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Direct quantification of PAHs in biomass burning aerosols by desorption electrospray ionization mass spectrometry

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ABSTRACT

Desorption electrospray ionization mass spectrometry (DESI-MS) technique was applied to the quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) in biomass burning aerosols. Experimental conditions were optimized to enhance the detection efficiencies of PAHs. DESI-MS signal intensities showed good linear responses to the amount of PAHs in a dynamic range of four orders of magnitude and the detection limit is about 1 pg/mm^2. Mass concentrations of three-, four-, five-, six-ring PAHs in laboratory-made rice straw burning aerosols were directly measured by DESI-MS without any sample pretreatment. The results agree well with the parallel measurement by traditional GC–MS. DESI phenomenon was also observed for other compounds in biomass burning aerosols such as sugars, inorganic and organic acids. Potential applications of DESI-MS to the rapid analysis of multiple components in aerosol samples were discussed.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds typically containing two or more fused carbon rings that are formed during incomplete combustion from natural and anthropogenic sources. PAHs can be released to the atmosphere in the vapor phase directly from the combustion facility, or emitted with aerosol particles, and then evaporated or dissipated into the environment as well. Biomass burning for agricultural residue disposal produced a lot of different kinds of PAHs and was regarded as one of the major anthropogenic sources [1–3]. PAHs have been paid extensive attention [4–13] by scientists from different research fields due to their strong carcinogenic and mutagenic effects [5–8]. The four-, five- and six-ring PAHs have stronger carcinogenic effects than the two-, three- and eight-, nine-ring PAHs [6].

The traditional methods for the analysis of PAHs in aerosol samples include gas chromatography–mass spectrometry (GC–MS), capillary supercritical fluid chromatography (SFC), high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), capillary electrophoresis (CE), etc. Usually these methods involve several steps like extraction, concentration and pre-separation [10,12,13]. These pretreatment procedures are labor intensive and time consuming. Meanwhile, some components in the environmental samples could be lost in these procedures due to the volatility, fragility or limited extraction efficiency. Some alternatives to the solvent extraction approach have been used to transfer organic analytes from aerosol samples to analytical systems, such as thermal desorption and thermal extraction [14,15]. The new soft ionization technique: desorption electrospray ionization (DESI) developed by Cooks and co-workers [16–18] opened a door for the rapid analysis of trace amount samples under ambient conditions. Since its introduction, DESI has been applied in a number of research areas, including biological tissue imaging [19], high-throughput metabolomics [20–22], explosives detection [23,24] pharmaceutical analysis [18,25,26], and environmental monitoring [27].

We have applied DESI-MS for the first time to the atmospheric aerosols analysis [28]. In the previous short application note, we briefly reported the semi-quantitative estimation of the total amount of 16 U.S. EPA priority PAHs by DESI-MS in aerosol samples. In this paper, we present in detail the quantitative measurement on single PAH species in biomass burning aerosols with focus on the optimization of experimental conditions and the concentrations of the PAHs with the strongest carcinogenic effect. The DESI-MS results were compared with the traditional GC–MS measurement. Potential applications of DESI-MS to other components in biomass burning aerosols were also discussed.

2. Experimental

2.1. Sampling

Biomass burning aerosols were generated by the combustion of rice straw in a homemade burner. The burner can control the

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amount of the biomass material and the burning condition (flaming/smoldering). In this experiment, 20 g rice straw was burned each time under flaming condition. The low ratio of CO/CO_2 in gas phase by GC analysis indicated the rice residue was burned completely. The rice straw was collected from the rural areas of Shanghai. The moisture content of the rice straw is around 11%. Total suspended particulate (TSP) produced by the rice straw burning in the burner were collected on 90 mm diameter quartz fiber filters (Whatman Company, Maidstone, UK) by a medium-volume aerosol sampler (Beijing Geological Instrument Factory, Beijing) at the sampling speed of 100 l/min. The sampling time was about 5 min. All the filters were baked at 550 °C for 4 h before sampling in order to eliminate organic species. The filters were equilibrated in a desiccator for 24 h before and after the aerosol sampling and then weighed to determine aerosol mass. All the filter samples were stored at −18 °C until analysis. Field blanks were handled the same way as real samples with exposure to air for 5 min.

2.2. Sample extraction and GC–MS analysis

A quarter of each aerosol sample filters was extracted in a 10 ml extraction cell. The extraction was performed with a SFXTM 220 supercritical fluid extraction (SFE) System (ISCO Inc.) using SFE-grade CO_2 (purity >99.999%, total hydrocarbon <2 ppm, Yunguang Co., Shanghai). SFE was carried out in two steps: a 5-min period on static mode, followed by 30 min of dynamic extraction at 30 MPa and 80 °C. Supercritical fluid flow on dynamic step was held at 1.5 ml/min by a variable-flow restrictor. After extraction, all solutions were evaporated and adjusted to 200 μl in dichloromethane under a gentle stream of clean nitrogen. Residual grade dichloromethane was purchased from Sigma–Aldrich Lab (Milwaukee, WI, USA).

The analysis of the extraction was performed on GC–MS (Agilent, USA). A VF-5MS (Varian, USA) 30 m × 0.25 mm I.D. fused-silica capillary column with 0.25 mm film thickness was used. The carrier gas was high purity helium (99.9999%). The temperature program was first hold at 60 °C for 4 min, ramp to 300 °C at 10 °C/min and hold at 300 °C for 5 min. The injector temperature was set at 250 °C and 1 μl analyte was injected in splitless mode. The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The transfer line and ion source temperatures were set at 280 and 230 °C, respectively. A internal standard mixture (2000 $\mu g\,ml^{-1}$) in dichloromethane containing 1,4-dichlorobenzene-d4, Acenapthene-d10, Chrysene-d12, Naphthalene-d8, Perylene-d12 and Phenanthrene-d10 (Supelco, Bellefonte, PA, USA) was added in the concentrated extraction solution (200 μl) prior to GC–MS analysis. The MS was operated in the full-scan mode in the range m/z 40–500 for qualitative analysis. The quantitative analysis was processed in the selective ion mode (SIM). The chromatogram was divided into 10 groups according to the different retention time of PAHs. For every compound, the molecular ion was monitored for quantification and the most intense fragment ions were used for confirmation. The blank tests did not show any significant levels of any of the PAHs, and thus, contamination from the experimental procedure can be excluded.

2.3. DESI-MS analysis

The mechanism and experimental set up of DESI-MS has been described before [17,28]. Briefly, the experiments were carried out using a commercial Thermo Finnigan (San Jose, CA) LCQ Advantage ion trap mass spectrometer equipped with a DESI ion source. As shown in Fig. 1, the DESI ion source was modified from the original electrospray ionization (ESI) source by adding a 3D moving sample stage to the ESI manifold. The sample stage includes a sample holder, a horizontal rotating stage, and a 3D moving stage to manually control the sprayer–sample-mass spectrometer distance and the impact angles. The MS mass range was set to 50–500 (m/z), and spectra were collected for 1 min in spectral average mode. Data were acquired via the Xcalibur software interface for a total acquisition time of 0.6 s/spectrum.

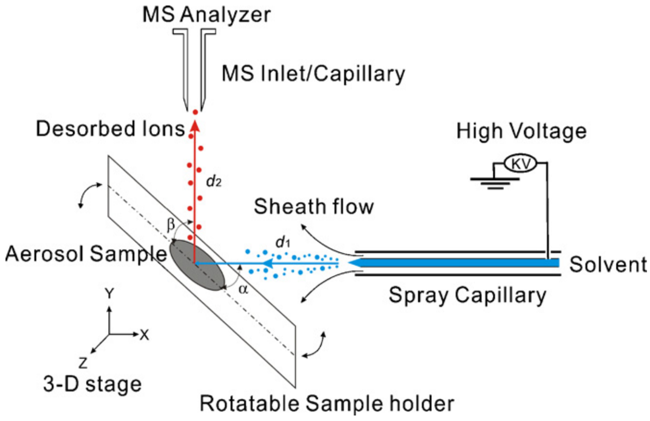

Fig. 1. Schematic of DESI source for aerosol sample analysis.

Experimental parameters for DESI-MS were first optimized to enhance the signal intensity by using a standard PAHs solution, with 16 EPA priority pollutants in methanol (EPA 610/525/550 PAH mixture, 100 ng/μl for each PAH, lot 323-55A), purchased from ChemService (West Chester, PA, USA). Diluted standard sample solution (10 μl) was deposited onto the substrate with a surface area of 1 cm^2. Then the substrate was attached to the 3D moving stage for DESI-MS analysis. Calibrations were carried out under the optimized experimental conditions between the signal intensities of target compounds and their amounts deposited on the substrate. After the calibration, a 1 cm × 1 cm piece was cut out from the aerosol sample filter and attached to the sample stage for DESI-MS analysis without any preparation or extraction. The quantity of PAHs in each aerosol sample can be calculated from the calibration curves. Typically, the DESI sampling spot in this analysis was about 1 mm^2 in area and the sampling duration for each spot was 5–10 s. DESI spectra were taken by scanning the whole analyzed sample surface and averaging the result for each spot.

3. Results and discussion

3.1. DESI-MS optimization

The experimental parameters for DESI-MS include chemical parameters (such as substrate for standard sample deposition, electrospray solvent, etc.), the geometric parameters of DESI, and the operation parameters of electrospray and mass spectrometer such as the sheath gas flow rate, heated capillary temperature, etc.

First, an appropriate substrate for standard sample deposition should be chosen. Insulator materials are preferred for the sample deposition surface in DESI-MS to avoid neutralization of the charge droplets on the surface [17]. In this study, the diluted standard PAHs solution was deposited on the quartz fiber filter, same as those for aerosol sampling. The selection of electrospray solvent, which is strongly dependent on the polarizability and the ionization cross-section of the analyte molecule, was a crucial factor for the signal intensity. PAHs are nonpolar molecules. However, their electron-rich carbon rings have both high proton affinities and low electron detachment energy, which suggest that they may have large cross-sections to form molecular or protonated molecular cations in the positively charged electrospray. We tested several different solutions such as methanol, hexane, cyclohexane, acetonitrile, acetic acid and ammonia water and their combinations as the spray solu-

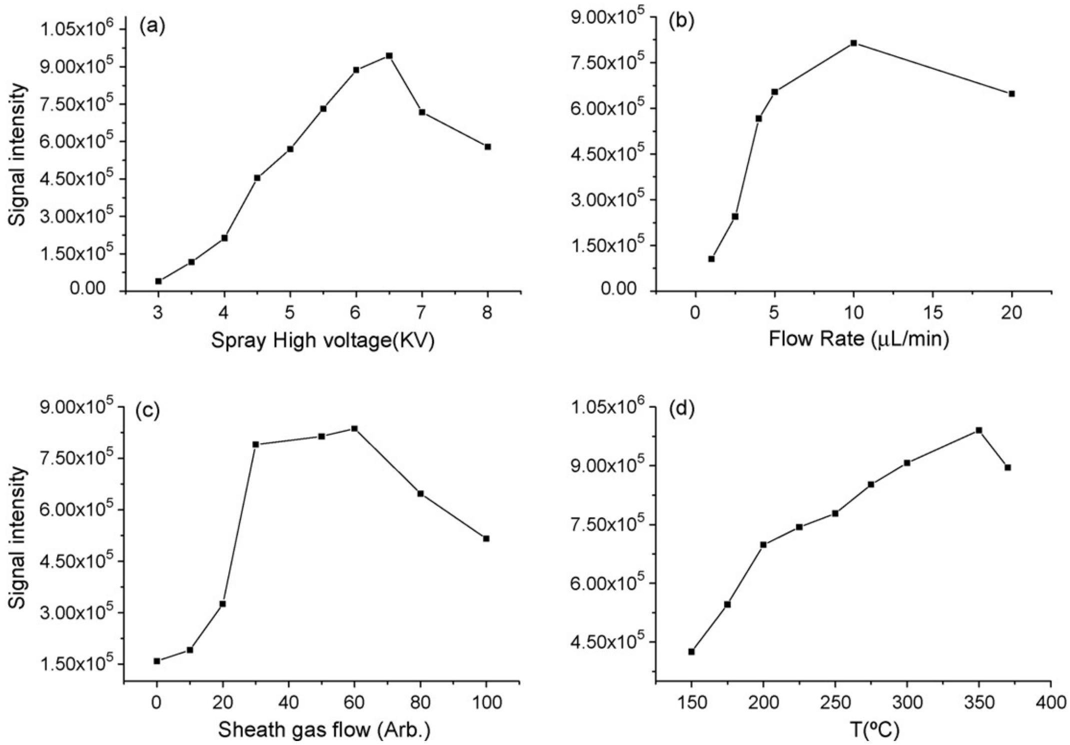

Fig. 2. Optimization of (a) electrospray high voltage, (b) solvent flow rate, (c) sheath gas flow rate and (d) temperature of heated capillary. For sheath gas flow rate, 10 arbitrary units equal to 3.5 l/min in this work.

tion and compared the signals in both positive ion and negative ion mass spectra. The methanol with 1% acetic acid solution gave the strongest signal for the molecular or protonated molecular cations of PAHs in positive ion mass spectrum. Hexane and cycloxane are not good solvents for stable electrospray because of their high volatilities. Pure methanol and acetonitrile can give cation signals of PAHs but not as strong as the solvent with acid addition. No strong signals were observed under negative ion mode for all the solvents.

As shown in Fig. 2a, total signal intensity of 16 PAHs increased steadily with the electrospray voltage and reached the maximum at 6.5 kV. Signal intensity decreased when the voltages >7.0 kV most because higher voltage yielded unstable Taylor cones and multi-pointed streams. The electrospray solvent flow rate is expected to have an effect on droplet size distribution and on the average charge carried by the droplets [26]. High electrospray solvent flow rate can produce a droplet size large enough for picking up and transporting analyte from substrate surface to MS analyzer as well as producing high analyte ion current. However, the desolvation efficiency decreases with the increasing flow rate. As shown in Fig. 2b, the best solvent flow rate in this experiment is 10 μl/min. The flow rate of sheath gas was also optimized in this study. The sheath gas is the inner coaxial nitrogen gas that sprays (nebulizes) the sample solution into a fine mist as it exits the electrospray tip. For a constant DESI solvent flow rate, adequate sheath gas flow rate can produce proper initial droplet size and enhance the signal sensitivity. The effect of the sheath gas flow rate is shown in Fig. 2c. Fig. 2d shows the temperature effect of the heating capillary tube after the inlet of mass spectrometer is shown in. Overall, higher signal intensity was achieved at high heating capillary temperature owing to more efficient desolvation.

The geometric parameters of DESI, including incident angle α, collection angle β, distance from sample to tip d_1, distance from sample to analyzer d_2 (as shown in Fig. 1), have important effect on the electrospray desorption process and the signal intensity. The optimum setting is 35° for α, 55° for β, 4–6 mm for d_1, and 1–3 mm for d_2 in this experiment.

3.2. Mass concentration calibration using standard sample solution

DESI is a very gentle ionization technique that produces ions similar to those obtained by ESI. As reported in our previous work [28], all the 16 PAHs were observed in the forms of molecular or protonated molecular ions under the optimized operating conditions, making the spectral assignment quite easy. The relative detection efficiencies for the 16 PAHs can be measured based on the signal intensities and are shown in Fig. 3. As labeled, some of the PAH signals are overlapped due to the same *m*/*z*. Since most of

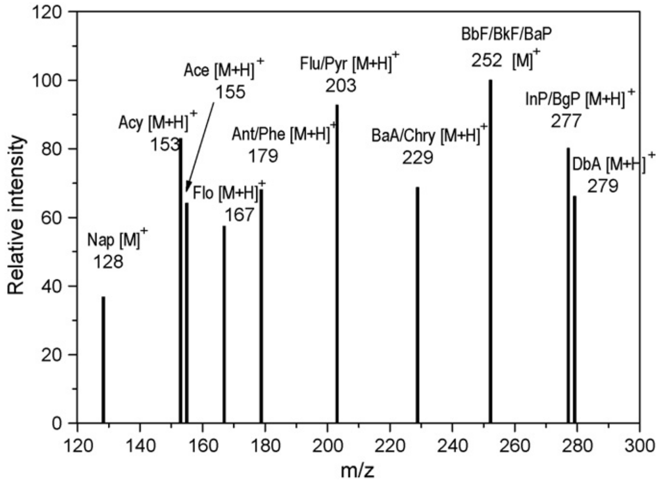

Fig. 3. Relative detection efficiencies of the 16 U.S. EPA “Priority PAH Pollutants” by DESI.

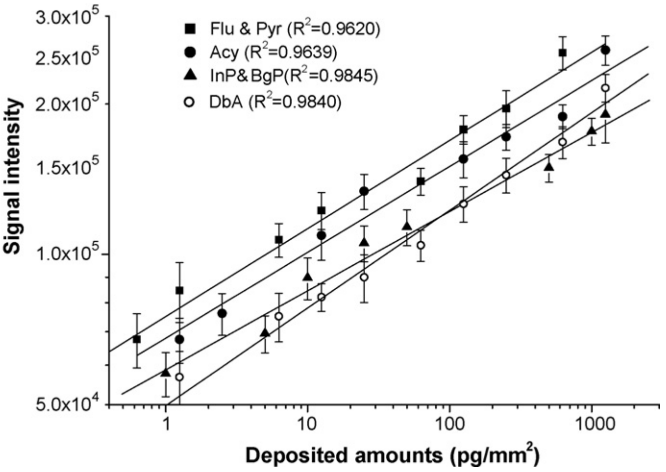

Fig. 4. Calibrations between DESI-MS signal intensities and deposited amount of PAH samples.

these overlapped ion species have similar molecular structures, it is hard to strictly measure the contribution from each species based on the MS/MS fragmentation spectra. Here, we assume that PAHs with same molecular weight have the same detection efficiency.

For natural surfaces, use of internal standards does not give strictly quantitative results in DESI studies [18]. In the case of aerosol samples, it is difficult to homogeneously disperse internal standard on the aerosol sample filter without destroying the original surface state. In this work, we used the standard solutions of PAHs with different concentrations deposited on the quartz fiber filter for calibration and attempted to gain a quantitative measurement of single PAH concentrations in aerosol samples from their ion signal intensities. A minimum of three continuous trials were conducted per experiment to get the relative standard difference (RSD). The amount of target compounds present on the substrate surface that showed mass signal three times higher than the peak-to-peak noise level of the baseline was considered as the limit of detection (LOD).

We focused on the PAHs with strongest carcinogenic effect. Acenaphthylene (Acy), fluorathene (Flu) & pyrene (Pyr), dibenz[a,h]anthracene (DbA), and indeno[1,2,3-cd] pyrene (InP) & benzo[g,h,i]perylene (BgP) were selected as the representatives of PAHs with three-, four-, five- and six-ring structures. Calibrations were carried out between the ion intensities and the sample amounts for these PAHs. As mentioned above, for the species with same molecular weight (Flu & Pyr, InP & BgP), we assume they have the same detection efficiency and calculate the total concentration for certain m/z. As shown in Fig. 4, DESI-MS demonstrated good linear responses to Acy, Flu & Pyr, DbA and InP & BgP in a dynamic range of four orders of magnitude. RSD was less than 15% for all the PAHs with LOD at about 1 pg/mm^2. No PAHs were observed beyond the LOD in the blank tests.

3.3. Measurement of PAHs in biomass burning aerosols by DESI-MS

In this work, we use the laboratory-made rice straw burning aerosols as the analog of ambient biomass burning aerosols. Fig. 5 shows a typical positive ion DESI spectrum of rice straw burning aerosols under the optimized conditions for PAH measurement. Only the 16 U.S. EPA “Priority PAHs Pollutants” were labeled. Each possible molecular or protonated molecular ion signal was identified by MS/MS fragmentation experiment. As shown in Fig. 5, PAHs can be selectively detected by DESI-MS under the optimized operating conditions despite of the complex ingredient of aerosols.

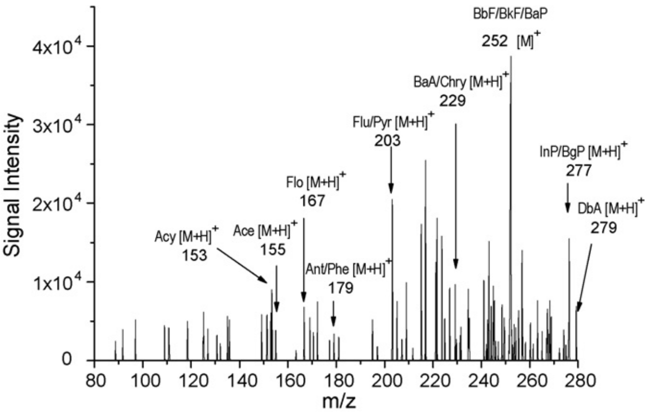

Fig. 5. Typical DESI-MS spectrum of PAHs from rice straw burning aerosols.

PAHs observed in this experiment can be divided into four groups according to the number of carbon rings they have: three-ring (Acy, acenaphthene (Ace), fluorine (Flo), phenanthrene (Phe), anthracene (Ant)), four-ring (Flu, Pyr, benzo[a]anthracene (BaA), chrysene (Chry)), five-ring (benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), DbA), and six-ring (InP, BgP). Two-ring structure naphthalene (Nap) was not observed because of its high vapor pressure and extremely low concentration in particle-phase [29]. We took Acy, Flu & Pyr, DbA, InP & BgP as the representative of each group. Firstly, their identities were confirmed by the MS/MS patterns as shown in Fig. 6. Then, mass concentrations of these PAHs in biomass burning aerosols were carefully measured by DESI-MS (as shown in Table 1).

Apparently, three-ring Acy has the lowest concentration, ranging from 0.8 to 26.1 μg/g with an average of 11.1 μg/g by DESI-MS. In some samples, Acy could not be detected by GC–MS method while it could be measured by DESI-MS. It should be noticed that the sample amount we used for DESI-MS measurement is only 1/15 of that for GC–MS method. The average mass concentrations of Flu & Pyr, DbA, InP & BgP in biomass burning aerosols are much higher than that of Acy. Combining with the relative intensities of other PAH species in Fig. 5, we may conclude that mass concentrations of four-, five-, six-ring PAHs, which have the strongest carcinogenic effects, are

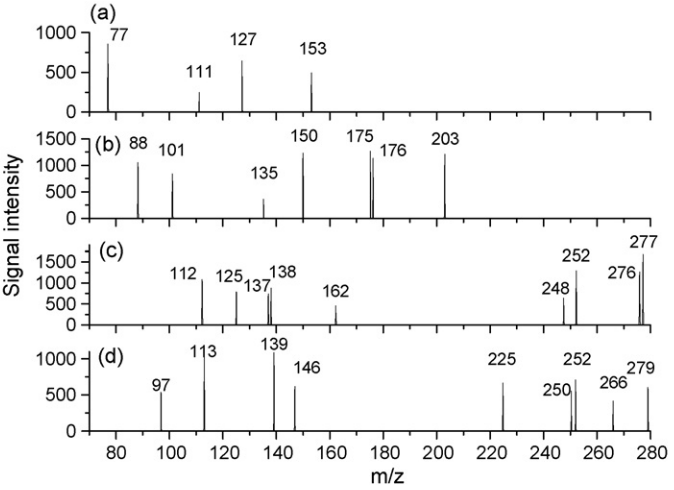

Fig. 6. The MS/MS investigation of (a) $m/z = 153$ [Acy+H]$^+$, (b) $m/z = 203$ [Flu, Pyr+H]$^+$, (c) $m/z = 277$ [InP, BgP+H]$^+$, (d) $m/z = 279$ [DbA+H]$^+$ peaks.

Table 1
PAH concentrations measured by DESI-MS and GC–MS.

Aerosol sample	Acy (μg/g)		Flu & Pyr (μg/g)		DbA (μg/g)		InP & BgP (μg/g)	
	DESI-MS	GC–MS	DESI-MS	GC–MS	DESI-MS	GC–MS	DESI-MS	GC–MS
1	26.1	20.4	104.8	93.6	44.1	96.4	227.9	210.3
2	11.2	6.4	45.2	52.2	66.1	82.5	7.7	10.0
3	24.7	27.0	197.5	215.1	75.4	68.6	9.4	11.6
4	14.0	8.1	108.0	119.1	46.1	36.7	139.5	163.2
5	12.5	19.6	188.5	193.8	9.6	13.4	116.5	125.6
6	11.0	6.6	124.7	93.0	42.6	35.3	131.1	117.5
7	1.3	–	128.2	160.5	34.1	42.1	95.1	106.2
8	3.9	–	249.6	270.2	14.0	12.2	20.5	21.1
9	5.0	–	110.3	122.1	11.3	8.9	63.7	60.4
10	0.8	–	11.0	9.9	24.6	16.2	17.9	14.5
Average	**11.1**	8.8	**126.8**	133.0	**36.8**	41.2	**82.9**	84.0

–: Below detection limit.

quite high in the aerosols emitted from rice straw burning even at flaming burning conditions.

As shown in Table 1, DISI-MS results agree very well with those by GC–MS. For some of the samples, the discrepancy between the two methods could be due to the different sampling areas (the inhomogeneity of the sample distribution on the filters). The difference between the surfaces of standard samples and the aerosol samples might also contribute to the discrepancy. The matrix effect of the aerosol sample (due to the other components in aerosols) could influence the quantitative accuracy of the DESI-MS measurement without using internal standard.

Biomass burning can significantly increase the input of organic aerosol components including PAHs to the atmosphere. In China, the annual crop residue yield exceeded 600 million tons from 2004 to 2006 [30], among which the rice straw yield is about 113 million tons per year. Most of the crop residues were burned for domestic energy or in the open field as a common way to eliminate waste after harvesting, which has been considered as a major air pollution source for local and regional environment [31]. In our study, TSP generated from rice straw burning is about 6.65 mg/g in average. The high concentrations of four-, five-, six-ring PAHs in the rice straw burning aerosols reveal that the crop residue combustion is an important source of PAHs in atmosphere and could have strong environmental effects.

3.4. *Possible applications of DESI-MS to other components in biomass burning aerosols*

The DESI phenomenon has been observed for a wide spectrum of compounds ranging from both polar and nonpolar small molecules to huge bio-molecules [16,18,19]. In this study, we also selectively detected some other components in the rice straw burning aerosols by changing operation conditions. Fig. 7 shows the typical DESI mass spectra for inorganic acids, organic acids and sugars in the rice straw burning aerosols. Both inorganic and organic acids showed strong signals as deprotonated molecular ions in the negative mass spectra while sugars were typically characterized by their protonated molecular ions in the positive mass spectra. All the labeled compounds are important components in biomass burning aerosols. For example, levoglucosan is a degradation product from cellulose and can be utilized as an indicator for the presence of biomass burning emission in the analysis of atmospheric aerosols [32]. The traditional analytical method for levoglucosan consists of extraction, silylation and analysis by GC–MS [32,33]. The preliminary data shown in Fig. 7 make us quite confident to extend the DESI-MS method to the rapid analysis of these compounds in aerosol samples.

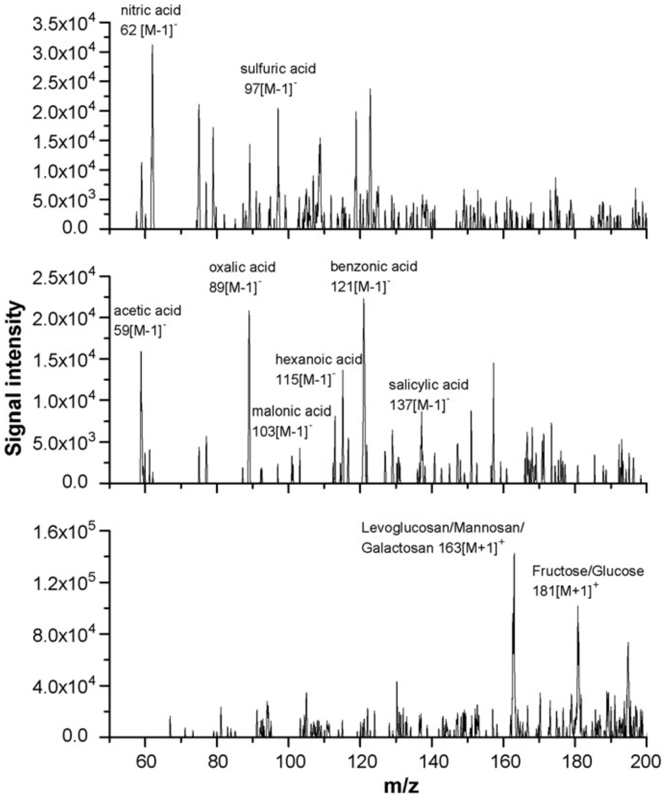

Fig. 7. DESI-MS spectra of (a) inorganic acids, (b) organic acids and (c) sugars from rice straw burning aerosols.

4. Conclusions

In this paper, we present in detail the quantitative measurement on PAHs in biomass burning aerosols by DESI-MS. Experimental conditions were optimized to enhance the detecting efficiencies of PAHs. Mass concentrations of three-, four-, five-, six-ring PAHs in rice straw burning aerosols were measured by DESI-MS and the results agree well with the traditional GC–MS measurement. The high concentrations of four-, five-, six-ring PAHs in the rice straw burning aerosols observed in this study suggest that the crop residue combustion is an important source of PAHs in the atmosphere and could have strong environmental effects. DESI phenomenon was also observed for other compounds in biomass burning aerosols such as sugars, inorganic and organic acids, which demonstrates the potential of DESI-MS for the rapid analysis of aerosol samples with multiple components.

Acknowledgments

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