



Direct detection of aromatic amines and observation of intermediates of Schiff-base reactions by reactive desorption electrospray ionization mass spectrometry

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ABSTRACT

The fast, sensitive detection for 6 aromatic amines and direct observation of intermediates of Schiff-base reactions were achieved through reactive desorption electrospray ionization mass spectrometry (reactive DESI-MS). Pure acetone was electrosprayed to impact the aromatic amines on the paper, allowing two reactions, a proton-transfer reaction and a Schiff-base reaction, to occur in these experiments. The former was used to detect the aromatic amines, and the protonated analytes generated were selected for the qualitative and quantitative analysis. The false-positive signals were excluded by tandem mass spectrometry. For the 6 analytes, linear signal responses were obtained, and each had a dynamic range of 5 orders of magnitude. The relative standard deviation (RSD) and limit of detection (LOD) for all the measurements were in 1.5–5.3% and 0.03–0.2 pg/mm² range, respectively. The latter is a nucleophilic addition reaction that occurred between the aromatic amines and the acetone. The carbinolamine intermediates of these reactions were directly detected and identified by reactive DESI-MS. The data show that reactive DESI-MS is not only a reliable, sensitive tool for chemical analysis, but also a valid and promising method for studying organic reactions simultaneously, especially for heterogeneous reactions that occurred at a solution/solid interface.

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1. Introduction

The unmatched abilities to detect, count, and characterize atoms and molecules make mass spectrometry (MS) a powerful and widely applicable analytical technology [1] for chemical analysis and also studying organic reactions [2]. Recently, a contemporary revolution occurred in MS with the introduction of new members to both the APCI and ESI families [3] of direct sampling desorption/ionization (DI) techniques [1], now known collectively as ambient mass spectrometry [3–6]. These techniques are different from the traditional atmospheric pressure ionization (API) sources, and they can be employed to analyze samples directly in their native status without sample pretreatment. The first landmark technique of ambient mass spectrometry is desorption electrospray ionization (DESI), which has become one of the most important DI techniques. Typical applications of DESI-MS include explosive detection [7,8], natural product analysis [9–11], pharmaceutical quality control [12–16], and tissue imaging [17–19]. The detection of trace analytes is an important part of DESI-MS, and the samples can be either solid or liquid mixtures. The spray solvent

is usually a methanol/water (1:1) mixture, and sometimes a little acid is added. In reactive DESI [20], instead of spraying only solvent on the sample surface, reagents are added into the solvent to react with the targeted compounds, and thus the selectivity and ionization efficiency of the analytes containing specific functional groups can be greatly improved by particular ion/molecule reactions [21,22]. For the detection of explosives on surfaces [20], the sensitivities for trinitrohexahydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were enhanced by adding chloride or trifluoroacetate (TFA) to the spray solvent. It was shown that when alkylamine was in the DESI spray solution, the sensitivity for artesunate molecules exposed on the tablet surface was increased 170-fold more than reagent-less DESI [23]. For imaging mass spectrometry, lipid alterations in injured rat spinal cord were mapped by reactive DESI-MS [24]. Reactive DESI-MS is also a useful tool for investigating the trace reactions: redox reactions [25], complex formation [23,26], chemical bond-forming reactions [21,22,27–29] and bimolecular reactions [30]. Because ambient mass spectrometry can provide transient detection to organic reactions [31], the detection of transient species in ultra-fast reactions can be achieved by reactive DESI-MS. For example, Zare et al. detected reactive intermediates formed in the secondary microdroplets on the millisecond timescale [32,33] and provided an extra case of DESI-MS for studying mechanisms of chemical reactions.

The class of aromatic amines has a special place among the chemical carcinogens, in terms of extent of use available scientific knowledge.

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Aromatic amines are widely used as raw materials and at an intermediate stage in the manufacturing of industrial chemicals such as pesticides, medicines, dyestuffs, polymers, surfactants, cosmetics and corrosion inhibitors [34]. They are also a common contaminant in several working environments: the chemical and mechanic industries and aluminum transformation. The relationship between arylamines and bladder cancer has been studied extensively [35]. Several analytical methods have been reported for the determination of aromatic amines. Among these methods, gas chromatography (GC) [36,37] and liquid chromatography (LC) [38,39] are common-used techniques. Capillary electrophoresis (CE) [40,41] and mass spectrometry [38] have also been employed. However, the sample pretreatment makes these methods time-consuming and laborious. Without any sample manipulation or sample-preparation steps, the ambient mass spectrometry (e.g., DESI-MS) may provide simple, high-throughput analysis for these compounds. Aromatic amines are also a reactant of a Schiff-base reaction, which is one of the most important reactions as the Schiff-base reaction has a wide variety of applications in many fields, such as in organic, biological, medicinal and analytical chemistry [42]. Snell proposed the generally accepted mechanism for this reaction [43], in which carbinolamine is the intermediate [44–46]. Several carbinolamine detection methods such as ultraviolet spectroscopy [47,48], Raman spectroscopy [49], and NMR [50–53] have been developed. All these methods have the complicated spectra, and the spectral features are easily interfered by those of the complex chemical components and/or the similar groups. While for the ultraviolet spectrometry, the evidence for the existence of the carbinolamine is indirectly obtained by the kinetic studies of the whole reaction process [54]. With the advantages of high sensitivity, selectivity and speed [1], MS is a very useful tool for studying the reaction mechanism. More importantly, MS can provide direct evidence for identifying the intermediate structure through the collision-induced dissociation (CID). Thus, ESI-MS was successfully used for the detection of carbinolamines in solution by Marquez et al. [55,56], though the detection is difficult [57] for the rapid decomposition of carbinolamines [51]. However, for heterogeneous reactions at a solution/solid interface, ESI-MS is not applicable, but such kind of reaction can be adequately investigated by reactive DESI-MS, with much shorter response time for the detection of the intermediate in a reaction [2]. Thus, in this paper the reactive DESI-MS was for the first time proposed to be used to study the Schiff-base reactions, especially for the several heterogeneous reactions. In addition, the simultaneous quantitative analysis of aromatic amines does not need sample pretreatment, which is necessary for the previous methods mentioned above.

In this study, pure acetone was used as the spray solvent and the reagent in reactive DESI-MS. The aromatic amine solutions were deposited on the paper. On the surface occurred two reactions: (1) the proton-transfer reaction, and (2) the Schiff-base reaction. The former reaction adds a proton to the aromatic amines similar to the traditional ESI-MS spray solvent. The aromatic amines were detected in this mode and the LOD is acceptable. In the latter reaction, the intermediates were observed directly and were proved to be the covalent carbinolamines by tandem mass spectrometry.

2. Materials and methods

2.1. Instrumental setup (DESI-MS)

All reactive DESI experiments were carried out using a commercial linear ion trap mass spectrometer (LTQ-XL, Finnigan Scientific, San Jose, CA) with a home-built DESI source. It consists of an inner capillary (fused silica, 100 μm i.d., 190 μm o.d.) for delivering the spray solvent and an outer capillary (stainless steel, 0.01 in. i.d., 1/16 in. o.d.) for delivering the nebulizing gas. The vertical distance between the sprayer tip and the sample surface was 2 mm. The horizontal distance between the sprayer and the inlet of the mass spectrometer was 4 mm. The angle between the sprayer and the paper surface was 45°. The

spray voltage was +3.5 kV. The nebulizing gas (N_2) pressure was 1.4 MPa. Pure acetone was used as the electrospray solvent, and its flow rate was 5 $\mu\text{L}/\text{min}$. The temperature and the voltage of the heated capillary of the LTQ instrument were maintained at 275 °C and 20 V, respectively. The tube lens voltage was 110 V. The default voltages for the conversion dynode, the detectors and the ion guide system were used without optimization. CID was performed with 20–32% (manufacturer's units) collision energy to the precursor ions, which were isolated with a mass window width of 1.6 m/z units. A Mathieu parameter q_z value of 0.25 was used during collisional activation. Positive ion detection mode was used for all the experiments. The Xcalibur software from Finnigan was used to control the instrument and to process the data.

2.2. Materials and reagents

Aniline (AR) was purchased from Fuchen Chemical Reagent Factory (Tianjin, China). The 2-aminonaphthalene, 2,4,5-trimethylaniline, 4-chloroaniline and 4-chloro-2-methylaniline (HPLC-grade) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 2-Nitroaniline (98%) was purchased from Alfa Aesar China (Tianjin) Co., Ltd. (Tianjin, China). Acetone (AR) was purchased from Zhongtian Chemical Co., Ltd. (Wuhan, China). Ethanol (AR) was purchased from Hengxing Chemical Preparation Co., Ltd. (Tianjin, China). Filter papers were purchased from Hangzhou Special Paper Co., Ltd. (Hangzhou, China).

2.3. Samples

Each of the 6 aromatic amines was dissolved in ethanol to prepare working solutions (1×10^{-4} g/mL to 1×10^{-8} g/mL). Filter paper was cut into 5 cm \times 1 cm pieces as the substrate. For each experiment, a 1 μL sample solution was deposited onto the filter paper, and the solution formed a sample spot about 10 mm².

3. Results and discussion

3.1. Sample blank

For this reactive DESI experiment, pure acetone was used as the reagent and spray solvent to replace the commonly-used methanol/water (1:1) mixture. The mass spectrum of the background was recorded without sample introduction (see Fig. 1). The generator of the primary ions of DESI is the electrospray (ESI), which is suitable and very effective for analyzing polar compounds and the signal intensity will be stronger with the increasing of the polarity. Though the polarity of acetone is weaker than methanol and water, the signal intensity is still strong under the optimal conditions (as shown in Fig. 1). The two obvious peaks at m/z 59 and m/z 117 are originated from the protonated acetone and the protonated acetone dimer, respectively. The higher intensity of the protonated acetone dimer (m/z 117) may be caused by pure acetone. These two kinds of ions can provide enough primary ions for further analysis of the aromatic amine samples. In the spectrum, there are other peaks with relatively high intensities, such as the ion of m/z 99, m/z 124, m/z 157 and m/z 173, etc. These peaks may be generated from the background of airborne compounds, and fortunately, no interference is observed.

3.2. The main reactions occurred in reactive DESI experiments

After the introduction of 6 aromatic amine samples (about 10 ng/mm²), the full scan spectra were obtained immediately and were shown in Fig. 2. In each spectrum, the base peak is the protonated molecule of the corresponding aromatic amine, such as the ions of m/z 94 in Fig. 2(a). The two main types of primary ions are protonated acetone and their dimers (Fig. 1), so the protons are

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