Research Article

Isomeric differentiation of polycyclic aromatic hydrocarbons using silver nitrate reactive desorption electrospray ionization mass spectrometry

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RATIONALE: Polycyclic aromatic hydrocarbons (PAHs) are nonpolar and difficult to detect by desorption electrospray ionization. We present a new detection method based on cationization with silver ions, which has the added advantage of being able to differentiate PAHs with the same mass but different structure.

METHODS: 9,10-Diphenylanthracene and triptycene, in addition to four different groups of PAH isomers: (1) anthracene and phenanthrene, (2) pyrene and fluoranthene, (3) benz[a]anthracene, benz[b]anthracene (tetracene), and chrysene (4) benzo[a]pyrene and benzo[k]fluoranthene, were deposited on a paper surface and bombarded with methanol droplets containing silver nitrate. The resulting microdroplets entered a quadruple mass spectrometer for mass analysis.

RESULTS: The mass spectrum shows $[PAH]^+$, $[Ag + OH + PAH]^+$, and $[Ag(PAH)_n]^+$ (n = 1, 2) (and $[PAH + O_2]^+$ in the case of benz[b]anthracene) ions. PAHs having a bay structure, such as phenanthrene, showed a different tendency to interact with silver ions from those PAHs having a linear arrangement of the fused benzene rings, such as anthracene. The ratios of the $[PAH]^+$ peak intensity to that of $[Ag–PAH]^+$, $[Ag + OH + PAH]^+$, $[Ag(PAH)_2]^+$, and $[PAH + O_2]^+$ were used to differentiate the PAH isomers sharing the same molecular formula with different structures. For isomeric mixtures the $[PAH]^+$ to $[Ag + OH + PAH]^+$ ratio was found to be the most useful parameter. The uncertainty in the mole fraction of an isomeric mixture was ± 0.09, ± 0.13, ± 0.25, and ± 0.1 for phenanthrene-anthracene, fluoranthene-pyrene, benz[a]anthracene-chrysene, and benzo[a]pyrene-benzo[k]fluoranthene, respectively.

CONCLUSIONS: A simple method has been developed for the detection of PAHs in desorption electrospray ionization mass spectrometry based on Ag(I) cationization. The method showed a capability to differentiate PAHs isomers (having the same molecular mass) in isomeric mixture with an uncertainty in the mole fraction of about ± 0.1. At high inlet temperature and voltage, this method showed better sensitivity but less ability to differentiate between isomeric species. Copyright © 2012 John Wiley & Sons, Ltd.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most prevalent forms of aquatic environmental contaminants, originating from natural sources such as volcanic activity or from anthropogenic sources such as incomplete combustion of fossil fuels, oil refining, motor vehicle exhaust, coke production, and other industrial activities.[1] Because of their effect as carcinogens,[2] PAHs are included in the US Environmental Protection Agency (US EPA) top pollutants list.[3] Of particular interest, PAH isomers (same molecular mass but different structure) were found to have different poisonous effects.[2,3] Consequently, there is much interest in being able to detect, quantitate, and differentiate PAHs based on their molecular mass and structure.

Recently, Takats *et al.*[4] reported desorption electrospray ionization (DESI) as a new soft ionization technique for the analysis of samples under ambient conditions. In DESI, charged droplets in a stream of gas are directed at the analyte of interest, which has been deposited on a surface. The impact of these droplets on the surface produces secondary microdroplets that contain the extracted analytes from the surface which become gas-phase ions upon desolvation.[4,5] Reactive DESI is a new development in DESI experiments that selectively targets a specific molecule on the surface.[6] In reactive DESI, instead of spraying only solvent onto the sample surface, specific reagents are added into the solvents that can selectively react with target molecules on the surface to form derivatized products. The advantages of this method are that analytes can be detected directly from their original source with no sample preparation and that it provides high sensitivity and short analysis times. Reactive DESI has also been used to detect reaction intermediates.[7–9]

DESI is considered to be a soft ionization technique, so it has limited applications to nonpolar molecules such as PAHs. DESI was first used by Chen *et al.*[10] to detect PAHs. Their approach was to use a methanol/acetic acid solution as the solvent spray to form cationic or protonated PAHs. Although the method was capable of detecting some PAHs, it provided

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a poor signal-to-noise ratio and low sensitivity. The Ag(I) ion has been previously found[11] to show a strong affinity toward aromatic compounds like PAHs arising from a number of fundamental intermolecular forces.[12] Recent theoretical studies have shown that electrostatic interactions are the main factors in cation aromatic π-interactions.[13,14] Ag(I) can cationize PAHs, yielding charged Ag-PAH complexes. An increase in Ag(I) affinity was observed with increasing number of fused benzene rings in the PAHs, despite the fact that the ion-induced dipole interactions were noticeably weakened for larger PAHs. Ng *et al.*[15] successfully used silver ions in electrospray ionization (ESI) mass spectrometry for the detection and differentiation of PAHs. However, this method requires a relatively large amount of sample to enable a continuous direct spray of the solution mixture into the mass spectrometer. This added an environmentally unfriendly procedure that also required the instrument to be cleaned after each experiment, especially when using real samples in which PAHs reside, such as smoke, coal, and oils. More importantly, the method (ESI) of Ng *et al.* is not capable of distinguishing between isomers in a mixture of PAHs.[15] It might also be mentioned that silver ions have previously been used in DESI to enhance the detection of unsaturated fatty acid and fatty acid ethyl esters.[16]

In this study, we report the use of Ag(I)-reactive DESI-MS to detect and differentiate between isomeric PAHs deposited on a surface. In this approach, the silver ion is used as a cationization agent for aromatic compounds yielding $[PAH]^+$, $[Ag + OH + PAH]^+$, and $[Ag(PAH)_n]^+$ (n = 1, 2) complexes. The reported method offers high-speed, clean, and easy adaptability. It also shows a high efficiency and sensitivity toward analyzing and differentiating PAH isomers that exist separately or in an isomeric mixture. The $[Ag + OH + PAH]^+$ peak had not previously been reported when using the ESI method.[15] This peak is the most useful in the differentiation of PAH isomers present in a mixture using reactive DESI.

EXPERIMENTAL

Reagents and chemicals

All chemical compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA) and the solvents were supplied by Sigma-Aldrich and Fisher Scientific (Pittsburgh, PA, USA). The PAH samples were prepared in HPLC grade chloroform solvent (1 mg mL^{-1}). For DESI experiments, 15 μL of sample was deposited on paper that was affixed to a glass slide. After the samples had completely dried in air, they were examined using DESI-MS. A stock solution of silver nitrate was prepared in HPLC grade methanol. In this experiment, 9,10-diphenylanthracene (DpA) and triptycene (Tryp) were used in addition to four different groups of PAH isomers: (1) anthracene (Anth) and phenanthrene (Phen), (2) pyrene (Pyr) and fluoranthene (Fluo), (3) benz[*a*]anthracene (BaA), benz[*b*]anthracene (BbA) and chrysene (Chry), and (4) benzo[*a*]pyrene (BaP) and benzo[*k*]fluoranthene (BkF) to study the ability of this method to detect and differentiate the isomeric PAHs. Separate isomer solutions along with isomeric mixture solution were used.

DESI-MS equipment and conditions

Reactive DESI experiments were performed in positive ion mode using a quadrupole ion trap mass spectrometer, (Finnigan LCQ classic, Thermo Scientific, San Jose, CA, USA). The analyses of PAHs were carried out using a DESI spray solution of methanol, which contained typically 5×10^{-5} mol L^{-1} of the metal ion, with a flow rate of 20 μL min^{-1}. The DESI source, as depicted in Fig. 1, was positioned at a 45° angle to the surface, 1–2 mm above the surface, and at a distance of 3–5 mm from the inlet of the LCQ mass spectrometer. Nebulizer gas (nitrogen) was used at a pressure of 150 psi. Unless otherwise mentioned, the capillary voltage was 31 V, and the capillary inlet connected to the mass spectrometer was at a temperature of 150 °C.
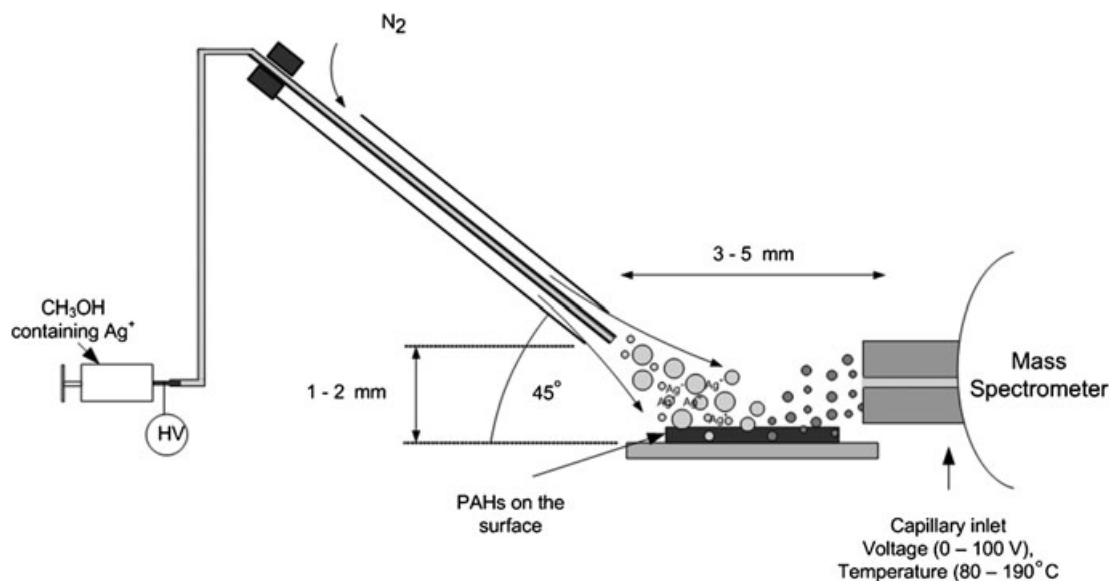

Figure 1. Schematic representation of reactive DESI of silver nitrate in methanol solution. PAHs are deposited on the surface and bombarded with methanol droplets containing Ag$^+$ ions.

RESULTS AND DISCUSSION

Because of the nonpolar structure of PAHs, direct analyses of these compounds in DESI-MS with spraying polar or nonpolar solvents had previously shown poor detection efficiency.[10] However, the π-electrons in their aromatic rings can be used to react with metal ions and produce ionic organometallic compounds. The silver ion proved to be the most efficient metal cationization agent for aromatic compounds, yielding [Ag(PAH)$_n$]$^+$ (n = 1, 2) complexes with PAHs. There are two possible bonding interactions in the Ag(I)-organic π-system such as PAHs. The first is a "σ-type bond" that is related to the transfer of a π-electron from the occupied 2p bonding orbitals of PAH into the vacant 5s orbital of the Ag$^+$ ion. The second is a "π-type bond", in which the 4d electrons of the Ag$^+$ ion transfer to the unoccupied π^* 2p anti-bonding orbital of the PAH. For arene systems like the PAHs, σ-type bonding is more probable owing to the availability of π-electrons in PAHs and the tendency of silver ions to accept electrons.[17]

Methanol containing silver ion as the spray solvent showed high efficiency for the study of PAHs in reactive DESI. Typical DESI spectra of the deposited triptycene and 9,10-diphenylanthracene are shown in Figs. 2(a) and 2(b), respectively. In general, the main peaks in the spectra were [PAH]$^+$, the silver complexes [Ag(PAH)$_n$]$^+$ (n = 1, 2) and [Ag + OH + PAH]$^+$. The peaks for the silver ion and its complexes appeared as two intense peaks (with a 2 m/z units difference) caused by the two approximately equally abundant stable isotopes of silver; ^{107}Ag and ^{109}Ag. Tandem mass spectrometry (MS/MS) experiments were used to confirm the peaks for the complexes, [Ag(DpA)$_n$]$^+$ (n = 1, 2), (see Figs. 2(c) and 2(d)). This method was used to differentiate four different groups of

isomeric PAHs: (1) anthracene and phenanthrene, (2) pyrene and fluoranthene, (3) benz[a]anthracene, benz[b]anthracene and chrysene, and (4) benzo[a]pyrene and benzo[k]fluoranthene, as shown in Figs. 3(a), 3(b), 4, and 5, respectively. Low intensity but persistent [nMethanol + mAg + xPAH]$^+$ cluster peaks (where n, m, and x are unknown) were recorded mainly at m/z 444 and 623. In the case of benzo[b]anthracene (m/z 228), two other intense peaks were observed at m/z 259 and 260. High-purity deuterated methanol (CD$_3$OD) showed no shift in the peak positions. This result suggested that the origin of the 32 m/z units difference is from molecular oxygen. Comparisons of the results shown in Figs. 3–5 provided convincing evidence for the power of reactive DESI-MS with silver ions to distinguish between different, already separated, PAH isomers.

We have explored whether different DESI-MS conditions provide more sensitivity in detecting PAHs and in distinguishing between the different isomers. The effect of the spray solvent containing silver nitrate was studied as a function of solvent polarity for toluene, chloroform, methanol, dimethylformamide, acetonitrile, and water (results are not shown here). Saturated silver nitrate solutions were prepared with chloroform and toluene solvents owing to the low solubility of AgNO$_3$ in these solvents. These spray solutions showed no success in detecting PAHs. Mixture of methanol/chloroform or methanol/toluene (with different proportions) showed that by increasing the proportion of chloroform or toluene with respect to methanol, the intensity of [PAH]$^+$ and the [Ag(PAH)$_n$]$^+$ (n = 1, 2) complexes dramatically decreased caused by the nonpolar nature of these solvents which restricts the dissociation of silver nitrate. On the other hand, water, acetonitrile, and dimethylformamide solvents showed less intense peaks than methanol which
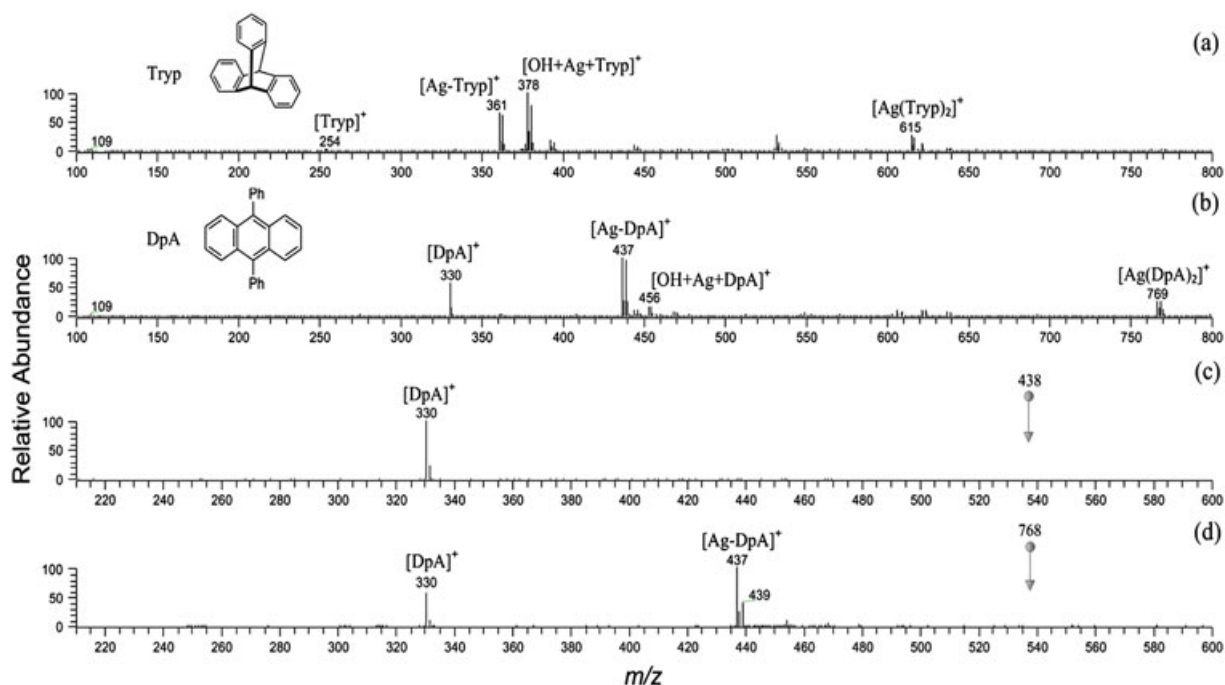

Figure 2. DESI-MS spectra of (a) triptcyne and (b) 9,10-diphenylanthracene. MS/MS data are shown in (c) and (d) for m/z 438 and m/z 768 for 9,10-diphenylanthracene, respectively. Inlet temperature = 150 °C, inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.
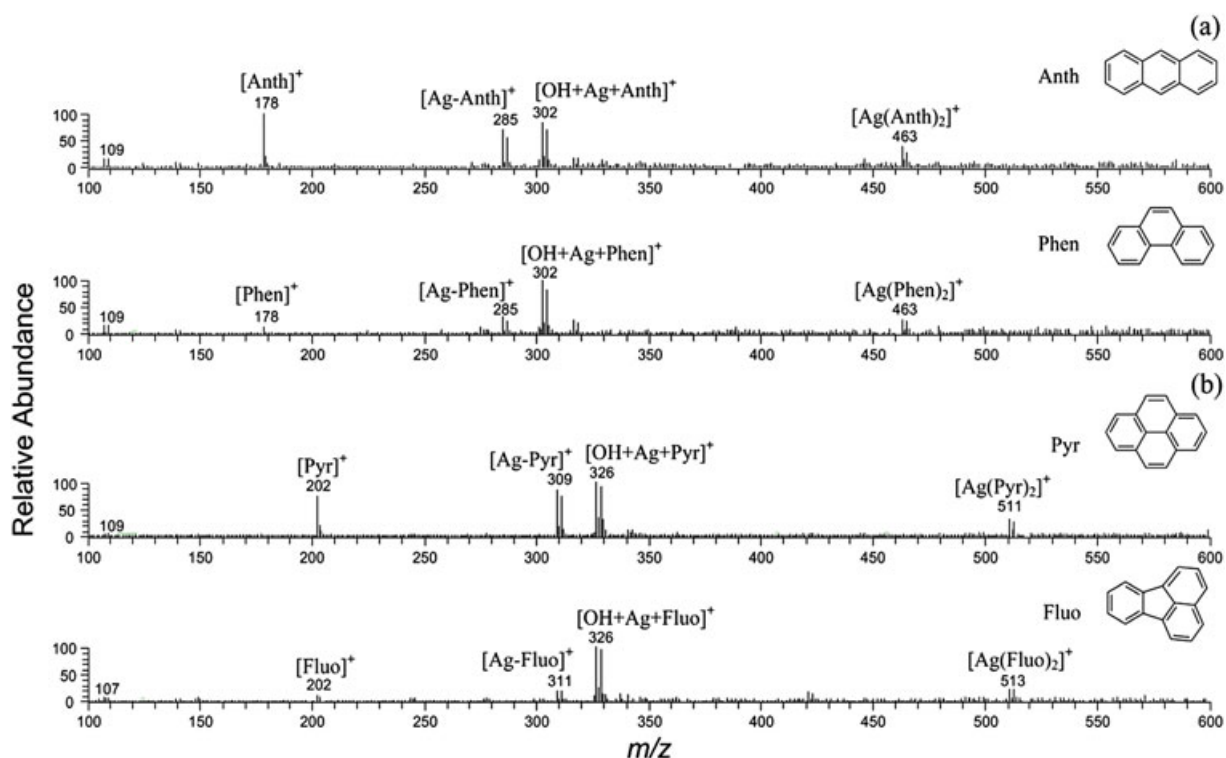
Figure 3. DESI-MS spectra of the isomer pairs: (a) anthracene and phenanthrene, and (b) pyrene and fluoranthene. Inlet temperature = 150 °C, inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.
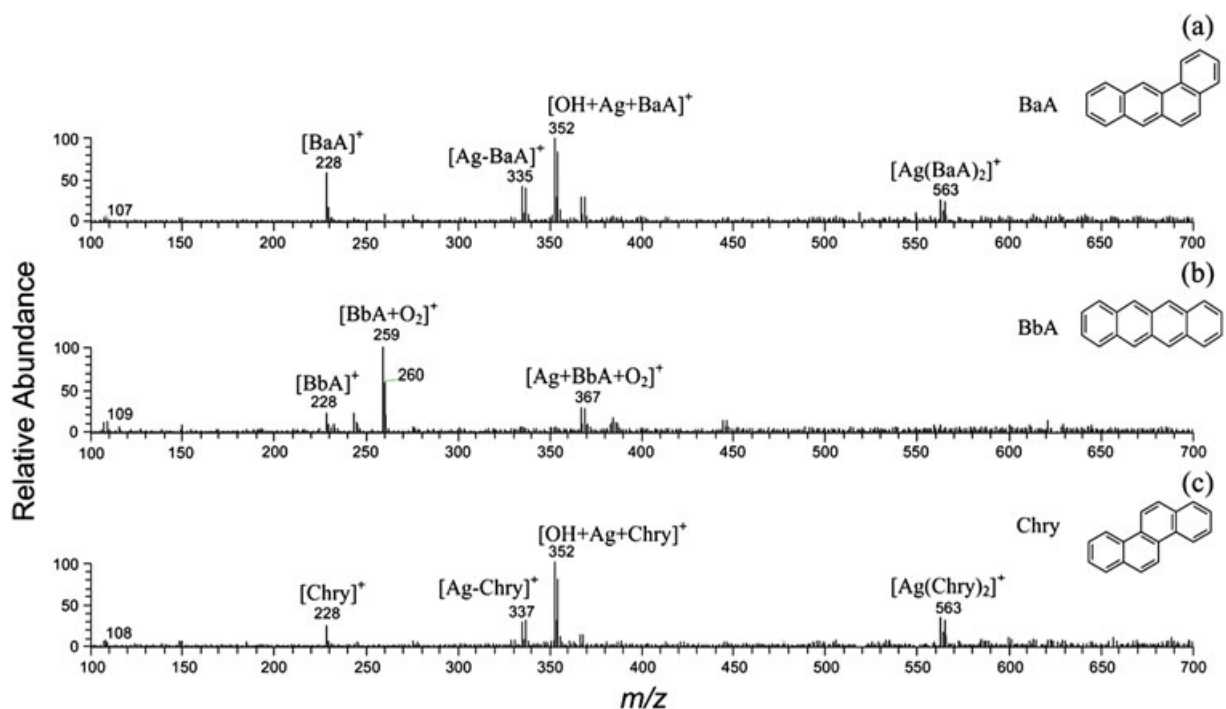

Figure 4. DESI-MS spectra of (a) benz[a]anthracene, (b) benz[b]anthracene, and (c) chrysene. Inlet temperature = 150 °C, inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.
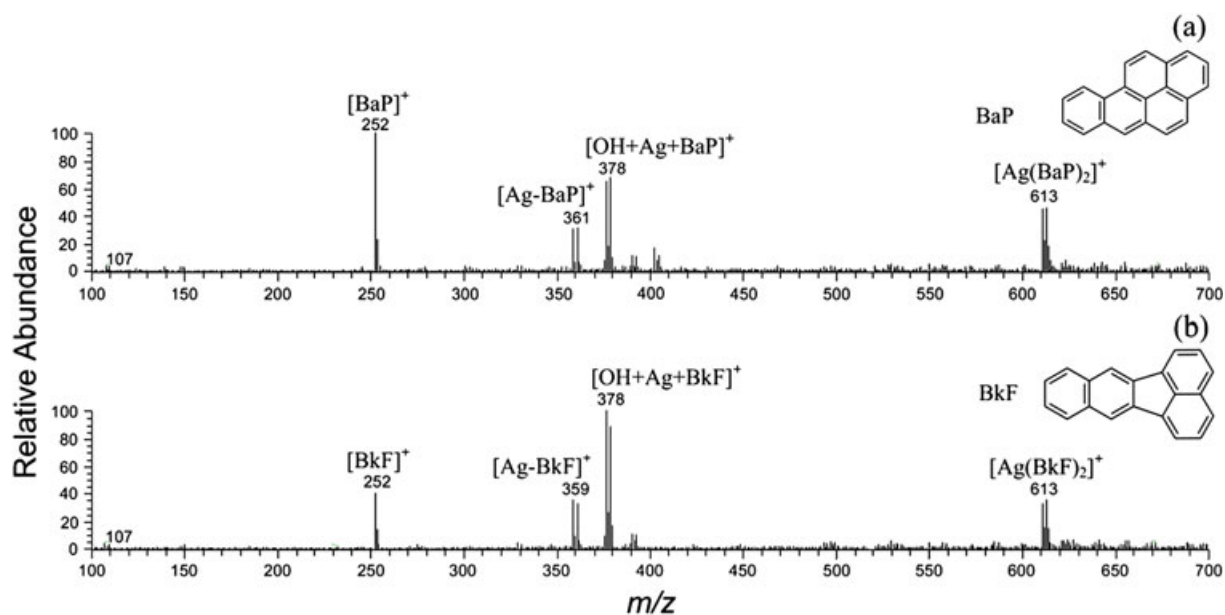
Figure 5. DESI-MS spectra of (a) benzo[*a*]pyrene (BaP) and (b) benzo[*k*]fluoranthene (BkF). Inlet temperature = 150 °C, inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.
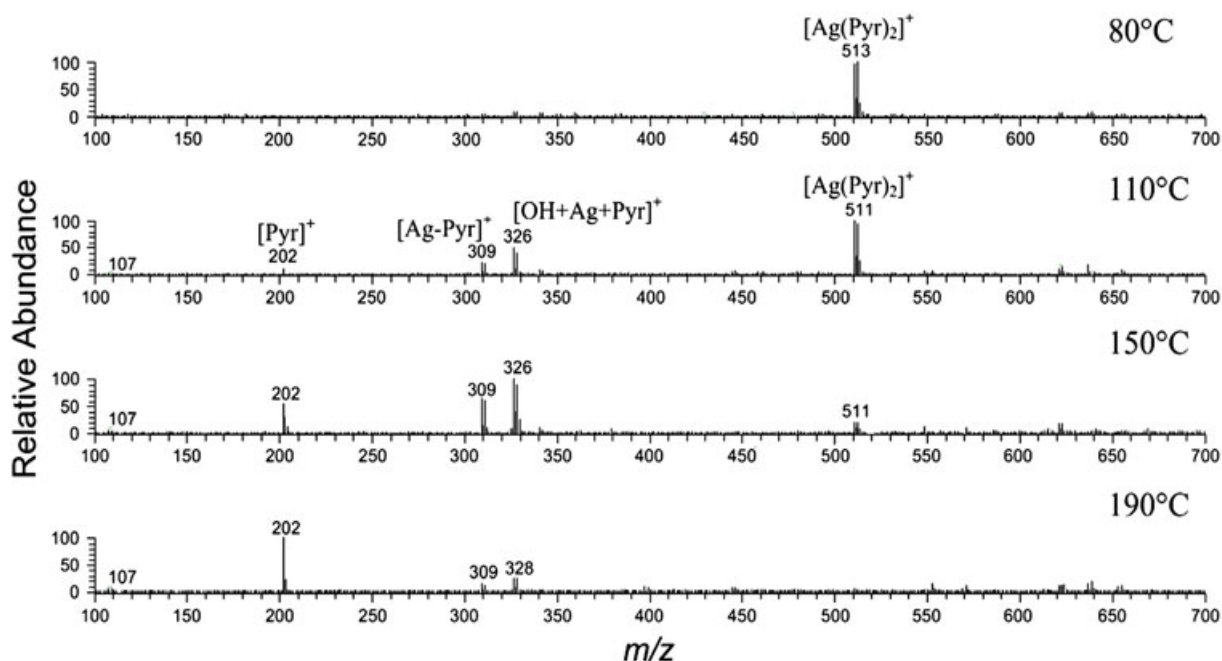

Figure 6. Effect of inlet temperature on ratio of pyrene peak intensities. Inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.

can be explained by the high solvation effect on the silver ion making it less available for reacting with PAHs. We reached the conclusion that methanol is the best spray solvent, presumably because of its relatively medium polarity.

We also examined how the voltage applied to the spray solution affects detection of PAHs. We found no effect on the peak ratio between the [PAH]$^+$ ion and PAH complexes with the silver ion (results not shown here). However, a voltage of 5 kV provided the highest sensitivity for all peaks and was chosen for all other experiments.

Figure 6 shows the effect of temperature on the detection of pyrene. At 80 °C, the [Ag(Pyr)$_2$]$^+$ complex was the only peak in the spectrum. At 110 °C, the [PAH]$^+$ ion and the [Ag-Pyr]$^+$ complex started to appear in the spectrum although the [Ag(Pyr)$_2$]$^+$ complex was still the major peak. At 150 °C, the intensity of the [Ag(Pyr)$_2$]$^+$ complex reduced and the intensity of [PAH]$^+$ and [Ag-Pyr]$^+$ complexes grew dramatically. Finally, at 190 °C, the [Ag(Pyr)$_2$]$^+$ complex had almost disappeared and the [PAH]$^+$ ion was the overwhelmingly dominant peak. We imagine that collisional breakup of the [Ag(Pyr)$_2$]$^+$ complex is
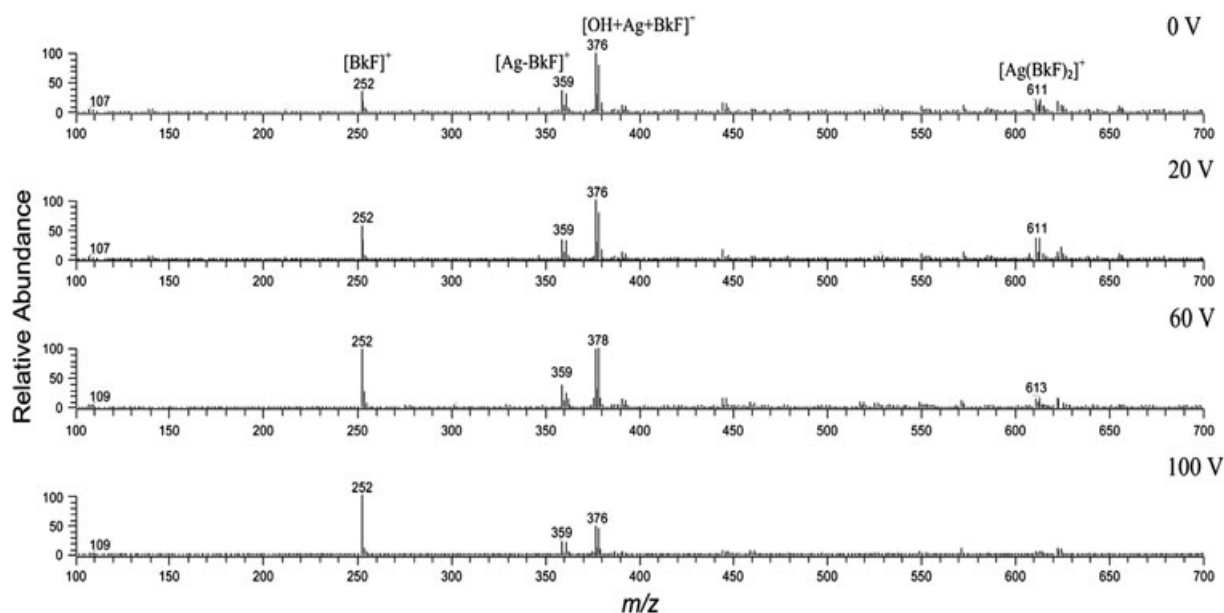
Figure 7. Effects of inlet voltage on benzo[*k*]fluoranthene peak intensities. Inlet temperature = 150 °C, and the applied voltage to the spray solution = 5 kV.

occurring and the efficiency of this process increases with internal excitation of the $[Ag(Pyr)_2]^+$ complex, that is, with increasing temperature. In this scenario, the temperature results are consistent with "σ-type bonding" as the mechanism for $[Ag(PAH)_n]^+$ (n = 1, 2) complexation.

One of the important parameters affecting the peak intensities of the $[PAH]^+$ ion and the $Ag(PAH)_n^+$ (n = 1, 2) complexes was the voltage applied to the inlet capillary of the mass spectrometer. The results for benzo[*k*]fluoranthene are shown in Fig. 7 for 0, 20, 60, and 100 V. Increasing this voltage resulted in an increase in the overall sensitivity of the instrument, as well as an increase in the $[PAH]^+$ peak intensity. This behavior suggests that with increasing inlet voltage, the reduction-oxidation reaction between silver ions and the PAHs becomes more preferable than complexation (because of the relatively high reduction potential of the silver ion). The temperature and voltage of the inlet to the mass spectrometer played a significant role in tuning the method for either high isomeric differentiation at moderate temperature and voltage (150 °C

and 31 V) or high detection efficiency, at higher temperature and voltage (190 °C and 100 V). Furthermore, at higher inlet temperature and voltage, the spectrum became less complicated where mainly $[PAH]^+$ ions appeared.

As previously reported by Cooks and coworkers,[18] PAHs with a bay structure (like phenanthrene) showed a different affinity to make a complex with the silver ion from linear PAHs (like anthracene). The arrangement of the phenyl rings changes the peak intensities for the $[PAH]^+$ ion and its complexes with silver, providing a good tool for differentiating isomers. R_1, R_2, R_3, and R_4 denote the ratios of the peak intensity of $[PAH]^+$ to that of $[Ag–PAH]^+$, $[OH + Ag + PAH]^+$, $[Ag(PAH)_2]^+$, and $[PAH + O_2]^+$, respectively. Table 1 lists the values of R_1, R_2, R_3, and R_4 for isomeric PAHs at an inlet temperature of 150 °C and a capillary inlet voltage of 31 V. The $[OH + Ag + PAH]^+$ peak, which had not previously been reported,[15,18] provided the best ratio to distinguish isomeric mixtures of PAHs. The uncertainties in R_1 and R_3 were in the range of ±10 to ±40%, reflecting an uncertainty in the isomeric

Table 1. Values of ion intensity ratios used to differentiate PAH isomers. R_1 = ratio of intensity of $[PAH]^+$ to $[Ag + PAH]^+$; R_2 = ratio of intensity of $[PAH]^+$ to $[OH + Ag + PAH]^+$; R_3 = ratio of intensity of $[PAH]^+$ to $[Ag(PAH)_2]^+$; and R_4 = ratio of intensity of $[PAH]^+$ to $[PAH + O_2]^+$

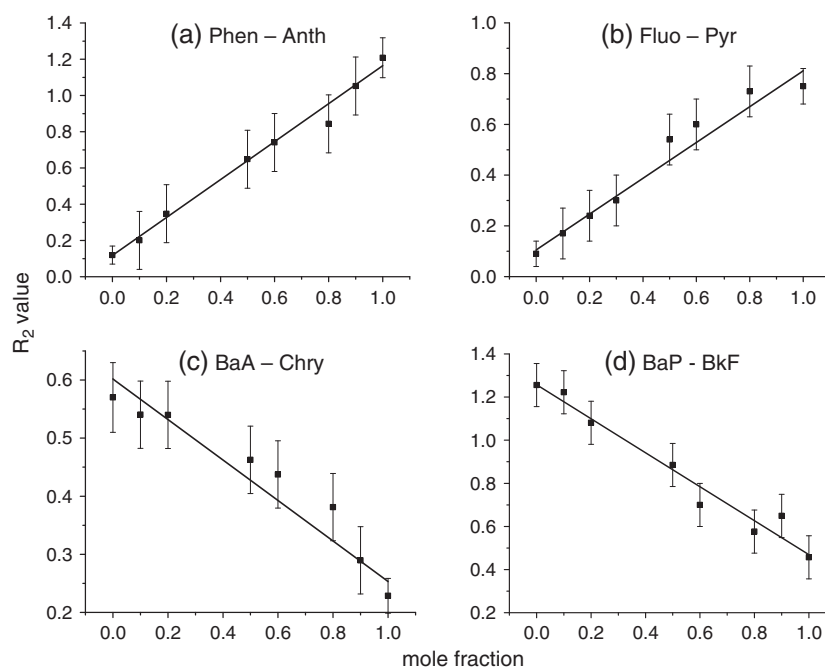|	Ion intensity ratio			
R_4	R_3	R_2	R_1	PAH
-	2.76 ± 0.28	1.21 ± 0.11	1.70 ± 0.16	Anthracene (1)
-	0.47 ± 0.11	0.12 ± 0.01	0.51 ± 0.21	Phenanthrene (1)
-	2.15 ± 0.15	0.75 ± 0.08	0.99 ± 0.05	Pyrene (2)
-	0.30 ± 0.09	0.09 ± 0.02	0.48 ± 0.17	Fluoranthene (2)
-	1.32 ± 0.39	0.23 ± 0.03	0.90 ± 0.13	Chrysene (3)
-	2.28 ± 0.39	0.57 ± 0.06	1.28 ± 0.27	Benz[*a*]anthracene (3)
0.24 ± 0.06	-	-	-	Benz[*b*]anthracene (3)
-	1.91 ± 0.22	1.26 ± 0.15	2.67 ± 0.53	Benzo[*a*]pyrene (4)
-	1.09 ± 0.24	0.46 ± 0.05	1.12 ± 0.14	Benzo[*k*]fluoranthene (4)

Figure 8. Isomeric differentiation of a mixture containing two PAH isomers using silver nitrate reactive DESI. The R_2 value is plotted against the mole fraction for (a) phenanthrene/anthracene, (b) fluoranthene/pyrene, (c) benz[a]-anthracene/chrysene, and (d) benzo[a]pyrene/benzo[k]fluoranthene. The lines drawn in the plots are the best fits. Inlet temperature = 150 °C, inlet voltage = 31 V, and the applied voltage to the spray solution = 5 kV.

differentiation mole fraction of greater than ±0.30. Benz[b]anthracene was the only isomer among those with a molecular mass of 228 that showed a peak at m/z 260 and 259 ($[PAH + O_2]^+$ and ($[PAH + O_2–H]^+$), respectively, which was uniquely expressed by R_4 in Table 1. R_2 was found to have the least uncertainty for isomers in separate solution (within ±10%). It was used successfully to distinguish the isomeric mole fraction of PAHs in an isomeric mixture. Figure 8 shows the linear response of R_2 for different isomeric ratios of (1) phenanthrene and anthracene, (2) fluoranthene and pyrene, (3) benz[a]anthracene and chrysene, and (4) benzo[a]pyrene and benzo[k]fluoranthene. The confidence in computing the mole fraction of an isomeric mixture was within ±0.09, ±0.13, ±0.25, and ±0.1 for Phen-Anth, Fluo-Pyr, BaA-Chry, and BaP-BkF, respectively. The large uncertainty in determining BaA-Chry was caused by the small difference in R_2 between the two isomers.

The peaks corresponding to $[PAH + OH]^+$ and $[PAH + O_2]^+$ are believed to be formed by the oxidation of PAH during DESI. Several studies have been conducted to understand the oxidation of some organic compounds by DESI.[19,20] Cooks and coworkers attributed this oxidation to an electric discharge between the sprayer tip and the mass spectrometer inlet and between the inlet and the glass substrate.[20] Thus, the yield of these oxidation products is expected to be sensitive to the voltage applied and to the separation distances.

The metal ions Fe(III), Co(II), and Ni(II) were also investigated as spraying solutions in methanol. Because of its low ionization energy, benz[b]anthracene was detected using any of the above metal ions with a relatively high intensity. With the exception of Ag(I) the trend of the sensitivity of these metal ions to PAHs agreed relatively well with the standard reduction potentials. The silver ion provided not only much higher sensitivity, but also the capability to differentiate isomers. These results suggest that the formation of the $[PAH]^+$ ion is governed by both the relatively high reduction potential of the silver ion and the ability of the silver ion to form complexes with PAHs.

CONCLUSIONS

We have reported the application of metal ions in methanol as a reactive DESI solution for the detection of PAHs. The silver ion provided the best results in terms of intensity of PAH peaks and the ability to distinguish PAH isomers. The interaction between the silver ion and PAHs results in three main complexes $[Ag(PAH)_n]^+$ (n = 1, 2), and $[OH + Ag + PAH]^+$. The intensity ratio of the $[PAH]^+$ ion to these complexes varied according to the structure of the PAH (mainly the arrangement of the phenyl rings). A moderate mass spectrometer inlet temperature and voltage provided the best conditions for distinguishing between isomers in a mixture of PAHs. If isomeric differentiation is not a concern, high temperature and voltage showed higher sensitivity for the detection of PAHs with mainly the $[PAH]^+$ ion appearing in the mass spectrum.

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