Application Note

Advion

LC-MS DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN WATER(EPA 610 MIX)

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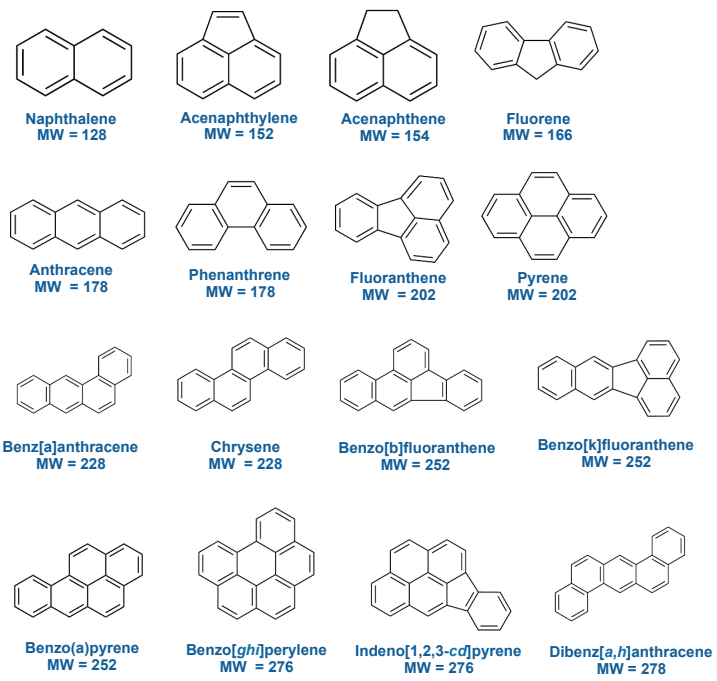
INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are neutral compounds containing multiple aromatic fused rings that are present in fossil fuels and can be formed from the incomplete combustion of organic material. In recent years, it has been well documented that several PAHs can be potentially carcinogenic via exposure or ingestion. The EPA has classified seven PAHs (benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) as Group B2, probable human carcinogens.[1,2]

Cooking meats or other foods at high temperatures over an open flame has also been found to increase the formation of PAHs[3]. In addition, PAHs have been found to be present in some drinking water supplies[3]. Environmentally, PAHs have been listed as a pollutant of concern to EPA's Great Water Program due to their persistence in the environment, their potential to bioaccumulate, and their toxicity to humans and the ecosystem[4].

This application note will demonstrate the LC/MS determination of 16 PAHs (EPA 610 Mix) in the EPA priority target list using the Advion expression Compact Mass Spectrometer (CMS) coupled to an Agilent 1220 Liquid Chromatography (LC) system. The detection limits for the16 PAHs in a water matrix were achieved at the low ppb level.



EXPERIMENTAL SETUP FOR ADVION LC/CMS ANALYSIS

LC conditions:

Solvent A: Water
Solvent B: Acetonitrile
Flowrate: 200 uL/min
Column: Agilent Eclipse PAH 100 x 2.1 mm, 3.5um particles

MS Conditions:

Ion Source: Positive APCI
Capillary Temperature (°C): 100
Capillary Voltage (V): 180
Source voltage offset (V): 20
Source voltage span (V): 0
Gas Temperature (°C): 400
Corona Discharge (uA): 5

Gradient:

Time (min)	%B
0.0	60
3.5	100
15	100
15.5	60
20	60

SUMMARY

The Advion expression CMS coupled to liquid chromatography can be an effective tool for the determination of PAH's in water matrices.

The detection limits of PAHs in water were demonstrated to be in the low ppb levels.

The ease-of-use, affordability and capability of the Advion expression CMS makes it a viable option for PAH analysis.

FIGURES

1. Examples of LC-MS Determination of PAHs

The nonpolar, PAH compounds normally are not ionized in electrospray ion source. Under APCI source conditions with heated nitrogen nebulization gas all 16 PAHs (MW from 128 to 278) were detected as radical cations, $M^{\bullet+}$ via initiated by the corona discharge.[5] In these LC-MS experiments, protonated molecule $[M+H]^+$ ions were not observed, which suggests the protonation process in APCI is not dominant under these conditions.

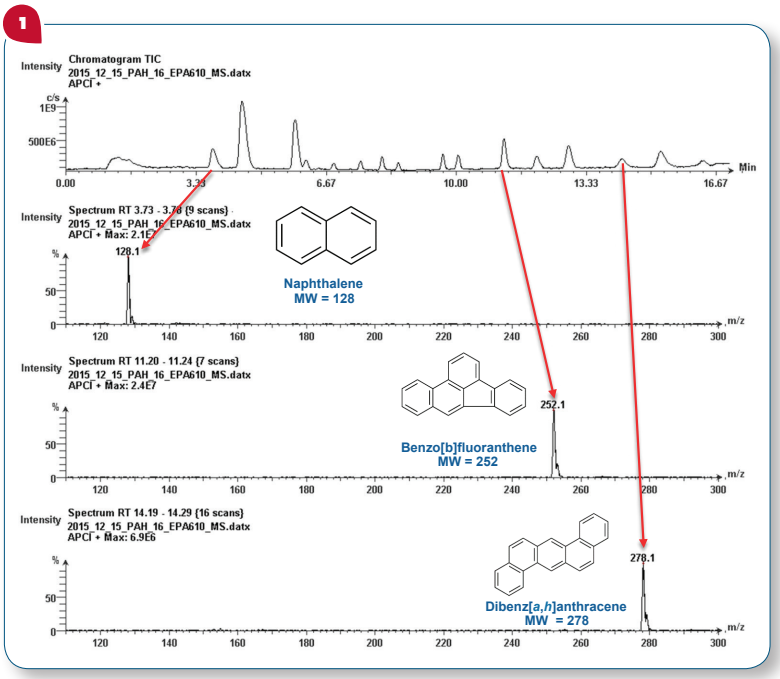
The mass spectra for three of the PAH's are shown in Figure 1: Naphthalene at m/z 128; Benzo[b]fluoranthene at m/z 252; and Dibenz[a,h]anthracene at m/z 278 are easily detected.

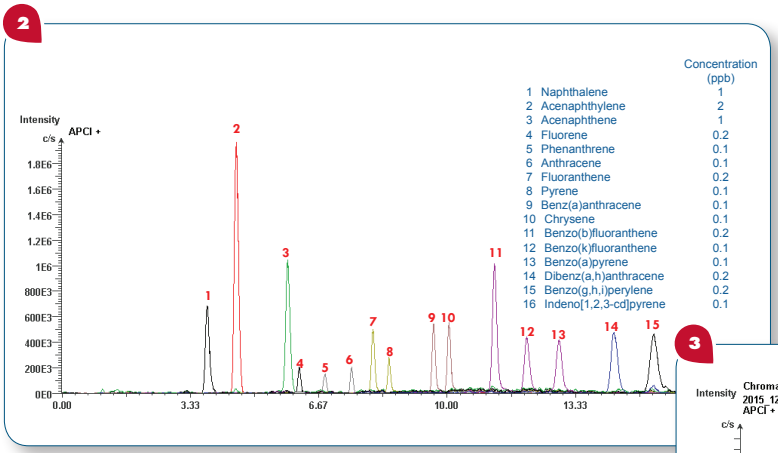
2. LC/SIM analysis of 16 PAHs spiked into tap water

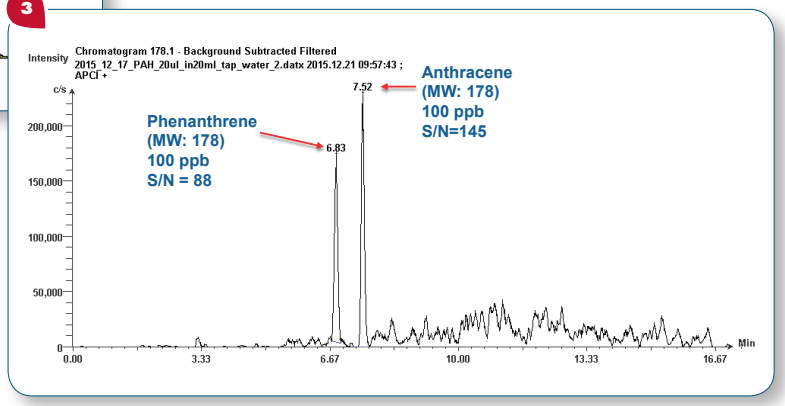
All16 PAHs were well separated and differentiated as shown in Figure 2. EPA 610 mix from Sigma was diluted by a factor of 1000 in tap water and used as a fortified sample for the analysis. The LC/SIM chromatograms of the fortified PAH sample is shown in Figure 2, with the concentration listed for each compound from low ppb to high ppt level.

3. Example of PAH detection limits at pg/uL levels

The two isobaric PAHs, phenanthrene and anthracene with m/z 178.1 were well separated with retention times of 6.83 min and 7.52 min, respectively. At 100 ppb, phenanthrene had a S/N of 88 and anthracene a S/N of 145. Therefore, the detection limits of these compounds can be demonstrated to be in the low pg/µL level in the water matrix. Note: Phenanthrene and anthracene were used in the figure below as they do not respond as well as the other PAH's under these ionization conditions. From this, it can be concluded that the detection limits of most PAHs in water using the Advion expression CMS would be in the low ppb regime.







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