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Electrospray mass spectrometric determination of polycyclic aromatic hydrocarbons by detecting the π - π complexes with tropylium cation

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A method is presented for the determination of polycyclic aromatic hydrocarbons (PAHs) by detecting the PAH-tropylium (π donor- π acceptor) complexes using liquid chromatography-electrospray ionization-mass spectrometry. The complexes were formed by mixing with the tropylium cation after the separation of PAHs through reversed phase liquid chromatography. The detection limits, defined as three times the noise, in the selected-ion monitoring mode were 25–165 ng of the injected PAHs.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants whose carcinogenicity and estrogenicity have been extensively studied.^{1–3} In order to evaluate the risk of PAHs in the environment, various methods for the determination of PAHs have been used. Gas chromatography-mass spectrometry (GC-MS) is an excellent and powerful tool for the identification of PAHs because of its high separation efficiency.⁴ However, PAHs whose molecular mass lies beyond the range (~ 300 u) are difficult to characterize and detect by GC-MS.⁵ In addition, it was found that the partial decomposition of unstable species of PAH, such as nitrated PAHs, occurs in the injector, the column and interface of the GC-MS.⁶ This effect makes the identification and quantification of PAHs difficult. These problems are overcome by using high performance liquid chromatography (HPLC), because it can be carried out at room temperature. Therefore, the methods based on HPLC coupled with a UV detector have been extensively used for the analysis of PAHs in environmental samples.^{7,8}

The LC-MS method would supply more useful information for the analysis of PAHs because of the relatively high specificity of an MS detector in comparison with a UV detector. However, very few examples are known based on the detection of PAHs by LC-MS using several commercially available interfaces, including thermospray,⁹ liquid ionization¹⁰ and atmospheric pressure chemical ionization.⁵ Furthermore, there are few reports about the detection of PAHs using electrospray as the interface due to the difficulty of ionizing low polar compounds.¹¹

In this study, a novel approach to detecting and identifying PAHs by liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) is demonstrated.

The tropylium cation (TR^+) has been known as a strong π -acceptor, and it recognizes PAHs by π - π interactions, and almost quantitatively forms the $[\text{PAH}-\text{TR}^+]$ 1:1 cation complex.¹² On the other hand, ESI is a very powerful method for the characterization and identification of non-covalently bound polar species, because the technique is a very soft ionization method,¹³ and it is well known that ESI achieves the best sensitivity for compounds that are precharged in the solution.¹⁴ Therefore, the $[\text{PAH}-\text{TR}^+]$ complexes are expected to show high responses using ESI-MS.

By utilizing the characteristics of TR^+ and ESI, we determined PAHs by detecting the $[\text{PAH}-\text{TR}^+]$ complexes,

which were formed by mixing with TR^+ after separation of the PAHs through reversed phase liquid chromatography using ESI-MS.

Experimental

Materials

All solvents were of HPLC grade and other chemicals were of analytical-reagent grade. Three PAHs, pyrene, benzo(a)pyrene and coronene, were used as target compounds. Pyrene was obtained from Wako Pure Chemical (Osaka, Japan). Coronene and tropylium tetrafluoroborate were purchased from Tokyo Kasei (Tokyo, Japan) and benzo(a)pyrene was from Nacal tesque (Kyoto, Japan).

HPLC conditions

Liquid chromatography was carried out on an HPLC apparatus equipped with a Model L-7100 chromatograph (Hitachi, Tokyo, Japan) and Thermo Minder SM-05 (Taitec, Tokyo, Japan). A GL Science Inertsil ODS-2 semi-micro column (5 μm particle size, 150×1.0 mm id) was used for the LC separation of the PAHs. The column temperature was 30 °C. Methanol was used as the mobile phase and the flow rate was 0.02 ml min⁻¹. In LC-ESI-MS, post-column addition of 1.0 mM of the tropylium cation acetonitrile solution at 0.1 ml min⁻¹ was carried out using a Shimadzu LP-6A liquid delivery pump. The mobile phase was mixed in a tee (Yokogawa 0100-0782, stainless) with the tropylium cation solution.

ESI-MS

ESI-MS was performed using a Hitachi M-1200AP (Tokyo, Japan) mass spectrometer connected to a Hitachi L-7100 chromatograph. The multiplier and focus voltage were set at 2.5 kV and 120 V, respectively. The desolvator temperature was set at 400 °C. The vaporizer temperature was set at 300 °C. Flow injection analyses (FIA) of the PAHs were carried out in the presence or absence of TR^+ . In the case of FIA, methanol was used as the mobile phase and the flow rate was 0.05 ml min⁻¹. The drift voltage was set at 70 V, unless otherwise noted. For LC-ESI-MS, the drift voltage was fixed at 20 V. The injection volumes of the sample solutions in ESI-MS were 5 μl . When working in the selected ion monitoring mode (SIM), the $[\text{M}]^+$ and $[\text{M} + \text{TR}]^+$ ions were monitored depending on the target analyte.

Fig. 4 LC-ESI-MS chromatograms of pyrene, benzo(a)pyrene and coronene for the injection (5 μ l) of a standard solution of PAHs (0.2, 0.05 and 0.25 mM) by selected-ion monitoring (m/z 293, 343 and 391, respectively).

Table 1 Detection limits and calibration equations for PAHs obtained using LC-ESI-MS

Analyte	Monitor ion (m/z)	Retention time/min	Detection limit ^a		Calibration equation	Correlation coefficient (R^2)
			Concentration/mM	Injection/ng		
Pyrene	293	15.8	0.1	101	$y = 28737x - 138$	0.997
Benzo(a)pyrene	343	18.0	0.02	25	$y = 158800x - 82$	0.992
Coronene	391	34.6	0.2	225	$y = 45173x - 251$	0.990

^a Calculated as three times the baseline noise.

Fig. 5 Calibration graph for pyrene in the range 0.1–0.5 mM.

ble by the complexation with TR^+ , a strong π -acceptor and ionic group.

The detection of PAHs by monitoring host–guest complexes is a new application of ESI, and this method would contribute to

the analysis of low volatile or thermally unstable species of PAHs that are difficult to detect by GC-MS.

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