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Rapid Screening and confirmation analysis of polycyclic aromatic hydrocarbons (PAHs) with DART mass spectrometry

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Yu Takabayashi[1], Jun Watanabe[2], Motoshi Sakakura[3], Teruhisa Shiota[3]
1 SHIMADZU TECHNO-RESEARCH, INC., Tokyo, Japan;
2 Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan;
3 AMR Inc., Meguro-ku, Tokyo, Japan

AMR INCORPORATED

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Introduction

Recently, the regulation of the content of the polycyclic aromatic hydrocarbons (PAHs) in goods which may put into a mouth or may contact is advanced and the technologies of measuring PAHs quickly are being developed.
The ionizing principle of DART (Direct Analysis in Real Time) using the excitation helium gas is able to widely ionize the wide-range compounds and it may also be able to ionize the compounds which are not ionized by ESI. Since PAHs is ionizable by DART, PAHs can be quickly screened by holding up a sample directly to DART. In this research, the technique detected by DART-MS was developed coupling with LC and DART analysis after carrying out LC separation was performed.

Methods and Materials

Commercial PAHs were used for the sample. The samples were applied to DART MS with the solution formed in suitable concentration or the powder formed. Small amount of the samples were picked up and held in the DART ionization gas stream using glass capillaries. In LC-DART MS analysis, the mixed-solution of PAHs standard was prepared and applied to HPLC. After carrying out chromatogram separation using a reverse phased column, LC-DART MS analysis was conducted by loading an eluate to a DART ionization area continuously.
DART OS ion source and single/triple quadrupole type mass spectrometer were used for this experiment. PAHs measured in the detection mode which performs a full scan mode with positive and negative simultaneous ionization.

MS condition (LCMS-2020; Shimadzu Corporation)

Ionization	: DART (Direct Analysis in Real Time)
Heater Temperature (DART)	: 300°C to 500°C
Measuring mode (MS)	: Positive/Negative scanning simultaneously

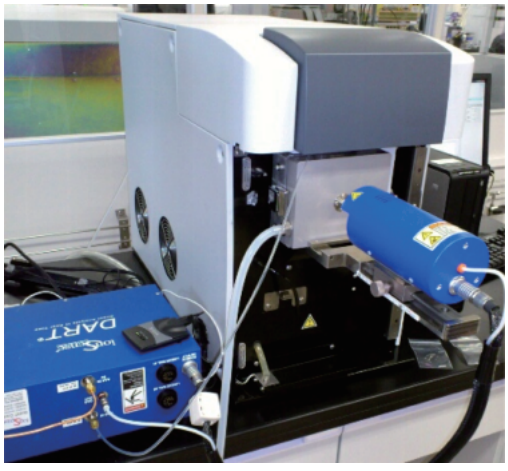

Figure 1 DART-OS ion source & LCMS-2020

High Speed Mass Spectrometer

Ufswitching
High-Speed Polarity Switching 15msec
Ufscanning
High-Speed Scanning 15,000u/sec

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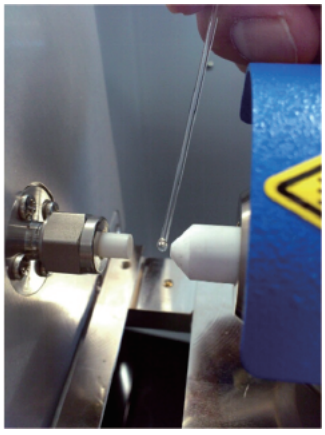
Result

First, in order to verify whether PAHs ionizes in DART, PAH standard reagents were analyzed in DART-MS. Benzo[a]anthracene, acenaphthene, anthracene, etc. were used as typical PAHs. When benzo[a]anthracene was analyzed, in the positive spectrum, the signal at m/z 229 which is equivalent to [M+H]+ was detected. Moreover, in the negative spectrum, the signal at m/z 243 which is equivalent to [M+O-H]- was detected. Similarly, acenaphthene and anthracene could also be ionized by DART-MS and were able to be assigned as molecular related ion. Additionally pyrene and fluoranthene were also examined. As each of these is structural isomers mutually in structural-formula C16H10, in the negative spectrum, the signal of [M+O-H]- is detected by m/z 217 in each other, and either was not able to identify whether the detected signal is pyrene or fluoranthene in analysis by DART-MS without chromatogram separation.



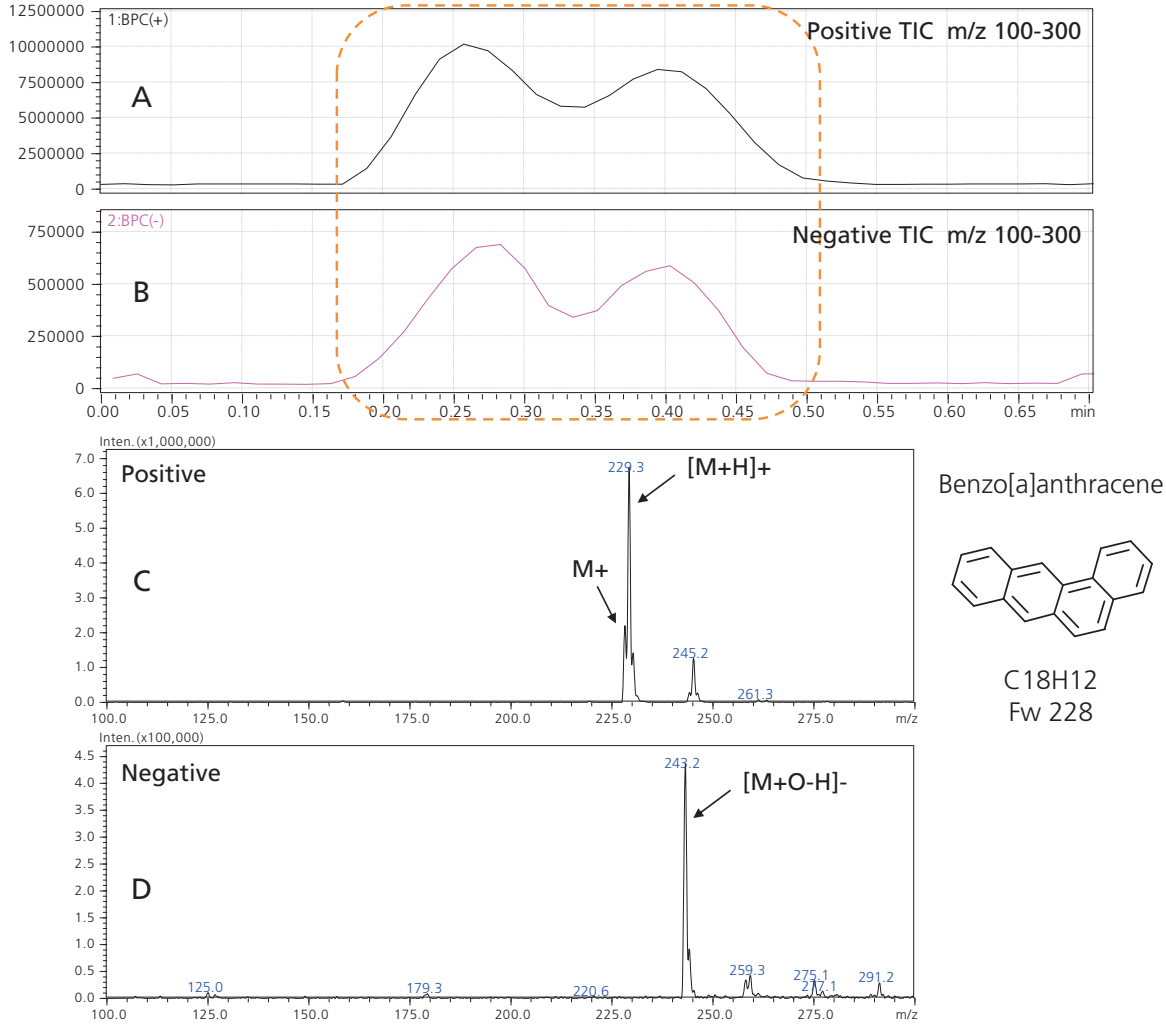


Figure 2 DART mass chromatogram and mass spectrum of Benzo[a]anthracene
A: positive mass chromatogram, B: negative mass chromatogram (The area with the orange dashed line is the time when sample was held in DART.)
C: positive mass spectrum, D: negative mass spectrum

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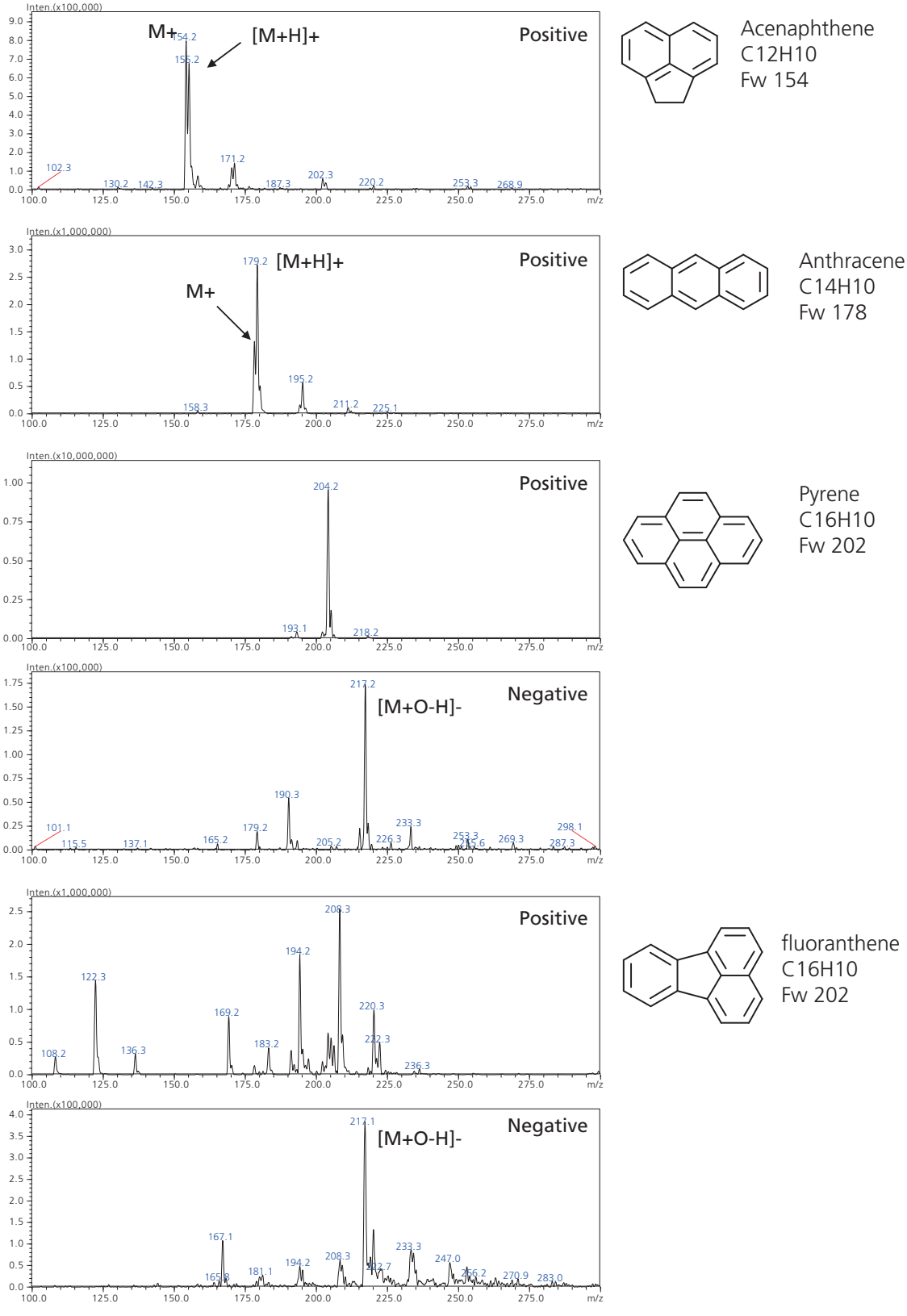

Figure 3 DART mass spectra of acenaphthene (positive), anthracene (positive), pyrene (positive/negative) and fluoranthene (positive/negative)

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Then, it examined the sample applied to DART separating with LC in order to perform chromatogram separation. As the suitable flow rate for DART ionization was thought to be approximately 10uL/min, the splitter located between column and DART ionization stage. Furthermore, the closed interface was adopted for sensitivity improvement.

Analytical Condition

Column	: Unison UK-C8 (2.0mmI.D. x 100mm, 3um, Imtakt Corporation, Kyoto, Japan)
Mobile phase	: 1mM Ammonium formate / Acetonitrile=75/25
Flow rate	: 0.2mL/min (to DART: 0.01mL/min)
DART heater temperature	: 500°C
Ionization	: Positive/Negative SIM mode

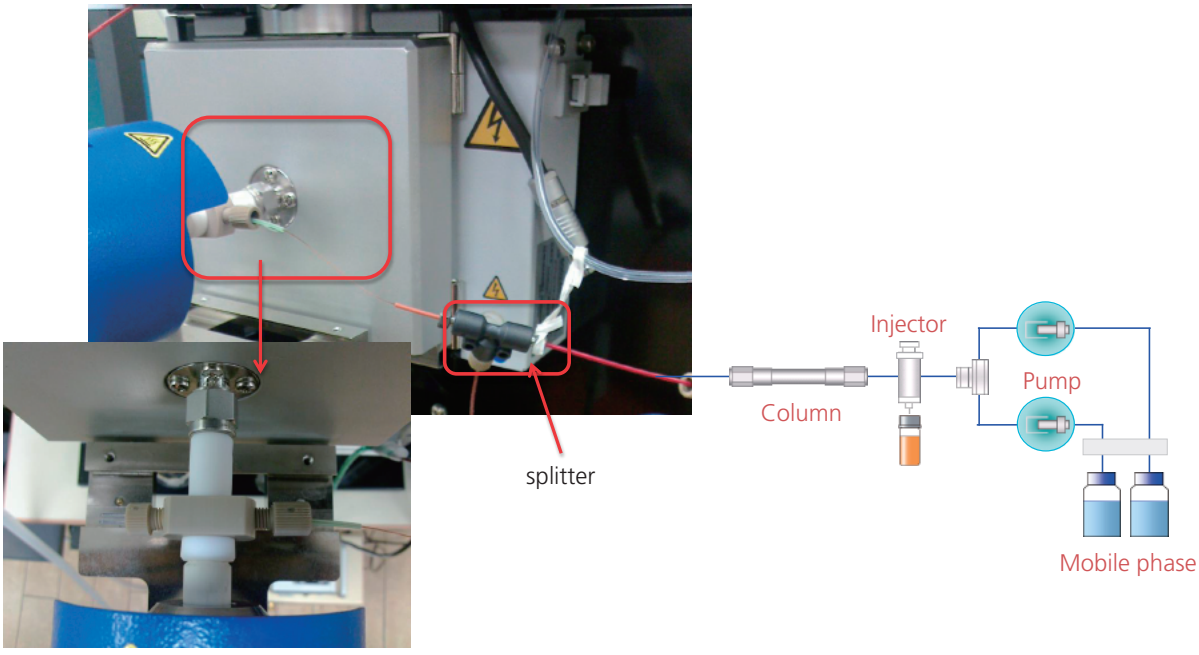

Figure 4 DART devices integrated with HPLC (AMR Inc.)

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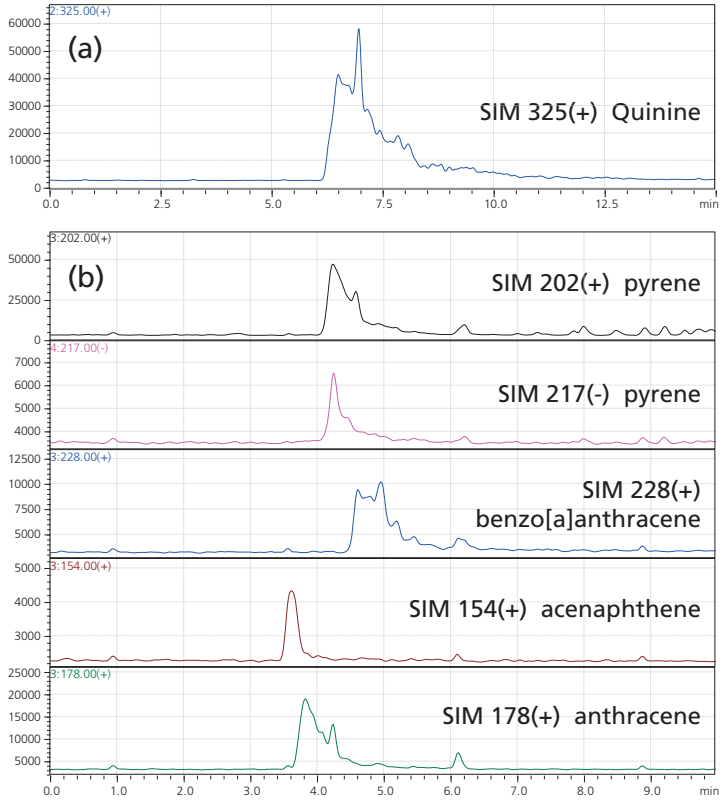

Figure 4 LC-DART mass chromatogram
(a) Typical compound for DART; Quinine
(b) PAH mixture (4 compounds)

As a result, by measurement of each PAHs standard reagent, each retention time was able to be confirmed and also each PAH was able to be detected in each retention time in the measurement using a PAH mixed sample. The conclusion of this examination was understood that DART MS is effective in quick screening, and also LC-DART MS is effective in the confirmation analysis of detected PAHs in analysis of PAHs.

Conclusions

DART mass spectrometer coupled with HPLC was valuable for confirmation analysis of polycyclic aromatic hydrocarbons (PAHs)

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