer GSM with a 4 mm long reaction region, a 5.5 cm long drift region and a 0.5 mm long collector region. The device is operated at a temperature of 340 K. At a frequency of 30 Hz, a short injection field is used after pulsed ionization (field strength 500 V/cm) to inject the ions into the drift region, where a permanent field of about 200 V/cm forces the ions toward the collector region. In the reaction region a small field of 3 V/cm prevents drift losses before injection. On their way through the drift region the ions collide with air molecules (drift tube and reaction region are at atmospheric pressure) flowing at 200 ml/min opposite the ion drift direction. The flow rate is controlled by a mass flow controller. In the collector region the ions experience a field of 1000 V/cm moving the ions to the detector, which is a simple Faraday cup.

In the reaction region, a pulsed electron gun emits free electrons that lead to the formation of reactant ions. The electron gun has been improved by replacing the original filament that initially emits electrons by glow discharge with a new barium electrode. Now very strong electron pulses can be generated with a pulse duration of only 0.2 μs at a voltage of 4.5 V supplied to the filament. The potential difference accelerating the electrons is set to 7 kV so that their average kinetic energy is similar to that of beta-radiation emitted from commercial tritium sources.

Different analyte concentrations are generated by mixing dry air (water concentration at 292 K below 200 ppbv, dew point of 181.1 K) with a gas mixture composed of dry air and analytes (generated via gas evaporation in a permeation oven into a constant air flow of 100 ml/min). The concentrations have been verified with an Ion Science Tiger Select photo ionization detector (PID) and a Draeger chip measurement system (CMS). For benzene and toluene a total mixed flow of 230 ml/min is used for each substance. The sample gas flow into the reaction region of the IMS is 40 ml/min. For the investigation of a benzene/toluene mixture 115 ml/min of the benzene sample gas flow and 115 ml/min of the toluene sample gas flow are mixed together giving the final gas flow of 230 ml/min.

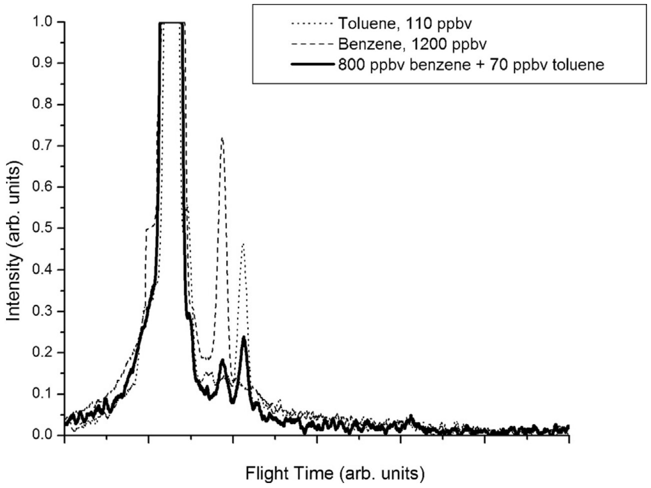

Fig. 1. IMS spectrum of benzene, toluene, and a mixture of both. The given concentrations are the concentrations in each analyte's gas flow.

3. Results and discussion

BTX (i.e. benzene, toluene and xylene and mixtures of these substances) detection using IMS is, in principle, not new. A common problem that has been described in previous papers are the quite similar ion mobilities of benzene and toluene (e.g. in ref. [11] the time of flight of benzene and toluene is given to be ca. 1.06 times the time of flight of the reactant ions; in ref. [9] the peaks are better separated with a reduced mobility of 1.94 cm^2 V^{-1} s^{-1} for benzene, 1.89 cm^2 V^{-1} s^{-1} for toluene and 2.07 cm^2 V^{-1} s^{-1} for the reactant ions) leading to product ion peaks very close to the RIP [11]. Using optical ionization techniques such as UV lasers (e.g. Nd:YAG with wavelengths at 266 nm after frequency doubling [12]) or UV lamps [15] leads to ion mobility spectra with clearly separated peaks. However, detection limits in the low ppb-range are difficult to achieve with these ionization sources and additional instrumentation is required. Furthermore, today's UV lamps need to be changed after several months of operation. Thus, despite their success other ionization sources are still in the center of interest. Corona discharge ionization sources also show good results [9], but their operation in the negative mode is more complicated. A more recent development is using direct current glow discharge [10], which does not have these disadvantages but similar good characteristics regarding the detection of benzene and toluene. However, for corona discharge and especially for hard ionization techniques different ionization mechanisms (e.g. due to ozone formation, or Penning ionization and vacuum ultraviolet photoionization) can lead to different spectra. The general interest is to have similar ionization mechanisms as the well known radioactive sources since these mechanisms are well understood and give excellent detection limits.

The electron gun used in our set up has two advantages over radioactive sources, while the average electron energy is similar to e.g. tritium sources: (1) It can be operated in a pulsed mode, where the duration of the electron pulse can be varied, and (2) the electron beam intensity can be controlled. For benzene this offers the possibility to increase the electron beam density and reactant ion density respectively until benzene can be detected in spite of its low ionization efficiency. Unfortunately, a general consequence of very high reactant ion densities is an increased coulomb repulsion leading to a broad RIP which prevents high resolution as required to separate the benzene peak from the RIP [20]. Fig. 1 shows IMS spectra of benzene, toluene and a mixture of both as they are typically obtained with our set up. Fig. 2 shows how pulsed operation of the electron