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Desorption Electrospray Ionization Tandem Mass Spectrometry for Detection of 24 Carcinogenic Aromatic Amines in Textiles

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Because of its significant advantages including minimal sample pretreatment, easy ambient sample manipulation, high sensitivity, high specificity, and high throughput, desorption electrospray ionization tandem mass spectrometry (DESI-MS^n) has been successfully applied for the fast nondestructive detection of carcinogenic aromatic amines on various textile samples. Under the optimized experimental conditions, 24 aromatic amines were directly detected as protonated molecules by using a mixture of methanol/water/acetic acid (49:49:2, v/v/v) as the electrospray liquid. The average analysis time for each sample was less than 30 s, making DESI-MS a high-throughput screening tool for textile examination. The false positive signals (having the same *m/z* values as those from the aromatic amines) could be excluded by using tandem DESI mass spectrometry. The detection limit for most of the aromatic amines in this study was on the order of low femtograms per squared millimeter by utilizing the characteristic fragments from DESI-MS/MS experiments. The typical RSD values for this method were found to be 5%∼10% for six measurements (S/N = 3) of the same sample. These results show that DESI-MS^n is reliable and the most sensitive analytical tool available for the rapid and nondestructive detection of carcinogenic aromatic amines on textile products. The technique has promising applications for inline quality monitoring in the textile industry.

Azo dyes, bearing the functional group R—N=N—R′, have been widely used in various industries such as nutrition, cosmetics, paper, pharmacy, printing inks, textile, and tannery. Of these industrial applications, the textile industry consumes 50% of the overall azo dye production.[1] Some azo dyes may react with substances excreted from human bodies (e.g., metabolites, sweat) to generate carcinogenic aromatic amines causing high risks to human health and the environment.[2−4] Therefore, the European Union banned the sale, importation, and use of textiles and leather which may produce any of the 24 carcinogenic aromatic amines (Table 1) when the products contact the human skin or oral cavity.[5−7] Similar actions are pending in other countries. Rapid and nondestructive detection of carcinogenic aromatic amines in textile products is thus of increasing importance. Currently, the screening of the toxic azo dyes in textiles is usually performed by monitoring the aromatic amines listed in Table 1. Typical methods used for the screening of azo dyes or carcinogenic aromatic amines include thin-layer chromatography,[8−10] high-performance liquid chromatography,[10−12] pyrolysis gas chromatography,[13] and capillary electrophoresis.[14,15] Common detection techniques include UV,[16,17] mass spectrometry,[2,5,11−13] and electrochemical detection.[14,15] With the exception of mass spectrometry detection, the limit of detection (LOD) is typically greater than 1×10^{-4} g/L for most techniques.[14,17] For traditional mass spectrometry approaches, such as chromatographic MS analysis, the sample preparation steps are critical for achieving reproducible

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Table 1. DESI-MS/MS Information for 24 Aromatic Amines

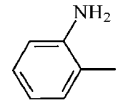
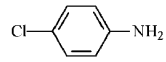
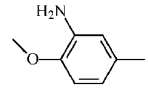
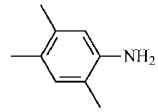
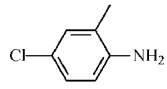
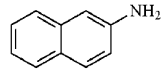
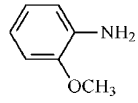
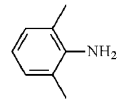
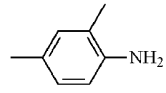
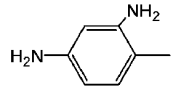
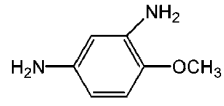
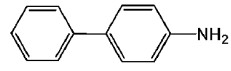
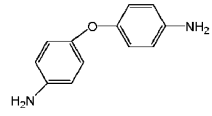
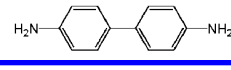
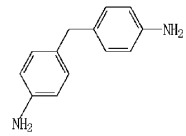
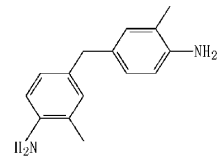
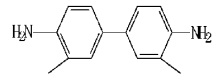
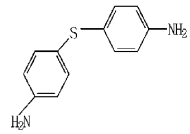
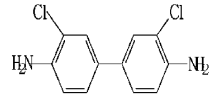
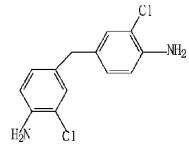
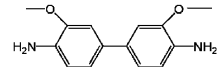
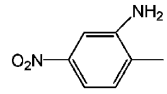
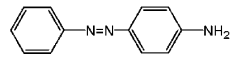
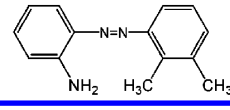
No.	Compound	Molecular structure	CE (%)	MW, $[M+H]^+$	Fragments (MS/MS)
1	o-Toluidine		23	107，108	93 $[M+H-CH_3]^+$ 91 $[M+H-NH_3]^+$
2	4-Chloroaniline		30	127，128	93 $[M+H-Cl]^+$ 111 $[M+H-NH_3]^+$
3	2-Methoxy-5-methylaniline		30	137，138	123 $[M+H-CH_3]^+$ 106 $[M+H-CH_3OH]^+$
4	2,4,5-Trimethylaniline		30	135，136	121 $[M+H-CH_3]^+$ 119 $[M+H-NH_3]^+$ 91 $[M+H-3CH_3]^+$
5	4-Chloro-2-methylaniline		30	141，142	125 $[M+H-NH_3]^+$ 127 $[M+H-CH_3]^+$ 107 $[M+H-Cl]^+$
6	2-Aminonaphthalene		30	143，144	117 $[M+H-HCN]^+$ 127 $[M+H-NH_3]^+$
7	o-Anisidine		30	123，124	109 $[M+H-CH_3]^+$ 92 $[M+H-CH_3OH]^+$
8	2,6-dimethylaniline		30	121，122	107 $[M+H-CH_3]^+$ 105 $[M+H-NH_3]^+$
9	2,4-dimethylaniline		30	121，122	107 $[M+H-CH_3]^+$ 105 $[M+H-NH_3]^+$
10	2,4-Diaminotoluene		33	122，123	108 $[M+H-CH_3]^+$ 106 $[M+H-NH_3]^+$
11	4-Methoxy-1,3-phenylene diamine		30	138，139	124 $[M+H-CH_3]^+$ 108 $[M+H-OCH_3]^+$
12	4-Aminodiphenylamine		27	169，170	153 $[M+H-NH_3]^+$ 92 $[M+H-ph]^+$
13	4,4′-Oxydianiline		30	200，201	184 $[M+H-NH_3]^+$ 108 $[M+H-ph-NH_3]^+$
14	Benzidine		30	184，185	168 $[M+H-NH_3]^+$ 151 $[M+H-2NH_3]^+$

Table 1. Continued

No.	Compound	Molecular structure	CE (%)	MW, $[M+H]^+$	Fragments (MS/MS)
15	4,4′-Methylenedianiline		30	198，199	182 $[M+H-NH_3]^+$ 106 $[M+H-ph-NH_3]^+$
16	3,3′-Dimethyl-4,4′-diamino diphenylmethane		30	226，227	210 $[M+H-NH_3]^+$ 195 $[M+H-CH_3-NH_3]^+$ 120 $[M+H-ph-CH_3-NH_3]^+$
17	o-Tolidine		27	212，213	196 $[M+H-NH_3]^+$ 181 $[M+H-CH_3-NH_3]^+$
18	4,4′-Thiodianiline		28	216，217	200 $[M+H-NH_3]^+$ 124 $[M+H-ph-NH_3]^+$
19	3,3′-Dichlorobenzidine		28	252，253	217 $[M+H-Cl]^+$ 182 $[M+H-2Cl]^+$
20	4,4′-Methylene-bis-(2-chloroaniline)		30	266，267	231 $[M+H-Cl]^+$ 140 $[M+H-ph-NH_3-Cl]^+$
21	3,3′-Dimethoxy -benzidine		26	244，245	230 $[M+H-CH_3]^+$ 213 $[M+H-CH_3-NH_3]^+$
22	2-Amino-4-nitrotoluene		30	152，153	136 $[M+H-NH_3]^+$ 107 $[M+H-NO_2]^+$
23	p-Phenylazoaniline		30	197, 198	181 $[M+H-NH_3]^+$ 170 $[M+H-N_2]^+$
24	4-Amino-2′,3-dimethylazo benzene		30	225, 226	211 $[M+H-CH_3]^+$ 209 $[M+H-NH_3]^+$ 196 $[M+H-2CH_3]^+$

spectra and reliable results.[18] The sample pretreatment procedures commonly include multiple steps such as sample shearing, extraction, chemical reduction, and preseparation, which are typically time-consuming and laborious. High-throughput, nondestructive analysis of textile samples is highly desirable, especially for cases where large numbers of samples require rapid analysis.

Ambient mass spectrometry, pioneered by Prof. Cooks et al. with the invention of the desorption electrospray ionization (DESI) technique,[19,20] has been of increasing interest in recent years. Following DESI, many techniques including direct analysis in real time (DART),[21,22] surface desorption atmospheric pressure chemical ionization (DAPCI),[23−26] extractive electrospray ionization (EESI),[27−29] low-temperature plasma (LTP),[30,31] electrospray

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assisted laser desorption/ionization (ELDI),[32−34] and easy ambient sonic ionization (EASI)[35−37] have been reported for rapid analysis of ambient, complex samples with minimal or no sample pretreatment. In a typical DESI experiment,[19,20] raw samples are placed on a precisely adjustable 3-D sample stage, on which the sample is easily accessible under ambient conditions. Solvents (typically a slightly acidified methanol/water solution or a basic methanol/water solution are used in positive or negative DESI-MS experiments, respectively) are electrosprayed as in a traditional ESI source. Charged droplets are then directed to impact the sample surface, where the desorption/ionization of the analytes occurs to produce analyte ions under the ambient conditions. After charge transfer, gas-phase ions and partially desolvated droplets containing the charged analytes are sampled through the ion optics system into the mass analyzer, where the charged analytes are liberated for mass analysis in high vacuum. Detailed mechanisms of DESI have been well-documented by Cooks et al.[38−41] The DESI technique makes it feasible for sensitive, direct, and nondestructive analysis of complex samples on solid surfaces with minimal sample pretreatment. Typical applications of DESI-MS include explosive detection,[42−45] natural product analysis,[46,47] pharmaceutical preparation analysis,[48−53] and tissue imaging.[54,55] DESI also enables rapid analysis of liquid mixtures, which are usually dried on solid substrates before the mixtures are subjected to the electrospray beam for desorption/ionization. With minimal sample pretreatment, even urine samples[56−59] and highly concentrated salt solutions[60] have been successfully analyzed by DESI-MS. Specific detection of trace analytes such as explosives[42−45] has been achieved using multiple stage tandem DESI-MS combined with selective ion/molecule reactions. Thus, DESI-MS provides the extremely valuable capabilities of direct mixture analysis, intrinsically high sensitivity, specificity, and high throughput.

The first example of DESI-MS for azo dye analysis was performed in 2006 to rapidly detect trace amounts of Sudan dyes in various food samples.[61] Since Sudan dyes may distribute unevenly on the surfaces of food samples,[61,62] it is recommended to screen multiple sample spots with large sampling areas to exclude false negative results. Methanol is often used in DESI experiments for rapid detection of analytes dissoluble in methanol. It is important to dispose of the food samples examined by DESI using methanol as the spray solvent due to possible chemical contamination, regardless of whether the food still passes the quality examination. However, volatile solvents such as methanol are suitable for DESI-MS analysis of textile products even though significant amounts of methanol are sprayed onto the samples, because textile products will not be swollen and usually the quality-control passed textiles will not be used until exposed to air for a relatively long time (months or longer). This ensures no safety concern when even a large amount of methanol is sprayed on the products. Therefore, DESI-MS was employed in this study to directly detect carcinogenic aromatic amines on various textile samples, and tandem DESI-MS was used to exclude false positive signals. The present results show that DESI-MS is a highly promising technique for quality control in the textile industry due

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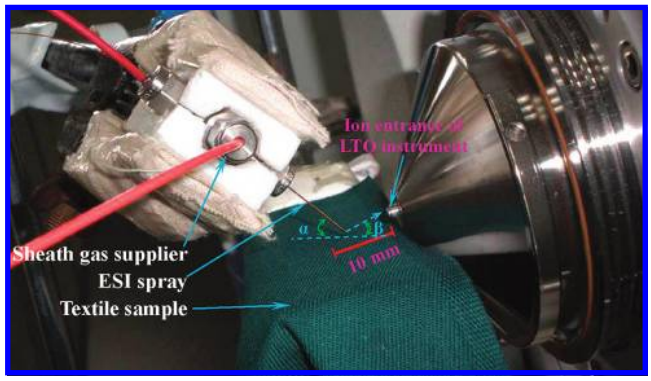

Figure 1. Open-air DESI setup for direct detection of aromatic amines in textile samples.

to its analytical merits such as high sensitivity, high specificity, high throughput, and nondestructive measurement.

EXPERIMENTAL SECTION

Instrumental Setup and Materials. The experiments were carried out using a LTQ-XL linear ion trap mass spectrometer (Finnigan, San Jose, CA) coupled with an in-house built DESI source (Figure 1). The Xcalibur software from Finnigan was used to control the MS instrument and to process the data. Acetic acid (analytical grade) and methanol (chromatography grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A total of 24 aromatic amines (chromatography grade) were imported from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The water used was deionized water provided by the chemistry facilities. Textile samples were obtained from local supermarkets.

The in-house built DESI source is an easily constructed open-air DESI source,[19,44,53,58,59,61] which is composed of two major parts: a traditional ESI source and a 3-D sample stage. The spray angle (α), ion uptake angle (β), the distance between the sprayer and the sample surface (d1), and the distance between the sample spot and mass spectrometer (d2) are important experimental parameters, which were optimized before the actual measurements. The 3-D moving stage facilitates the systematic optimization of all the parameters for analysis. The source optimization was performed by following the procedures described previously in detail.[44,47,53,58,61] Briefly, the ESI high voltage was 4.5 kV; the distances d1 and d2 were 1 and 4 mm, respectively; and the angles α and β were 30−50° and 10−20°, respectively.

Since the analytes are basic amines, the DESI-LTQ mass spectrometer was set to run in a positive ion detection mode. DESI-MS spectra were acquired in the mass range of m/z 50−600. The nebulizing gas pressure was 1.8 MPa. The capillary voltage was set to 44 V; the tube lens voltage was 90 V; and the temperature of the heated capillary was 280 °C. Solvents were electrosprayed onto the sample surface at a flow rate of 25.0 μL/min. The sample delivery was executed manually, which provides maximum flexibility for fast scanning across the whole sample surface. The mass spectra were collected with an average time of 1.5 min. Ions of interest were isolated with a mass-to-charge window width of 1.6 unit for collision-induced dissociation experiments by applying a collision energy (CE) of 20−30% (arbitrary units defined by the LTQ mass spectrometer).

Samples. A total of 24 carcinogenic aromatic amines were dissolved in methanol to prepare stock solutions (0.1 g/L, marked as numbers 1−24, respectively). The stock solutions were further diluted using a methanol and water (1:1, v/v) solution, and the working solutions were made at $1.0-20.0 \times 10^{-6}$ g/mL for actual measurements. For reference experiments, blank fabric textile samples were cut into 5 cm × 3 cm pieces for ease of sample delivery. For practical sample analysis, the textile samples such as clothes from various manufacturers were directly analyzed without any treatment. A 10−20 μL aliquot of each diluted aromatic amine working solution was deposited directly on the surface of various textile materials, including blank fabric textile samples, purses (leather), sleevelets (synthetic fiber), and shower caps (plastic). The samples were allowed to dry prior to analysis. No further pretreatment was performed.

RESULTS AND DISCUSSION

Optimizing DESI-MS. To optimize the DESI parameters, 50 μL of *o*-toluidine solution (1.0×10^{-6} g/mL) was deposited on a blank fabric textile sample (5 cm × 3 cm) forming a sample spot about 10 mm^2. After drying in air (~2 min), DESI-MS experiments were performed using a solution of methanol/water/acetic acid (49:49:2, v/v/v) as the electrospray liquid. Once the operation parameters were set to the aforementioned values, satisfactory DESI signals were generated, showing a predominant peak at m/z 108 from the protonated *o*-toluidine. The parameters including d1 (the distance between ESI tip and samples), d2 (the distance between the tip and MS inlet), α (spray angle), and β (ion uptake angle) were adjusted and validated by experimentally optimizing the signal of m/z 108. The mechanisms of how the electrospray voltage, the distances (i.e., d1 and d2), and the angles (i.e., α and β) affect the DESI signals have been discussed previously.[58,61,63]

The solvent infusion rate and the sheath gas pressure also play important roles in the formation of DESI signals. It was found that a highly stable signal of *o*-toluidine was detected when the methanol/water/acetic acid solution was electrosprayed with infusion rates varied from 20 to 50 μL/min, which were higher than a typical infusion rate of 2−5 μL/min. Textile fabric absorbs liquids such as the spray solution. In most cases, charged droplets need to wet the surface and enable local extraction to dissolve the analytes before DESI signals are obtained. The spray solution may evaporate into the air and spread quickly across the fabric around the sample spot; thus, a high solvent infusion rate is required to maintain the signal. Also, a relatively higher ESI sheath gas pressure facilitates the generation of a stable DESI-MS signal. Below a critical pressure of 200 psi, no stable signal was detected. The signal level was sustained when the sheath gas pressure varied from 250 to 300 psi and then decreased significantly (≥20%) when the sheath gas pressure was higher than 350 psi. The textiles usually have coarse surfaces, thus a higher projection velocity of droplets is required to impact the rough textured surfaces. Therefore, to achieve better desolvation for high solvent infusion rates, a high sheath gas pressure is preferred. When the sheath gas pressure was too high (≥300 psi), the signal drop was probably ascribed to the astray projection of ions, which could not be collected for mass analysis. Thus, the sheath gas pressure was set at 260 psi for a solvent infusion rate of 25 μL/min for the following experiments.

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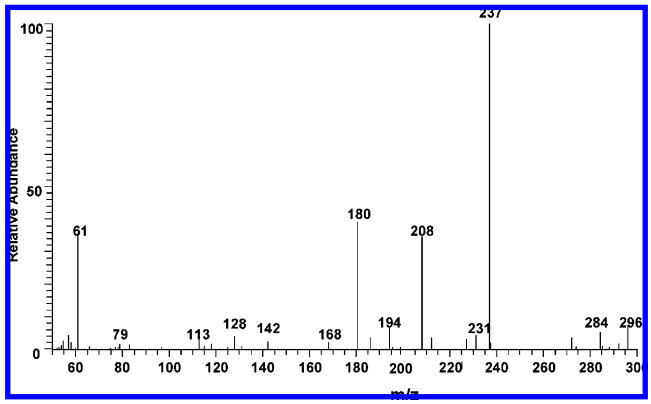

Figure 2. DESI-MS spectrum of a blank fabric textile sample.

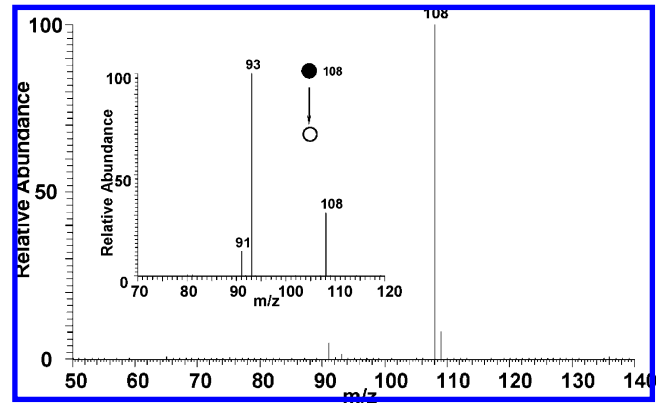

Figure 3. DESI-MS and MS/MS spectra of *o*-toluidine on the surface of a blank fabric textile sample.

A positive ion detection mode was employed in the current work for DESI-MS detection of the basic aromatic amines. It was found that acetic acid/methanol/water solutions produced signals of amines better than other solvents such as pure methanol or basic solvents (data not shown). Compared to the signal level obtained using pure methanol, the signal level was increased about 1.7 and 3.2 times without significantly increasing the noise levels when the content of acetic acid was 0.1% and 2%, respectively. With a further increase of acetic acid in the spray solution, a slight improvement of the signal intensity (≤4 times) was observed, showing no need to increase the acid content in the solution. Experimental data showed that methanol is also essential to the signal generation. To maximally stabilize a high level signal, methanol content should not be less than water in the electrospray solution, probably because the aromatic analytes are not likely to be dissolved by solutions with high water content. Therefore, the solution of methanol/water/acetic acid (49:49:2 v/v/v) was selected as the electrospray solution.

Sample Blank. Textiles are directly exposed to ambient air such that substances originating from the environment accumulate easily in textiles. Fabric textile samples containing no aromatic amines were obtained from Hangzhou Textile Research Institute (Hangzhou, China) and used as the blank samples for this study. The blank samples were kept in the same ambient environment as the commercial products. Accordingly, blank fabric textile samples might generate background peaks due to airborne compounds such as organic amines, which may result in false positive signals in the MS spectrum. Thus, it was necessary to perform reference experiments using authentic blank fabric textile samples containing no aromatic amine. Under the optimized experimental conditions, DESI-MS spectra were recorded from the blank fabric textile samples. As shown in Figure 2, peaks detected at m/z 61, 180, 208, and 237 dominate the DESI-MS spectrum. The peak at m/z 61 was ascribed to the protonated acetic acid ($[M + H]^+$), probably due to the relatively high acetic acid content in the electrospray solution. Other peaks were background signals, which were commonly detected from several authentic textile samples containing no aromatic amines. Multiple-stage MS experiments were performed on the individual peaks, which generated none of the characteristic fragments of aromatic amines (summarized in Table 1). Therefore, these data confirmed that the signals detected from the blank samples were not related to any of 24 aromatic amines listed in Table 1.

DESI-MS Analysis of 24 Carcinogenic Aromatic Amines. To record the DESI-MS spectra of the aromatic amines on textiles, each carcinogenic aromatic amine (100 ng) was deposited on different blank fabric textile samples to form a spot about 10 mm^2. Under the optimized experimental conditions, DESI-MS measurements were carried out for the 24 aromatic amines, individually. All the aromatic amines produced protonated molecules $(M + H)^+$ as the major type of ions observed in the DESI-MS spectra. For validation of the detection of the aromatic amines, CID experiments (MS/MS) were further performed on the corresponding protonated molecular ions to obtain information on the major characteristic fragment ions. For example, protonated *o*-toluidine molecules (m/z 108) dominated the DESI-MS spectrum (Figure 3) recorded using a blank textile sample contaminated with 100 ng of *o*-toluidine. Upon CID, the precursor ions of m/z 108 gave rise to the major fragment ions detected at m/z 91 and 93 (inset shown in Figure 3). The peak at m/z 91 was the ionic residue generated by the loss of NH_3 from the protonated *o*-toluidine (m/z 108). Similarly, the peak at m/z 93 was produced due to the cleavage of CH_3 from the precursor ions (m/z 108). Note that the relative intensity of the fragment of m/z 91 was about 10% of the intensity of m/z 93, indicating that the cleavage of NH_3 under the experimental conditions was much more difficult than CH_3. Further fragmentation was not observed in the DESI-MS/MS experiments, probably because the precursor ions (i.e., m/z 108) generated by DESI were not as highly energetic as those generated by electron impact ionization, showing the softness of DESI for the ionization of organic compounds. With the use of the same approach, a profile of the characteristic MS/MS fragmentation information on the 24 carcinogenic aromatic amines was achieved and summarized in Table 1.

As shown in Table 1, aromatic amines were easily detected as protonated molecules $(M + H)^+$, which generated their characteristic fragments in the CID experiments. These observations are in good agreement with the results obtained using LC−ESI-MS/MS.[12] However, unlike LC−ESI-MS/MS, DESI-MS requires no sample pretreatment to perform direct, nondestructive, and rapid detection of aromatic amines on various textile samples. This feature is highly attractive for inline product monitoring in the textile industry.

It is also worth noting that in the DESI-MS spectra the signal intensities of the protonated aromatic amines differ from each

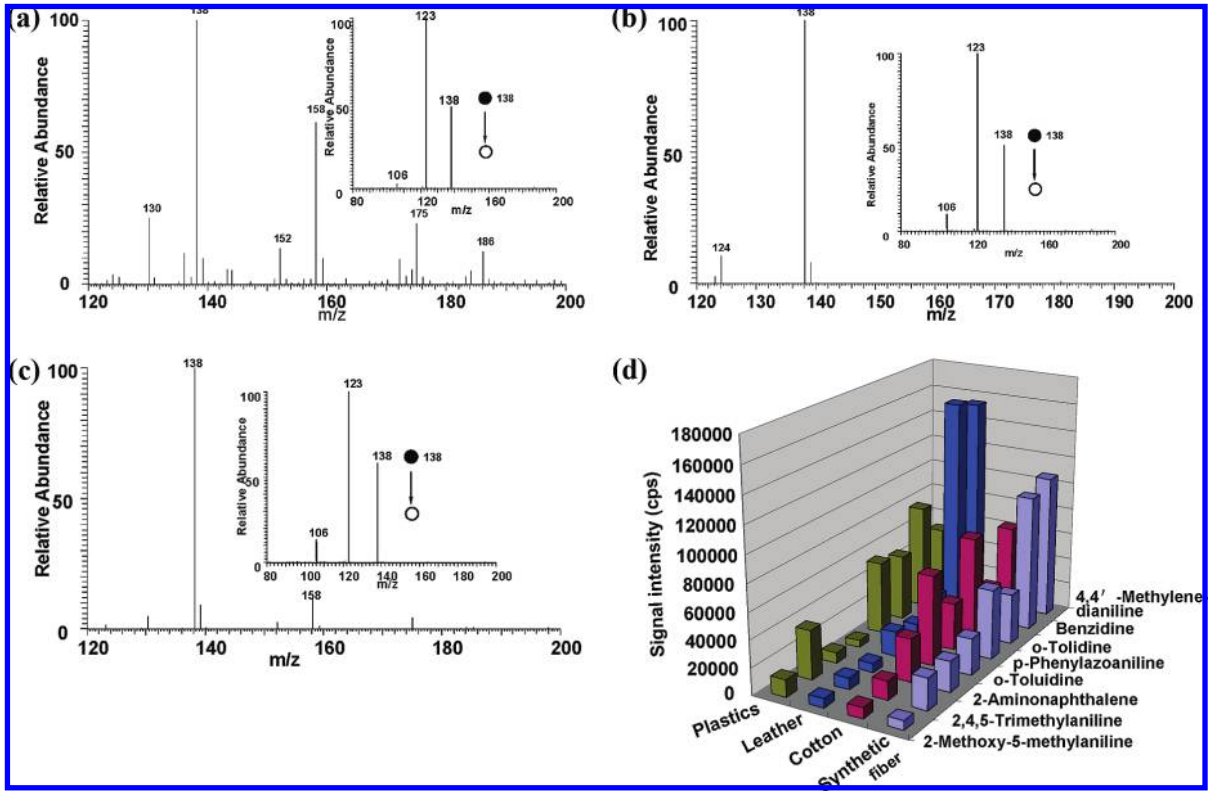

Figure 4. DESI-MS and MS/MS spectra of aromatic amines on various textile samples: (a) 2-methoxy-5-methylaniline on leather; (b) 2-methoxy-5-methylaniline on chemical fiber textile samples; (c) 2-methoxy-5-methylaniline on plastic Nylon textile sample; (d) signal responses of various amines detected on various textile samples.

other even though the signals are detected under the same experimental conditions and from the same textile surface. A possible explanation is that the volatility and/or gas phase basicity of the aromatic amines are different from each other, and thus the signal intensities recorded in DESI-MS vary to a certain degree depending on both the volatility and gas phase basicity of the analyte. In all the CID experiments, the CE applied to the precursor ions was 20−30%. Under such a mild CID condition, the precursor ions, which are usually molecules protonated on the ammonia group terminal, cleave neutral species such as NH_3 or CH_3 radicals, resulting in cation residues. The ionic residue usually contains 1−2 six-member or seven-member ring structures, depending on the molecular structure of the precursor ions, and thus stabilizes the resultant species. Therefore, no in-depth fragmentation of the ring structure was detected in the MS/MS spectra.

Effects of Substrate Materials. DESI-MS tolerates complex matrixes. No serious matrix effects were found in the previously reported DESI-MS measurements. In this study, the chemical composition of the textile samples varied dramatically; thus, the molecular interactions between the aromatic analytes and the fabric substrates could be quite different in terms of strength. Once the molecular interaction is sufficiently strong, no analyte can be efficiently desorbed for ionization. To study the possible effects caused by substrate materials, DESI-MS experiments were also carried out by depositing aromatic amines on different materials containing no aromatic amines. Each sample was then measured immediately, or kept in ambient air for measurements after 1 day, 2 days, 1 week, 2 weeks, and 3 weeks, respectively.

Figure 4a shows a DESI-MS spectrum recorded from leather when 10 μL of a 2-methoxy-5-methylaniline solution (1.0×10^{-6} g/mL) was directly deposited on a leather purse surface. The 2-methoxy-5-methylaniline on the leather surface generated protonated molecular ions of m/z 138, which was a predominant peak with the abundance of 6900 cps among several signals detected in the spectrum. With 25% CE in the CID experiments, the protonated 2-methoxy-5- methylaniline molecules produced fragment ions at m/z 106 and 123, by the loss of methanol and CH_3, respectively. In the MS^3 experiment, the fragment of m/z 123 lost methanol to yield a major fragment of m/z 91. This is consistent with the fragmentation pathways observed in our experiments. The abundance of the peak at m/z 123 was much higher than that at m/z 106, indicating the fragmentation pathway to cleave methanol was not favored under the conditions. Different DESI-MS spectra were recorded when the 2-methoxy-5-methylaniline solution was deposited on surfaces of different materials such as sleevelets (synthetic fiber, shown in Figure 4b) and shower caps (plastic, shown in Figure 4c), providing signal abundances of 6750 and 12 800 cps, respectively. The same fragment pattern was observed for the protonated 2-methoxy-5-methylaniline (m/z 138) as shown in the insets of Figure 4b,c. Also, the absolute intensities of the signal (m/z 138) differed from each other, probably because the analyte was desorbed for ionization with the highest efficiency from the plastic surface. Similar signal alterations were also found for most of the aromatic amines (Figure 4d) on surfaces of different textile materials. For the aromatic amines containing one benzene ring, the signal levels varied within 2-fold; but for the analytes containing two benzene rings (e.g., benzidine), especially those possessing

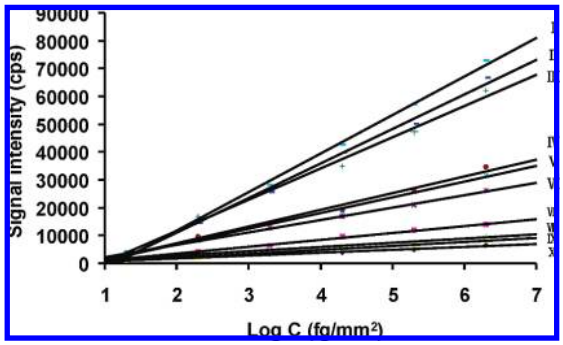

Figure 5. Linear responses of various aromatic amines on a cotton surface: I, *o*-tolidine, $y = 13\,853x - 15\,993$, $R^2 = 0.996$; II, *o*-toluidine, $y = 12\,424x - 3831$, $R^2 = 0.995$; III, 4,4′-methylenedianiline, $y = 11\,209x - 10\,835$, $R^2 = 0.992$; IV, *p*-phenylazoaniline, $y = 6021x - 4872.3$, $R^2 = 0.990$; V, 2-aminonaphthalene, $y = 5640.2x - 4576.9$, $R^2 = 0.993$; VI, benzidine, $y = 4488.5x - 2428$, $R^2 = 0.998$; VII, 2,4,5-trimethylaniline, $y = 2476.4x - 1415$, $R^2 = 0.994$; VIII, 4-methoxy-1,3-phenylene diamine, $y = 1524.3x - 266.54$, $R^2 = 0.988$; IX, 2-methoxy-5-methylaniline, $y = 1425x - 914.98$, $R^2 = 0.992$; X, *o*-anisidine, $y = 1015.7x - 228.54$, $R^2 = 0.994$. Each data point designates six measurements; the RSD values for the data points are in the range of 1.7−6.5%.

N═N groups (e.g., *p*-phenylazoaniline), the signal levels could vary in a wider range up to 5 times. For the same textile samples, signal levels of different aromatic amines also changed significantly as shown in Figure 4d. Among the aromatic amines tested, those containing two benzene rings such as 4,4′- oxidianiline gave the most abundant signals on different textile samples except for the cotton textile surfaces, probably because these compounds are easier to be desorbed from these substrates than the others. For all the textile materials examined, the analyte signals decreased slightly (10−20%) in the first 3 days after sample deposition; however, no further decrease was found when the sample was exposed to ambient air for more than 2 weeks. Probably under these conditions the aromatic amines had stabilized on the materials.

Signal Responses of Aromatic Amines on Cotton Substrate. DESI-MS was applied to investigating the signal responses of various carcinogenic amines on the same substrate. A linear dynamic signal response of *o*-toluidine was obtained by depositing trace amounts of *o*-toluidine onto the cotton surface, showing a linear range of about 6 orders of magnitude on a logarithm scale (Figure 5, curve II). Among the amines analyzed, *o*-tolidine showed the highest sensitivity as shown in Figure 5, curve I, probably because this compound, which contained two $-NH_2$ groups and two methyl groups, was more volatile and basic than others on the cotton surface. The LOD of *o*-tolidine on the cotton textile surface was 0.82 fg/mm^2 (S/N = 3, $n = 6$), which is equal to 0.0051 mg of aromatic amines per kilogram of raw cotton textile materials. Table 2 summarizes the data for six measurements of different amounts of *o*-toluidine on the cotton textile. As shown in Figure 5, curve III, the sensitivity of 4,4′-methylenedianiline, which also contains two $-NH_2$ groups, was relatively lower than that of *o*-toluidine or *o*-tolidine, possibly because the volatility of 4,4′-methylenedianiline is lower than *o*-toluidine and *o*-tolidine. The curves IṼVI indicate the sensitivity of these compounds is also low, probably because these compounds contain two benzene rings, which may result in a greater affinity for the cotton surface. The experimental data also suggests that the $-OCH_3$ group attached to the benzene ring of the aromatic amines may play an important role in the affinity of the molecules for the cotton surface. This might account for their low signal responses observed in DESI-MS experiments.

In summary, DESI provides high sensitivity for rapid detection of aromatic amines accumulated on textile surfaces. Tables S1−S9 in the Supporting Information provides the detailed data for the quantitatively linear signal responses of aromatic amines tested using DESI-MS. The relatively low RSD values obtained for the measurements demonstrate that the precision of DESI-MS measurements are acceptable for rapid detection of carcinogenic amines on textile materials. This work shows that DESI-MS is a promising technique to quantitatively detect carcinogenic aromatic amines in actual textile products without sample pretreatment.

Direct Detection of Carcinogenic Aromatic Amines on Actual Samples. Actual textile samples were purchased from markets, and DESI-MS analyses were performed on the samples without pretreatment in order to determine whether they contain any of the 24 carcinogenic aromatic amines. First, the DESI-MS spectrum is used to screen for the characteristic peaks corresponding to the protonated aromatic amines. Once a peak matching any mass-to-charge ratio of the protonated aromatic amines is found, MS/MS (CID) experiments must be performed to exclude false positives. For instance, a typical DESI-MS spectrum recorded from a blue cotton cloth sample is shown in Figure 6a, where numerous peaks were detected in the mass range of 100−300. Because the textile sample was analyzed without any pretreatment, it was common to have some peaks in the DESI-MS spectra which were unrelated to aromatic amines since many airborne contaminants produce signals in DESI-MS. Note that the homemade DESI source was of a simple, open-air configuration. It was found that aerosols and particles containing compounds of high proton affinities contributed signals in the mass spectrum once these compounds were involved in the spray. These compounds were probably ionized through an extractive electrospray ionization (EESI) mechanism as demonstrated previously.[64−68] Thereby, it is reasonable to regard EESI as a variant of DESI, which may generate ions of analytes by desorption/extraction in the air.

As shown in Figure 6a, peaks at m/z 108, 124, and 139 were found with significant abundances in the DESI-MS spectrum of the blue cotton cloth samples. Therefore, *o*-toluidine, *o*-anisidine, and 4-methoxy-1,3-phenylenediamine were expected to exist in the textile samples. CID experiments were further performed on the peaks at m/z 108, 124, and 139, and MS/MS spectra are illustrated in parts b, c, and d of Figure 6, respectively. By comparison of the reference spectra obtained using authentic compounds regarding the characteristic peaks and the relative abundances, it was concluded that the blue cotton cloth samples tested under this study contained *o*-toluidine, *o*-anisidine, and 4-methoxy-1,3-phenylenediamine. With the use of the calibration curves shown in Figure 5, the content of these amines were semiquantitated as 224.7, 23.4, and 19.7 fg/mm^2 for *o*-anisidine, 4-methoxy-1,3-phenylenediamine, and *o*-toluidine, respectively.

Analysis Speed. Direct DESI-MS measurements can start instantaneously, as long as samples are on the sample stage, without any sample preparation. Using the LTQ mass spectrom-

Table 2. Signal Responses of *o*-Tolidine Measured on Cotton Textile Surface Using DESI-MS

concentration of *o*-tolidine (fg/mm^2)	signal intensity of protonated *o*-tolidine molecules (*m*/*z* 213)						mean value	standard deviation	RSD (%)
20.0	4 190	4 270	4 250	4 280	4 110	4 220	4 220	63.2	1.5
200.0	15 300	13 900	14 600	15 100	15 700	14 800	14 900	622.9	4.2
2 000.0	27 800	26 900	28 400	29 100	28 700	28 200	28 183	767.9	2.7
20 000.0	43 600	44 700	43 100	42 400	41 500	40 100	42 567	1621.9	3.8
200 000.0	54 400	57 600	58 100	55 900	56 800	59 900	57 117	1892.5	3.3
2 000 000.0	71 400	70 500	75 400	73 600	72 700	74 300	72 983	1828.0	2.5

eter, the shortest scan time for the mass range of *m*/*z* 50−600 is less than 1 ms. However, the scan time in this study was set to 100 ms to ensure stable signals. The total analysis time required for screening and identification of 24 aromatic amines in one sample was about 30 s. Our data showed that for the final textile products, the aromatic amine contents have almost uniform distribution across the whole sample surface. For the aromatic amines generated naturally on the textile surfaces, the signal variation was about 10−20% for different sample spots on the same sample, and no signal variation higher than 50% was found for the samples tested. Thus, it is not critical to check every point of the sample surface for the quality control of commercial final products. However, in practical samples such as used clothes, the aromatic amine contents could vary dramatically, even as high as 2 orders of magnitude. In such cases, it is necessary to screen as many spots as possible to achieve a reasonable conclusion. To be noticed, traditional methods including GC, HPLC, and TLC require tedious sample pretreatments such as cutting the sample into small pieces (~1 cm^2) followed by solvent extraction, preconcentration, and sample separation.[18] These methods take more than half a day to complete the analysis of one textile sample. Obviously, these required steps decrease the throughput for sample analysis, and the destructive sample handling is not cost-effective for industry quality control. Thus, DESI-MS provides a reliable and high-throughput way to detect aromatic amines on textiles.

Detection Limit and Reproducibility. The DESI technique is of high sensitivity for most compounds which can be protonated. The limits of detection of DESI-MS were measured using blank samples deposited with diluted authentic aromatic amine solutions when the signal intensities reached 3 times the noise level. Table 3 shows the LOD of 10 aromatic amines examined in this study. Since all the aromatic amines are basic compounds of similar molecular structures, it is reasonable to conclude that all 24 carcinogenic aromatic amines can be detected by DESI-MS at concentration levels as low as tens of femtograms per millimeter

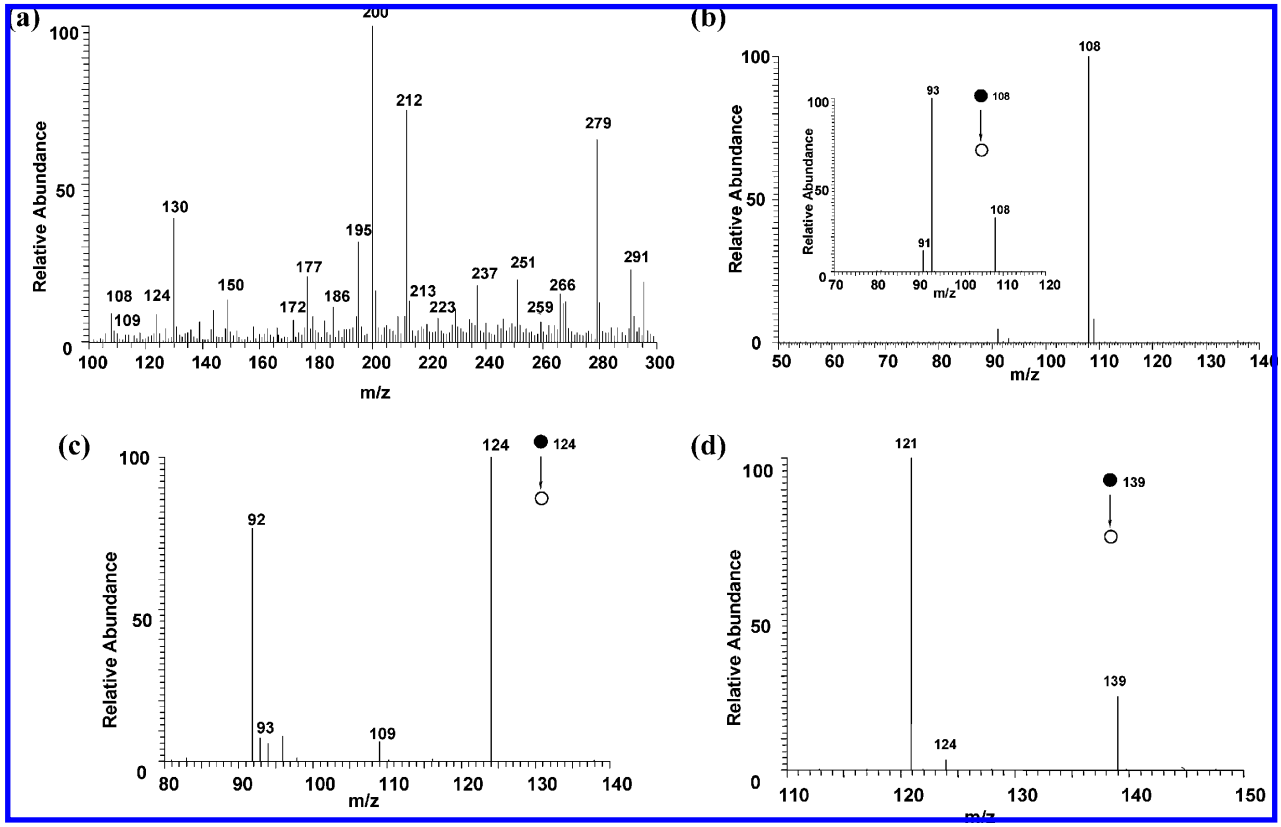

Figure 6. Mass spectra recorded from practical textile samples: (a) DESI-MS spectrum collected from a blue cotton sample; (b) DESI-MS/MS spectrum of *m*/*z* 108 detected in the blue cotton sample; (c) DESI-MS/MS spectrum of *m*/*z* 124 detected in the blue cotton sample; (d) DESI-MS/MS spectrum of *m*/*z* 139 detected in the blue cotton sample.

Table 3. LOD Values of DESI-MS for Detection of 10 Carcinogenic Aromatic Amines on the Surface of Cotton Textile

aromatic amines	LOD[a] (fg/mm^2)
o-tolidine	0.82
o-toluidine	0.9
4,4′-methylenedianiline	1.0
2-aminonaphthalene	1.2
benzidine	1.2
p-phenylazoaniline	1.2
2,4,5-trimethylaniline	2.0
4-methoxy-1,3-phenylene diamine	2.2
2-methoxy-5-methylaniline	2.5
o-anisidine	3.5

[a] The LOD was calculated using the equation LOD = $3\sigma c/S$, where σ was the standard deviation of the six measurements performed on the blank sample, c was the minimal concentration of a standard solution used to obtain the calibration curve; and S was the mean value of the signal of analytes at the concentration c.

squared, which is much lower than the concentration allowed in the textile samples. Since DESI generates protonated or deprotonated molecular ions, signal intensities are highly affected by the proton affinity (PA) of compounds under investigation. Compounds with high proton affinities, such as bases, are easy to ionize and achieve high-quality MS signals. Aromatic amines are typical basic compounds, which have high proton affinity and produce strong DESI-MS signals as shown in this study. For example, the PA values for *o*-toluidine, *o*-anisidine, and 2,6-dimethylaniline are 890.9, 905.2, and 901.7 kJ/mol, respectively. Their high PA values probably account for their low LOD values which are in the low femtogram per millimeter squared range.

In comparison with aromatic amines, azo dyes generally have lower proton affinities. Additionally, the molecular structures of azo dyes result in stong molecular interactions with fabric textiles, resulting in low desorption/ionization efficiency in DESI. However, previous studies showed that DESI provided high sensitivity for detection of Sudan dyes on food surfaces.[61] With the use of a methanol/water spray solution, our experiments showed that azo dyes absorbed on textile fabrics were generally detected with poor signals in terms of both absolute signal intensity and signal-to-noise ratio by DESI-MS. Although, the azo dyes newly deposited on the textile substrate could be detected without significant sensitivity loss. This data suggests that the sensitivity of DESI for azo dyes detection depends on many factors including the molecular structures, gas-phase basicities of the analytes, and the surface properties of the textile samples. To ensure high sensitivity for azo dye detection, azo dyes are usually reduced into aromatic amines using chemicals in the laboratory. However, this conversion is unlikely to occur using reactive DESI[69−71] under ambient conditions, because the reaction conditions (e.g., speed, reagents, and temperature) are not compatible with our open-air DESI source. Under the appropriate conditions, azo dyes can be naturally converted to aromatic amines by bacteria. Thus, the detection of carcinogenic aromatic amines usually means that the textile products have been contaminated by illicit azo dyes. Meanwhile, airborne compounds such as explosives and/or aromatic amines can easily accumulate in fabric textiles. Regardless of the original source of the aromatic amines, their presence poses high risk for end users of the fabric products. Therefore, DESI-MS is useful for fast screening of the presence of aromatic amines in clothes and garments.

Under the optimized experimental conditions, DESI-MS provided acceptable precision for multiple measurements. Typically, the relative standard deviation (RSD) of most aromatic amines present in various textile samples (e.g., synthetic fabrics, cotton, leather, and plastic) was in the narrow range of 5−10% for six measurements of the same authentic aromatic amine solution. These data suggest that DESI can be used for the quantitative detection of aromatic amines in textile samples when necessary.

CONCLUSION

This study investigated the DESI-MS signal responses and fragmentation behaviors of all 24 carcinogenic aromatic amines on textile samples. A full profile of the characteristic fragments of all the aromatic amines generated in DESI-MS/MS has been systematically studied for the first time. Under optimized experimental conditions, DESI-MS was able to rapidly detect aromatic amines in various textile products, providing linear signal responses with a dynamic range of 6 orders of magnitude. Acceptable RSD (5−10%) was obtained for DESI-MS measurement of aromatic amines on various textile surfaces. The LOD of DESI-MS for most of the 24 aromatic amines is about $1-4 \times 10^{-15}$ g/mm^2. Detection of 24 aromatic amines on the same textile sample can be completed within 30 s using DESI-MS/MS experiments. The experimental data shows that DESI-MS is a sensitive, easy operation, nondestructive, and highly cost-effective method for high-throughput detection of trace amounts of carcinogenic aromatic amines in textile products.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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