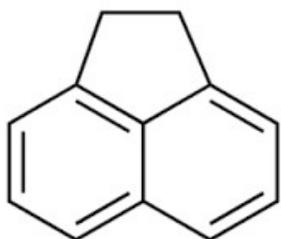


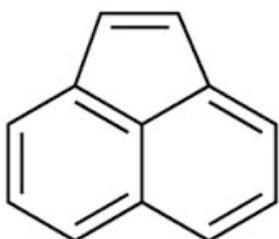
Using NIST Standard Reference Materials to Validate a Method for the Detailed Analysis of Polycyclic Aromatic Hydrocarbons in Environmental Matrices on a New GC Column Phase

Christopher Rattray, Jack Cochran

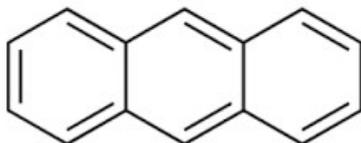
EPA 16 PAH



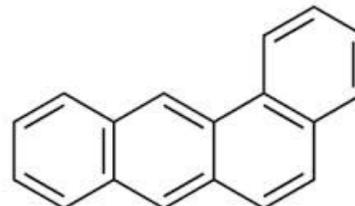
Acenaphthene



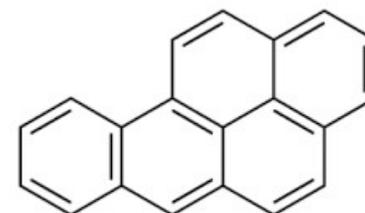
Acenaphthylene



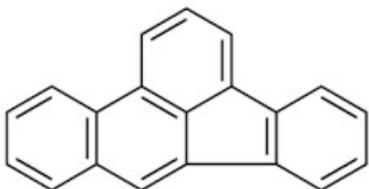
Anthracene



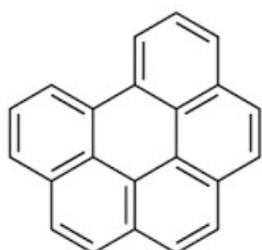
Benz[a]anthracene



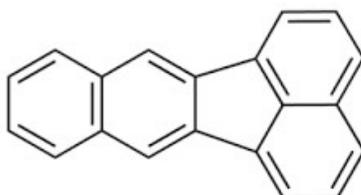
Benzo[a]pyrene



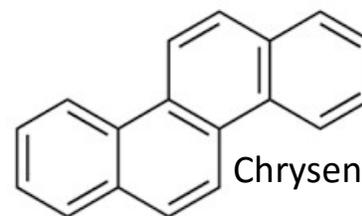
Benzo[b]fluoranthene



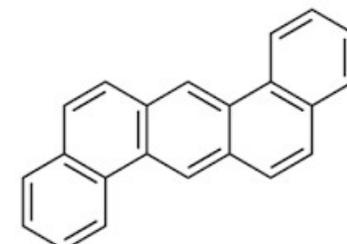
Benzo[ghi]perylene



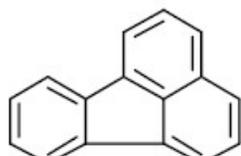
Benzo[k]fluoranthene



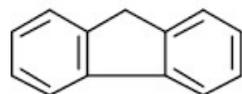
Chrysene



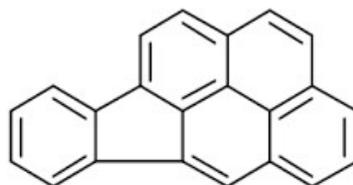
Dibenz[a,h]anthracene



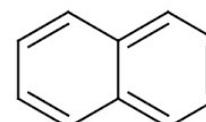
Fluoranthene



Fluorene



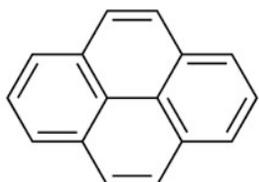
Indeno[1,2,3-cd]pyrene



Naphthalene



Phenanthrene



Pyrene

“Although the HPLC conditions described allow for a unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.”

[EPA Method 610](#)

6.2.6 - The extent of interferences that may be encountered using GC/MS techniques has not been fully assessed. **Although GC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.**

[Method TO-13A](#)

11.6.1.4 - Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different gas chromatographic retention times. **Sufficient gas chromatographic resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.** Otherwise, structural isomers are identified as isomeric pairs. The **resolution should be verified on the mid-point concentration** of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

[Method 8270D](#)



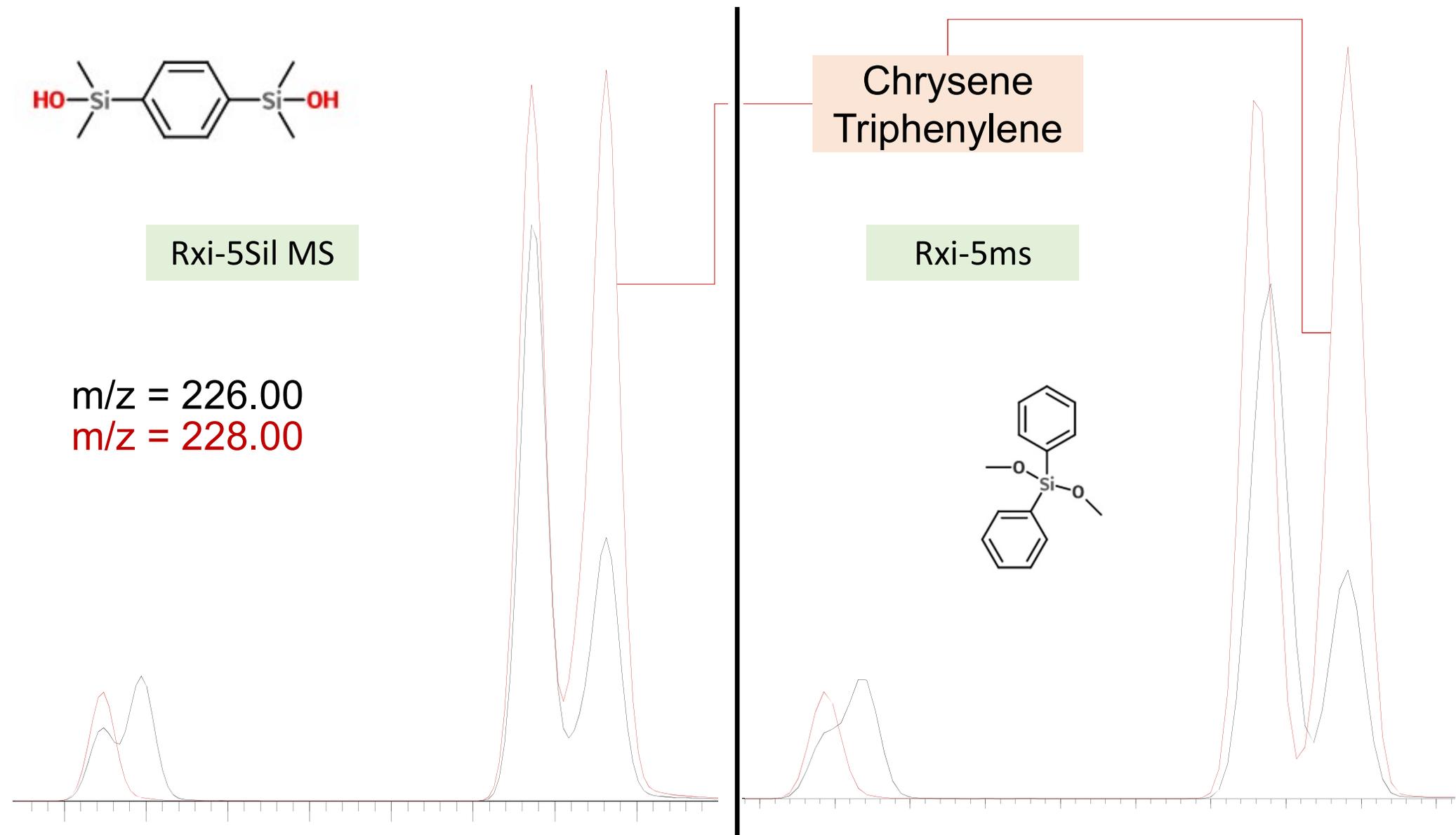
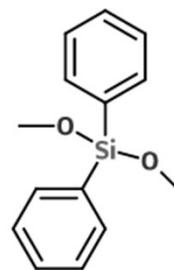
Rxi-5Sil MS

m/z = 226.00

m/z = 228.00

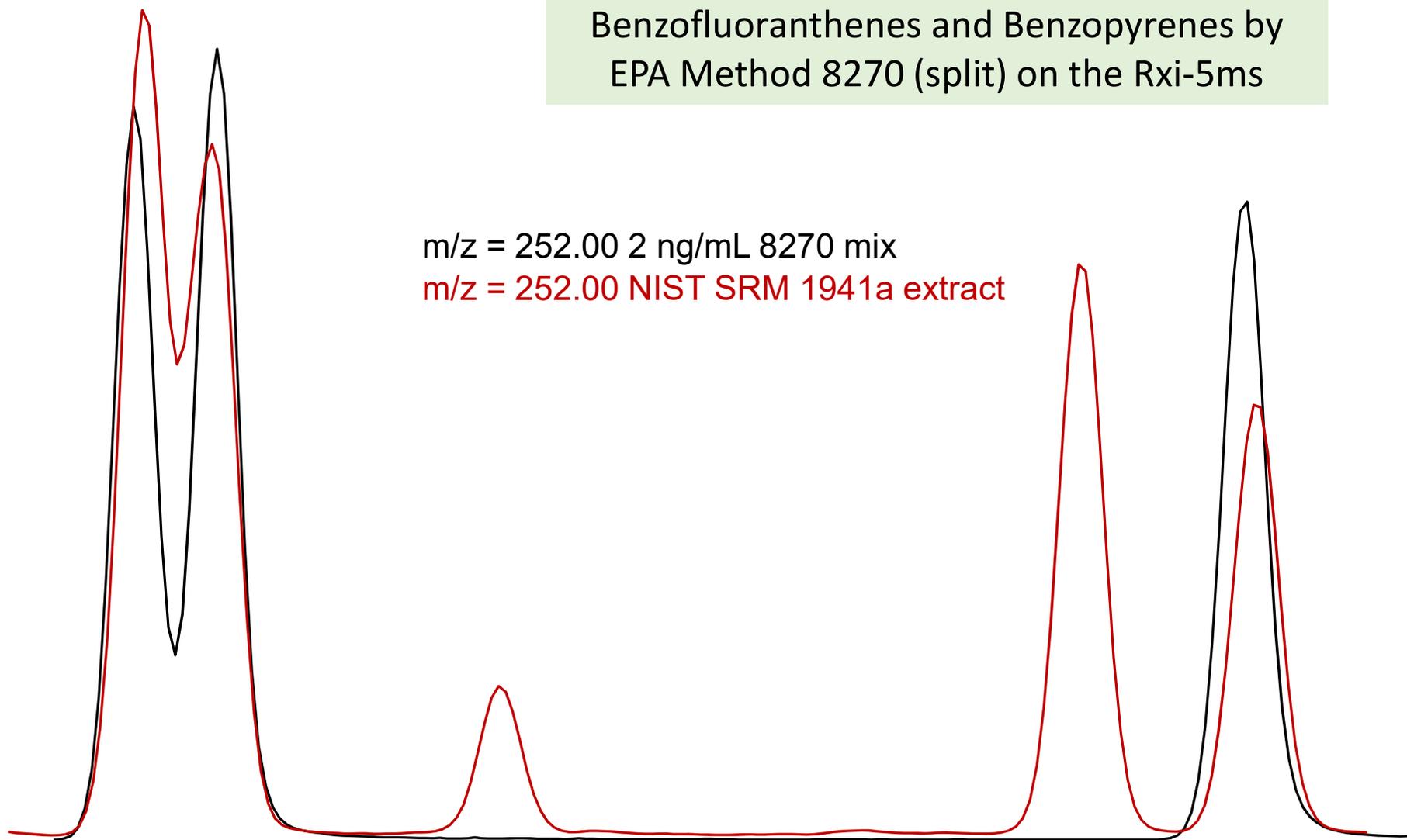
Chrysene
Triphenylene

Rxi-5ms



Benzofluoranthenes and Benzopyrenes by
EPA Method 8270 (split) on the Rxi-5ms

m/z = 252.00 2 ng/mL 8270 mix
m/z = 252.00 NIST SRM 1941a extract



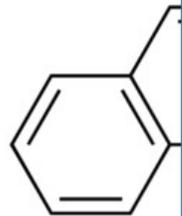
5.2 Interferences with GC-MS

Substances that co-elute with the target PAH may interfere with the determination. These interferences may lead to incompletely resolved signals and may, depending on their magnitude, affect accuracy and precision of the analytical results. Non-symmetrical peaks and peaks broader than the corresponding peaks of the reference substance suggest interferences.

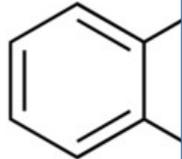
Chromatographic separation between dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene is most critical. Due to their molecular mass differences, quantification can be made by mass selective detection. When incomplete resolution is encountered, peak integration shall be checked and, when necessary, the baseline corrected. Sufficient resolution (e.g. not less than $R = 0,8$) between the peaks of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene as well as of benzo[*a*]pyrene and benzo[*e*]pyrene is to be set as quality criterion for the capillary column. Benzo[*j*]fluoranthene cannot be separated from benzo[*k*]fluoranthene and benzo[*b*]fluoranthene. It is possible that triphenylene is not completely separated from benzo[*a*]anthracene and chrysene. If this is the case, state this fact in the test report.

NOTE Benzo[*j*]fluoranthene, benzo[*e*]pyrene, and triphenylene are not part of the 16 target analytes.

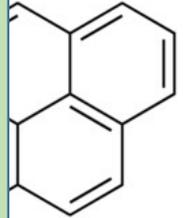
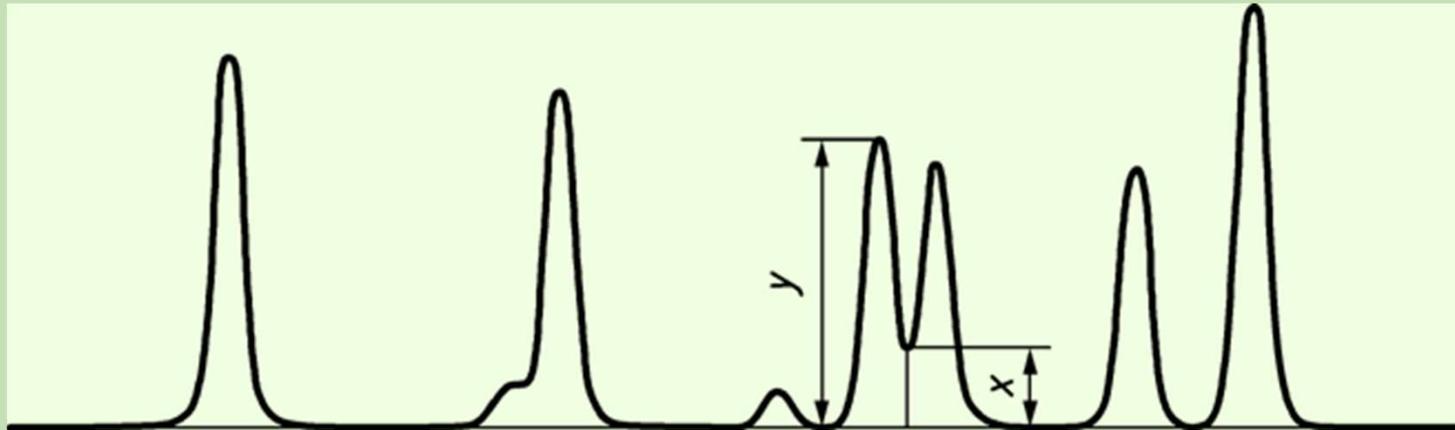
Additional PAH "Critical Peak Couples"



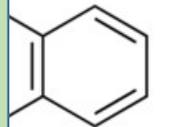
Phena



Anth



pyrene



pyrene

Per NF ISO 28540, PAHs are considered resolved when the peak valley height relative to the highest peak ($X/Y * 100\%$) is less than 25%

Chrysene



National Institute of Standards & Technology

Certificate of Analysis

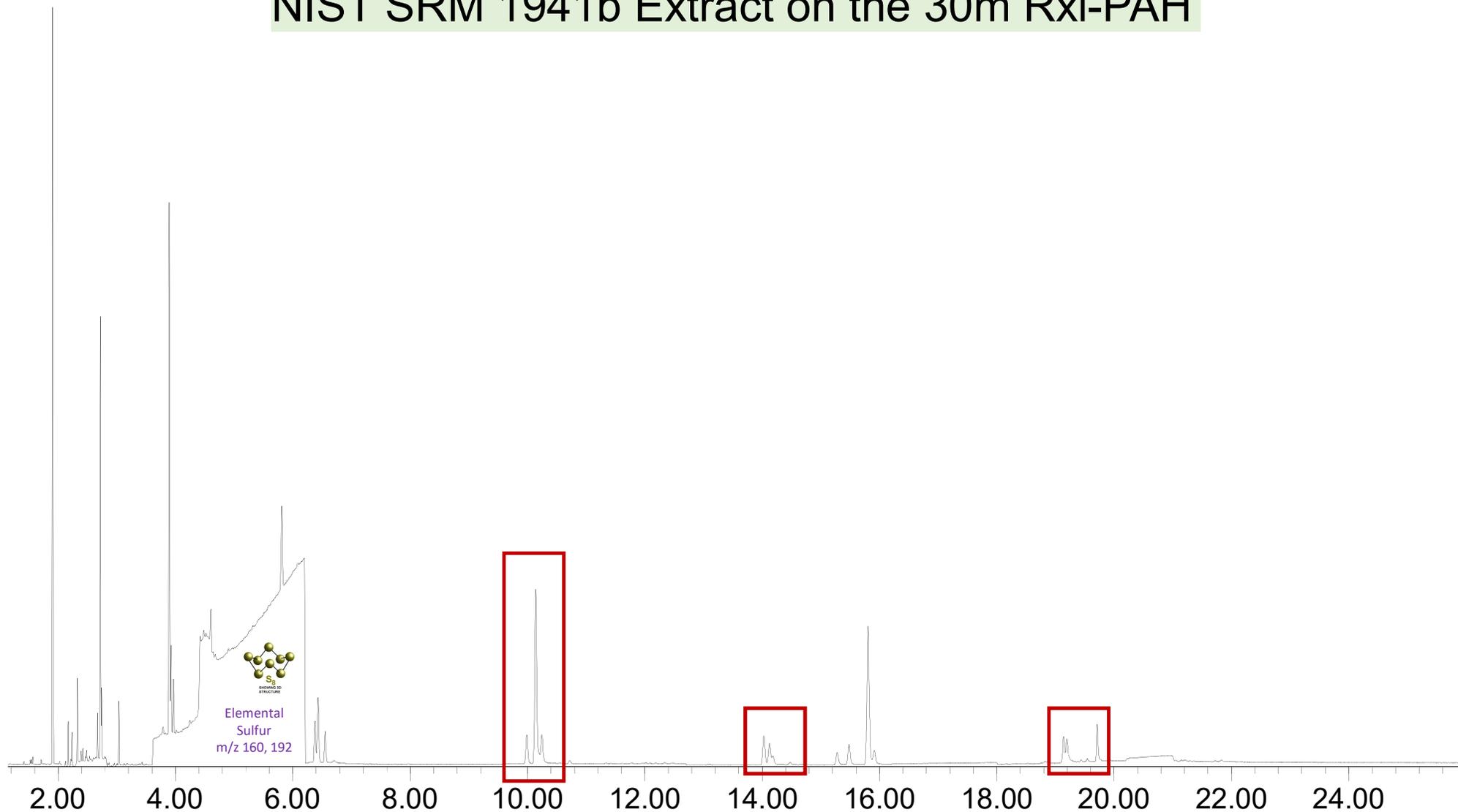
Standard Reference Material[®] 1941b

Organics in Marine Sediment

This Standard Reference Material (SRM) is marine sediment collected at the mouth of the Baltimore (MD) Harbor. SRM 1941b is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in marine sediment and similar matrices. Information values are also provided for total organic carbon (TOC), total carbon, hydrogen, and nitrogen. All of the constituents for which certified, reference, and information values are provided in SRM 1941b were naturally present in the sediment before processing. A unit of SRM 1941b consists of a bottle containing 50 g of radiation-sterilized, freeze-dried sediment.

Certified Mass Fraction Values: Certified mass fraction values for PAHs, PCB congeners, and chlorinated pesticides are provided in Table 1 through Table 3. The certified values for the PAHs, PCB congeners, and chlorinated pesticides are based on the agreement of results obtained at NIST from two or more chemically independent analytical techniques along with results from an interlaboratory comparison study [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1].

NIST SRM 1941b Extract on the 30m Rxi-PAH

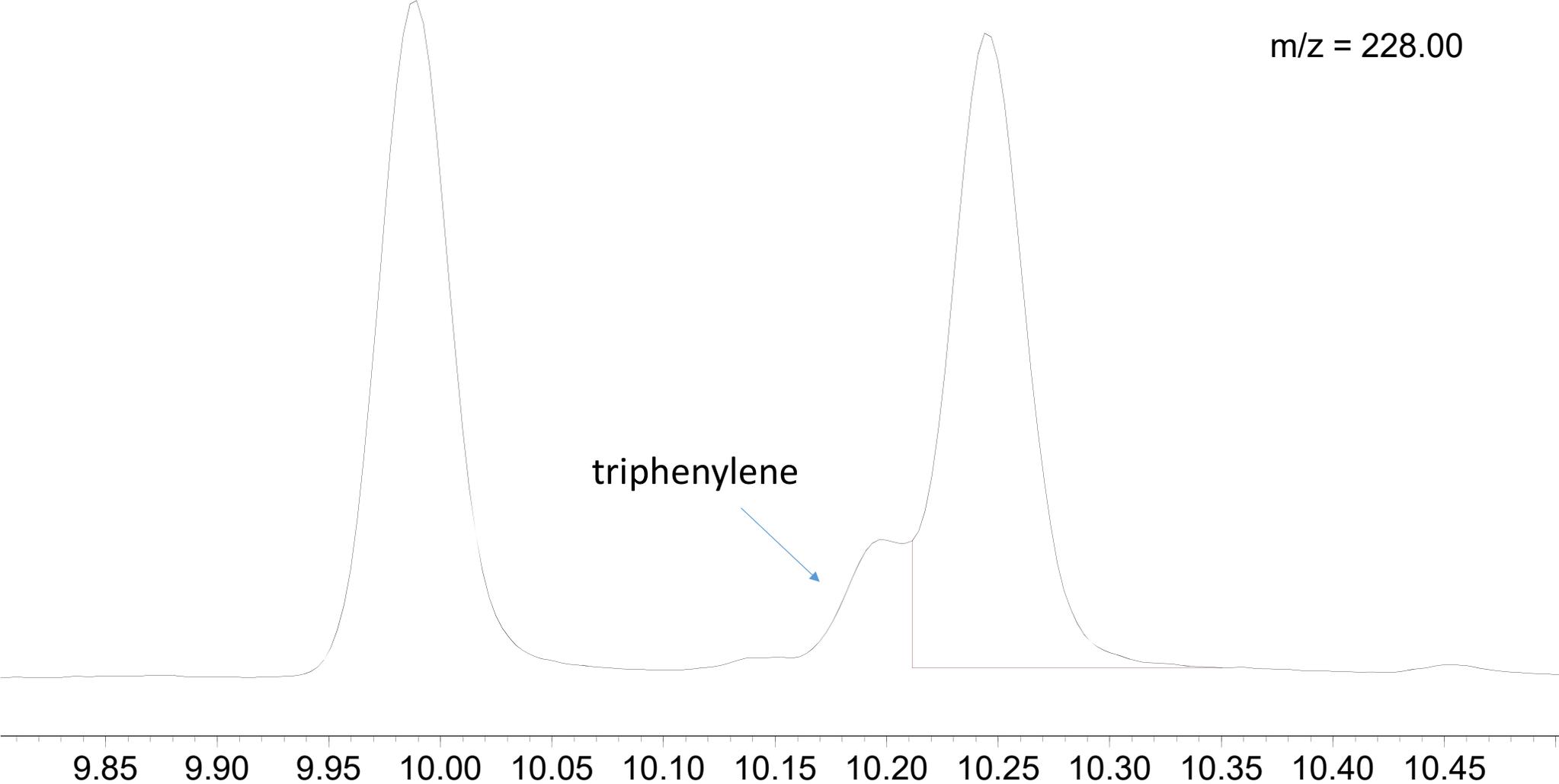


Benz[a]anthracene

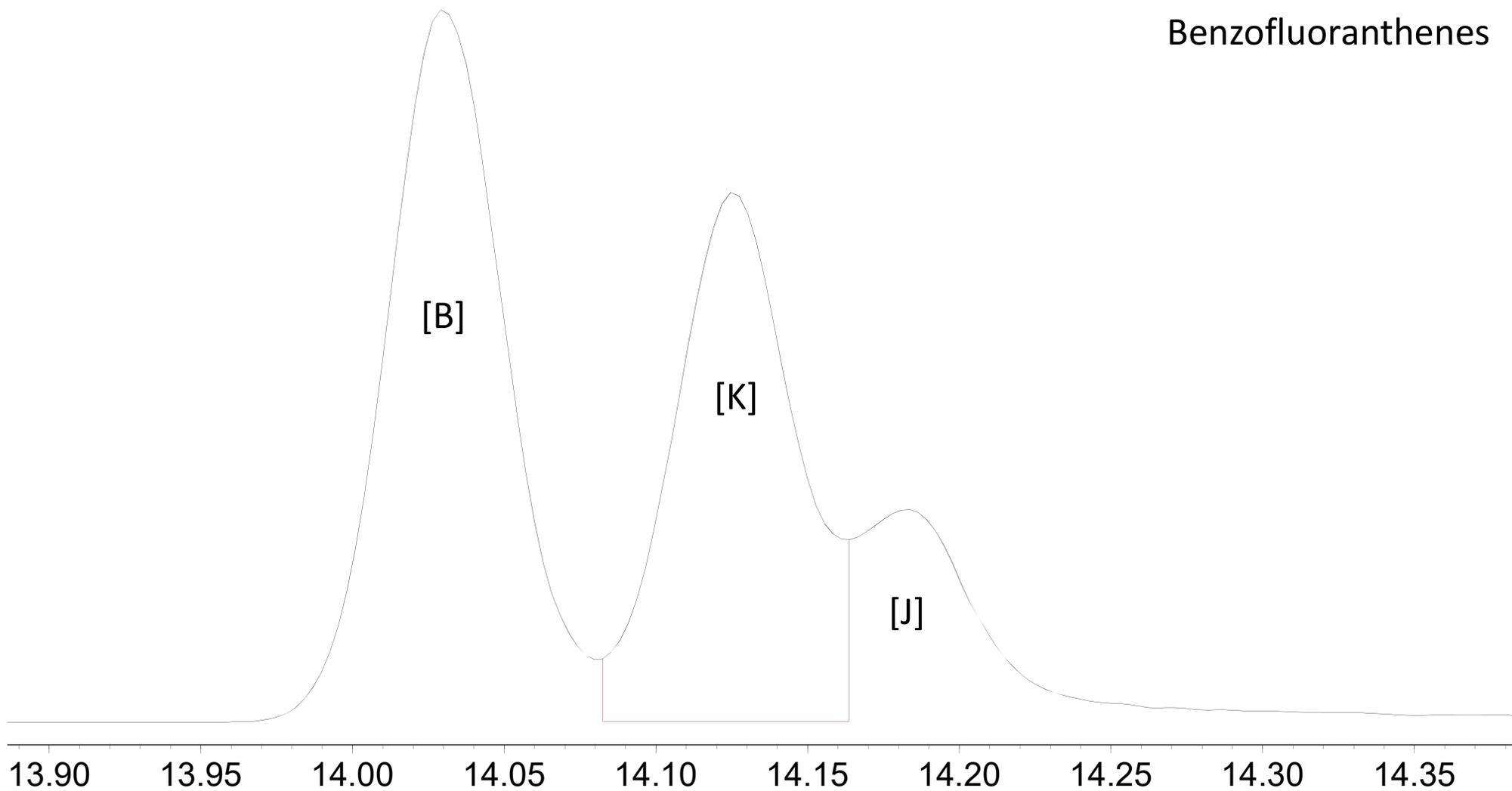
Chrysene

m/z = 228.00

triphenylene

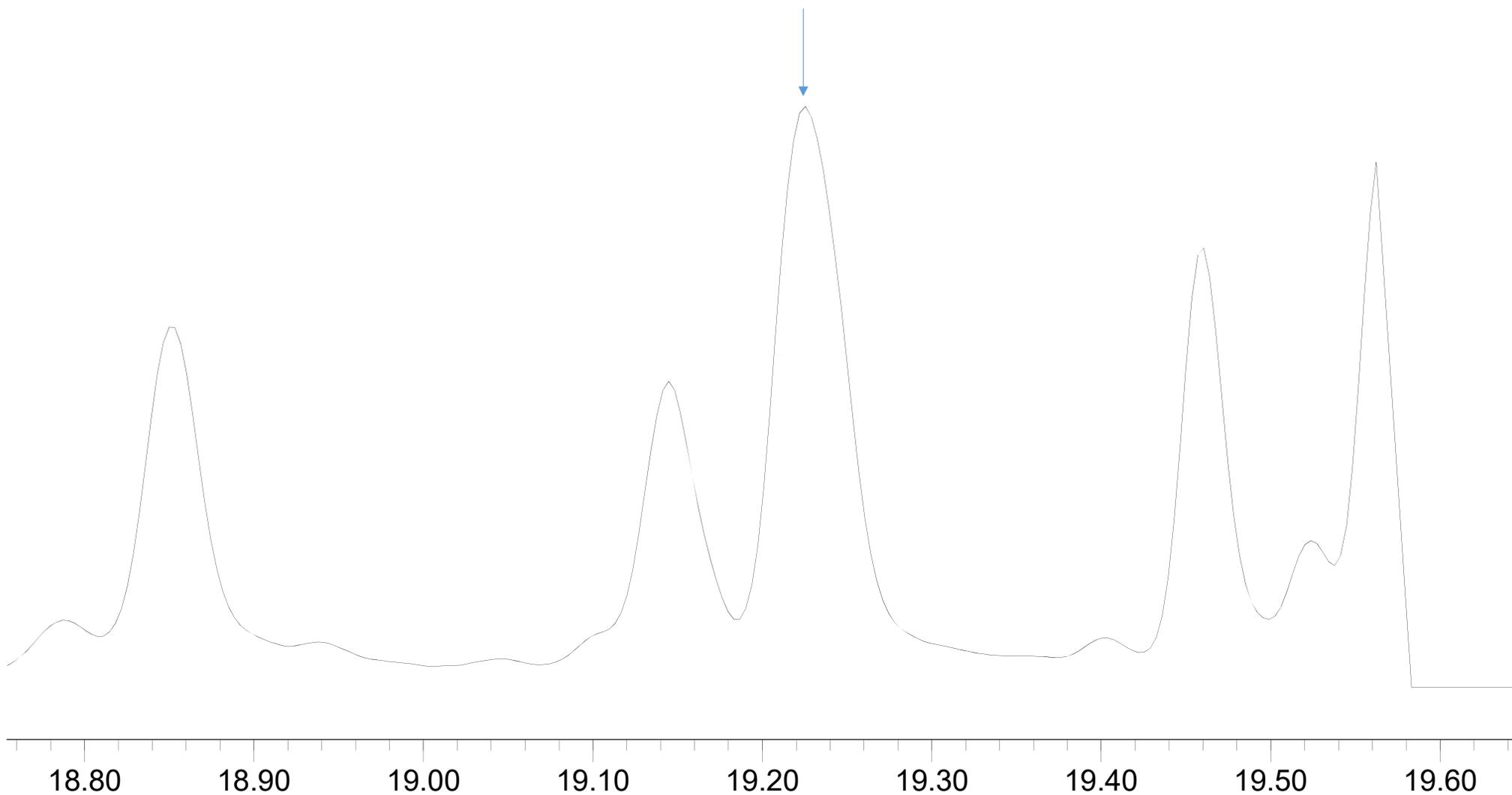


m/z = 252.00
Benzofluoranthenes



Dibenz[ah]anthracene – suspected coelution

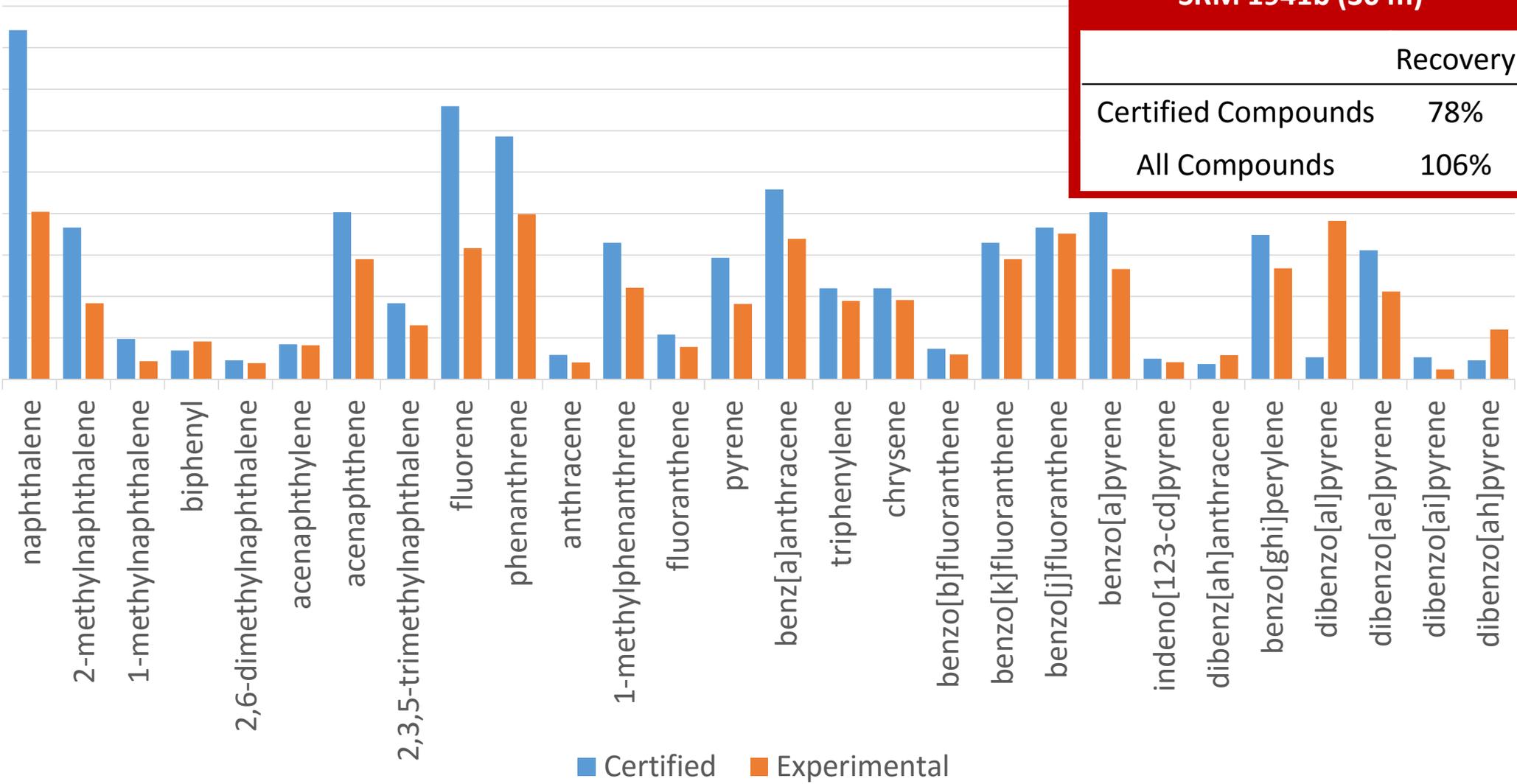
m/z = 278.00



NIST SRM 1941B

Method Performance Summary
SRM 1941b (30 m)

Recovery	
Certified Compounds	78%
All Compounds	106%



GC_EV1394 Detailed PAHs on 60m Rxi-PAH

60 m x 0.25 mm ID X 0.10 μ m Rxi-PAH
1 μ L injection split 10:1
1.95 mL/min He

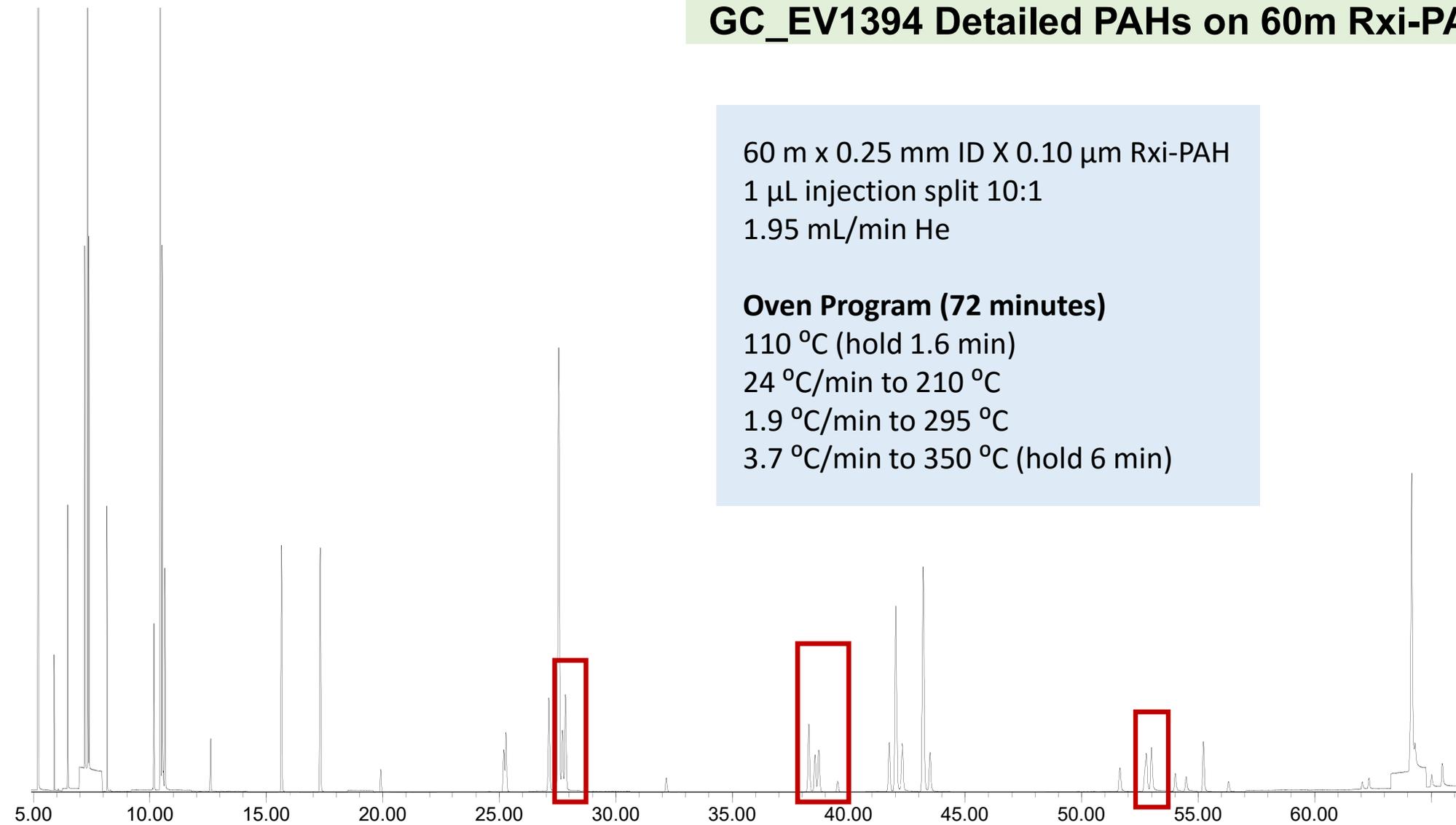
Oven Program (72 minutes)

110 $^{\circ}$ C (hold 1.6 min)

24 $^{\circ}$ C/min to 210 $^{\circ}$ C

1.9 $^{\circ}$ C/min to 295 $^{\circ}$ C

3.7 $^{\circ}$ C/min to 350 $^{\circ}$ C (hold 6 min)



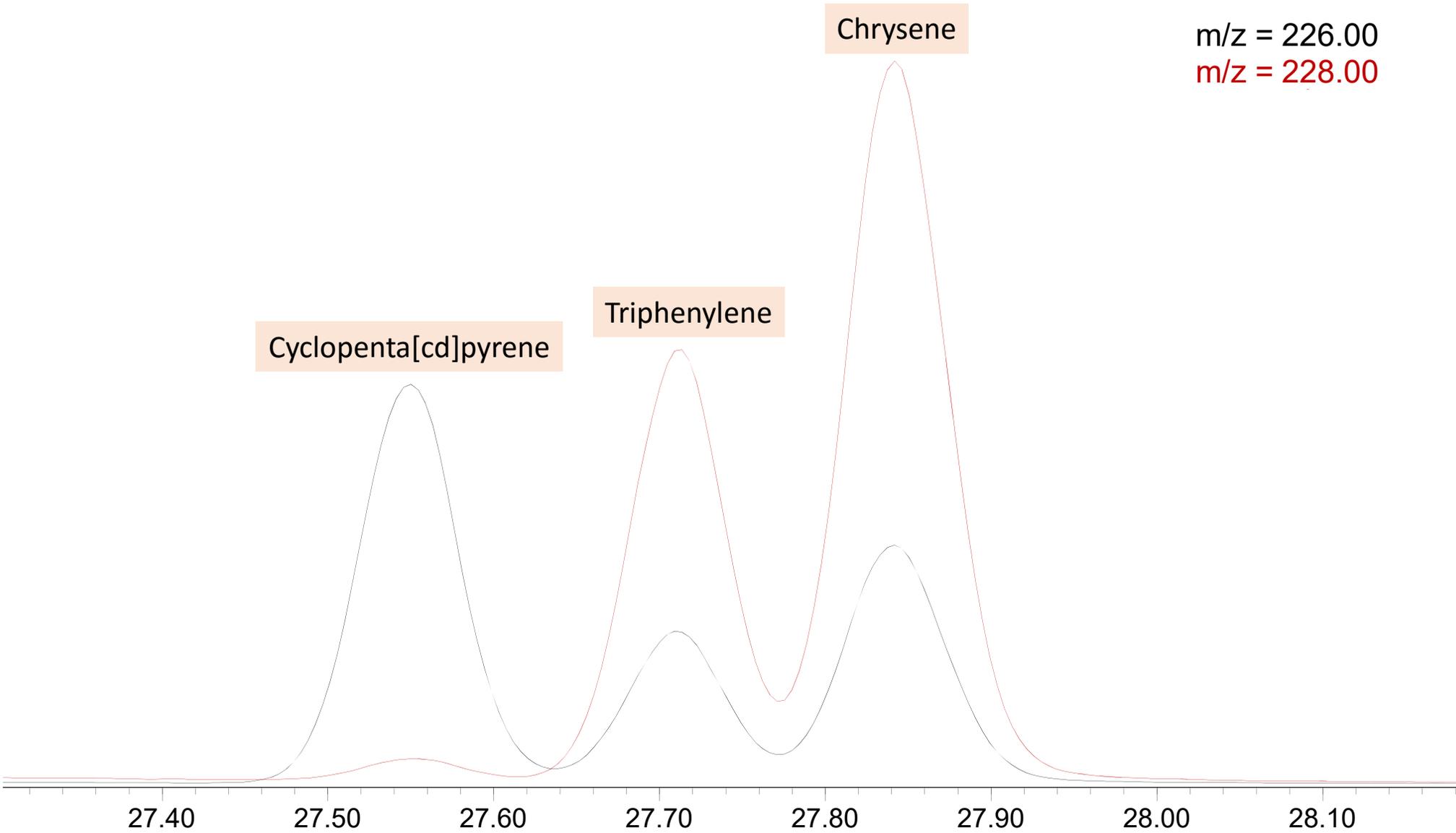
Cyclopenta[cd]pyrene

Triphenylene

Chrysene

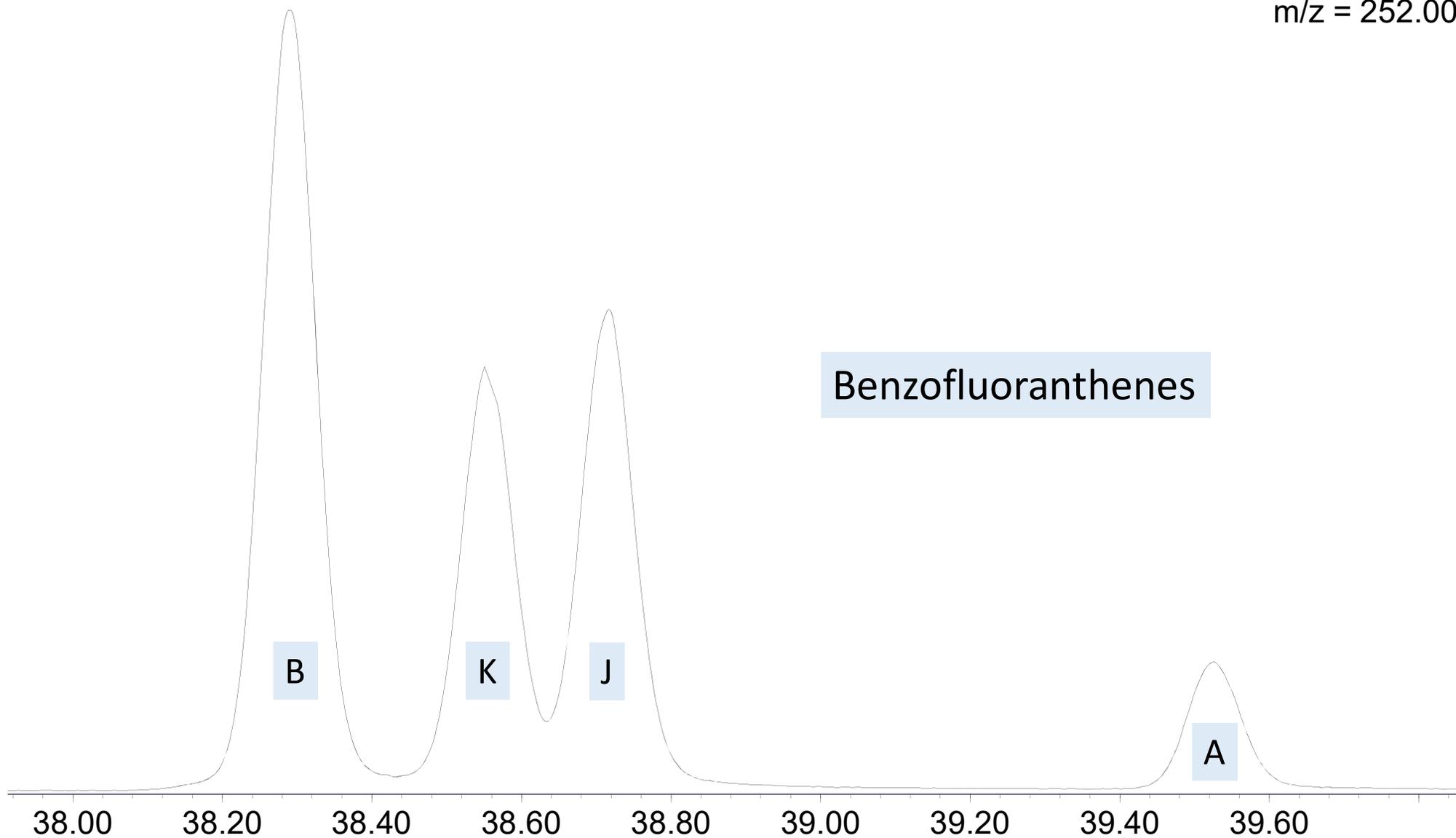
m/z = 226.00

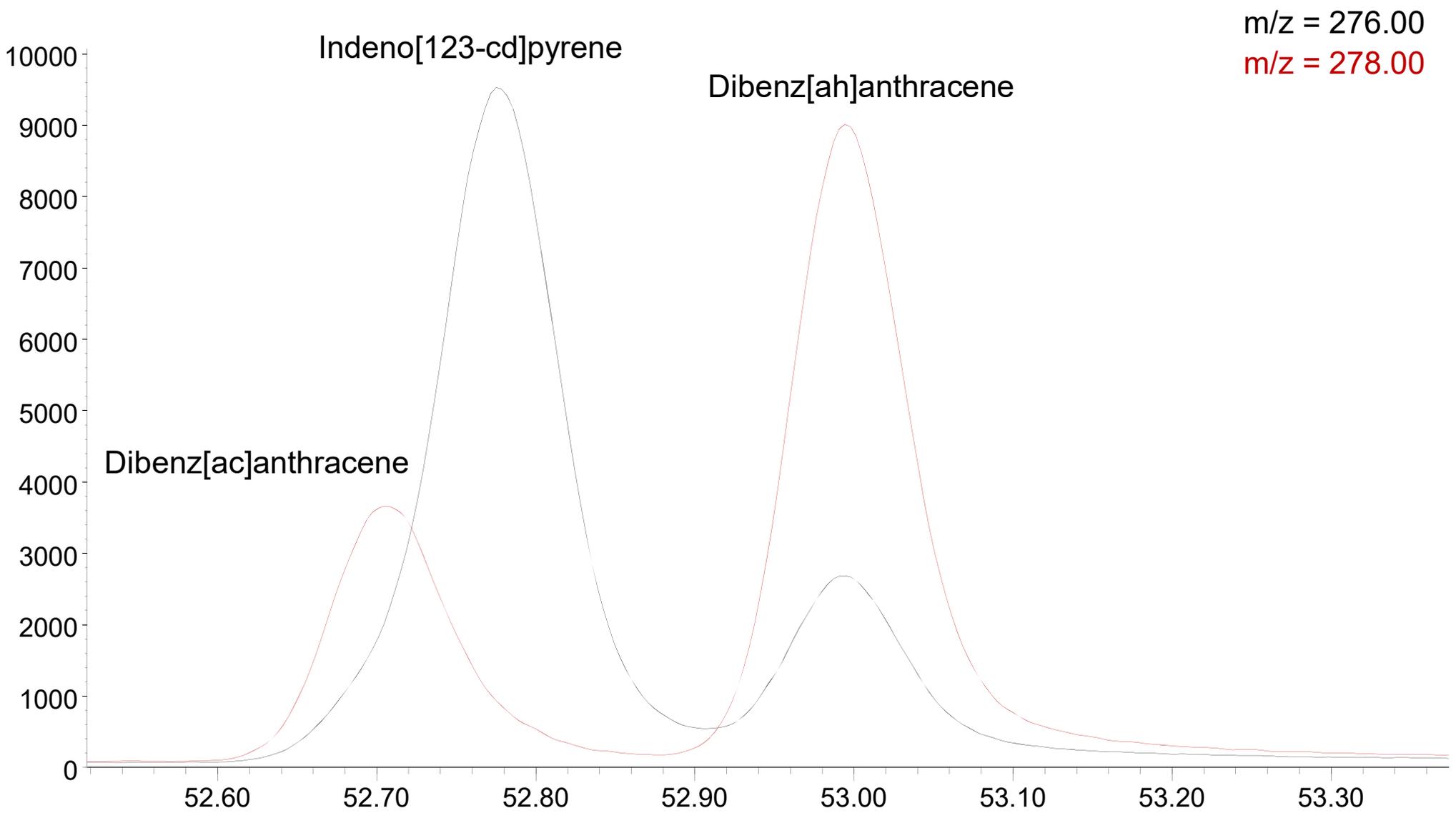
m/z = 228.00



m/z = 252.00

Benzofluoranthenes





Indeno[123-cd]pyrene

Dibenz[ah]anthracene

Dibenz[ac]anthracene

$m/z = 276.00$

$m/z = 278.00$



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1975

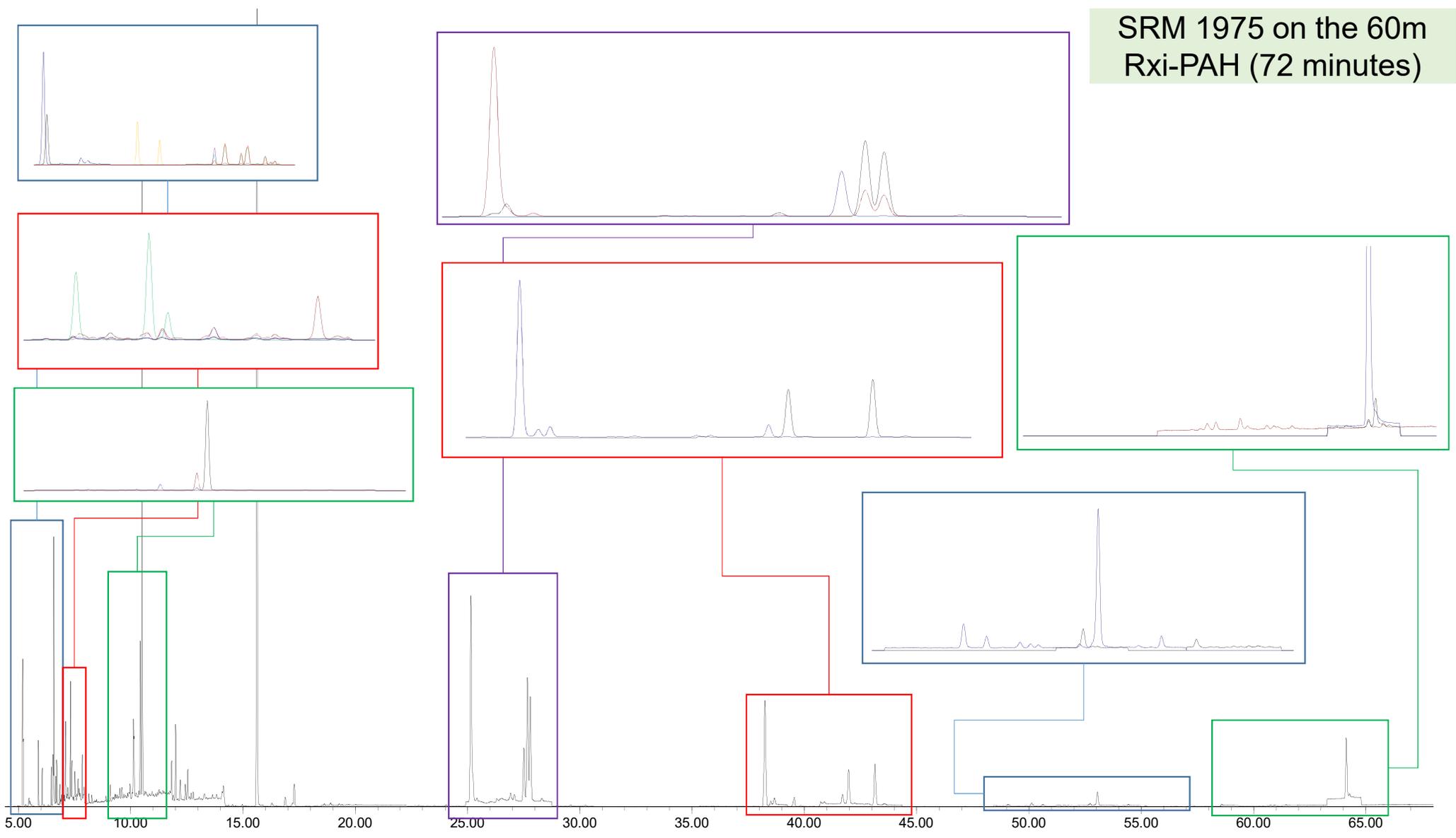
Diesel Particulate Extract

This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted PAHs in diesel particulate extracts and similar matrices. In addition to certified, reference, and information values for selected PAHs and nitro-substituted PAHs, reference values are provided for extract residue mass, and mutagenic activity. All of the chemical constituents for which certified and reference values are provided in SRM 1975 were naturally present in the particulate material before extraction. A unit of SRM 1975 consists of four ampoules, each containing approximately 1.2 mL of a dichloromethane extract of diesel particulate matter collected from an industrial diesel-powered forklift.

Diesel particulate matter from the same lot of material that was used to prepare SRM 1975 is also available as SRM 2975, Diesel Particulate Matter (Industrial Forklift) [1].

Certified Concentration Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

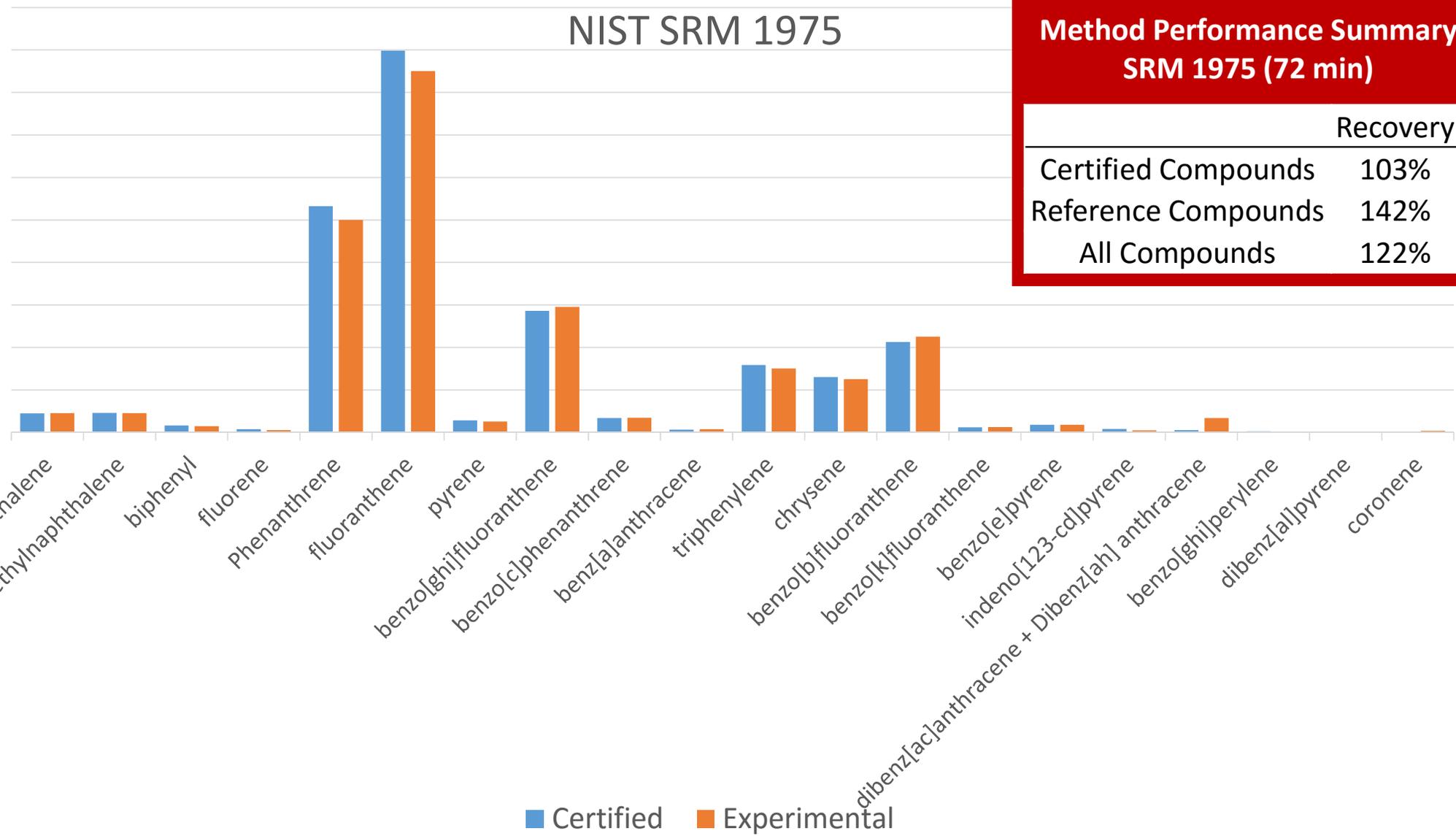
SRM 1975 on the 60m
Rxi-PAH (72 minutes)



NIST SRM 1975

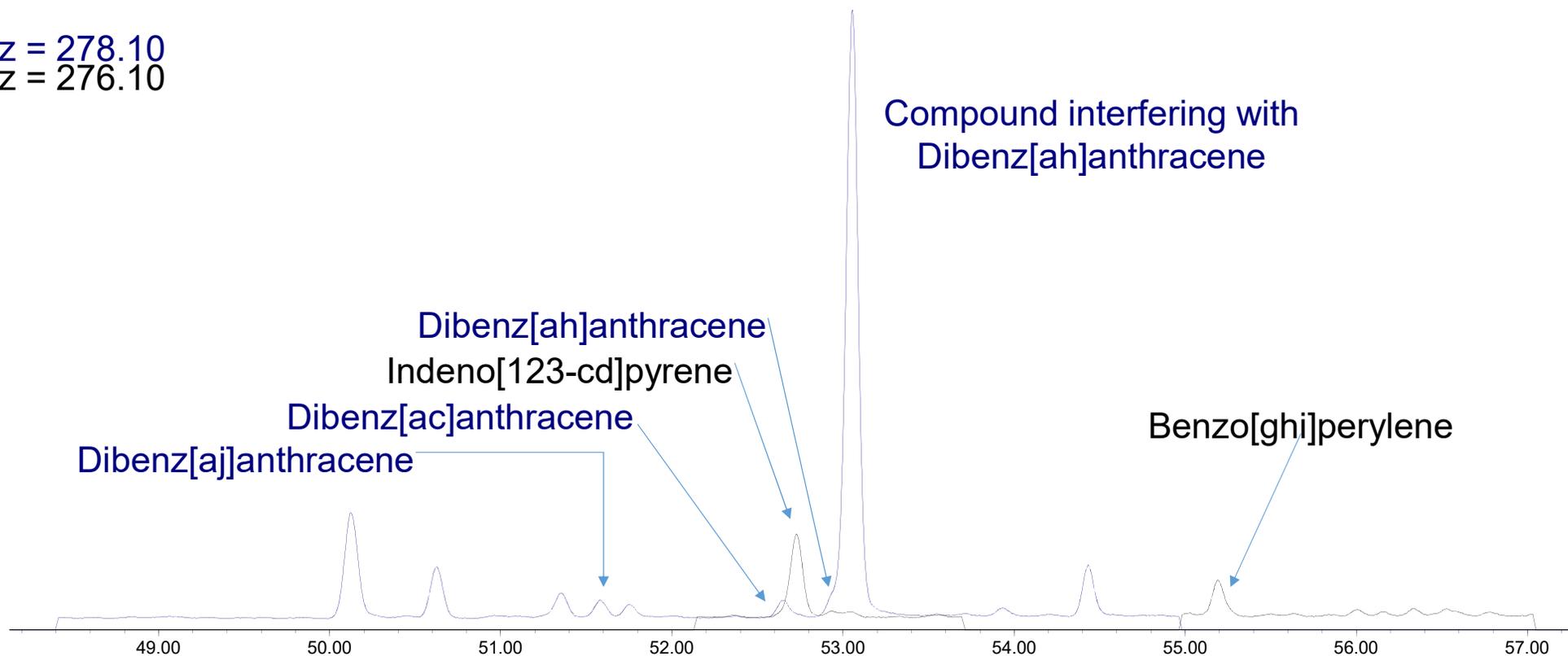
Method Performance Summary
SRM 1975 (72 min)

	Recovery
Certified Compounds	103%
Reference Compounds	142%
All Compounds	122%

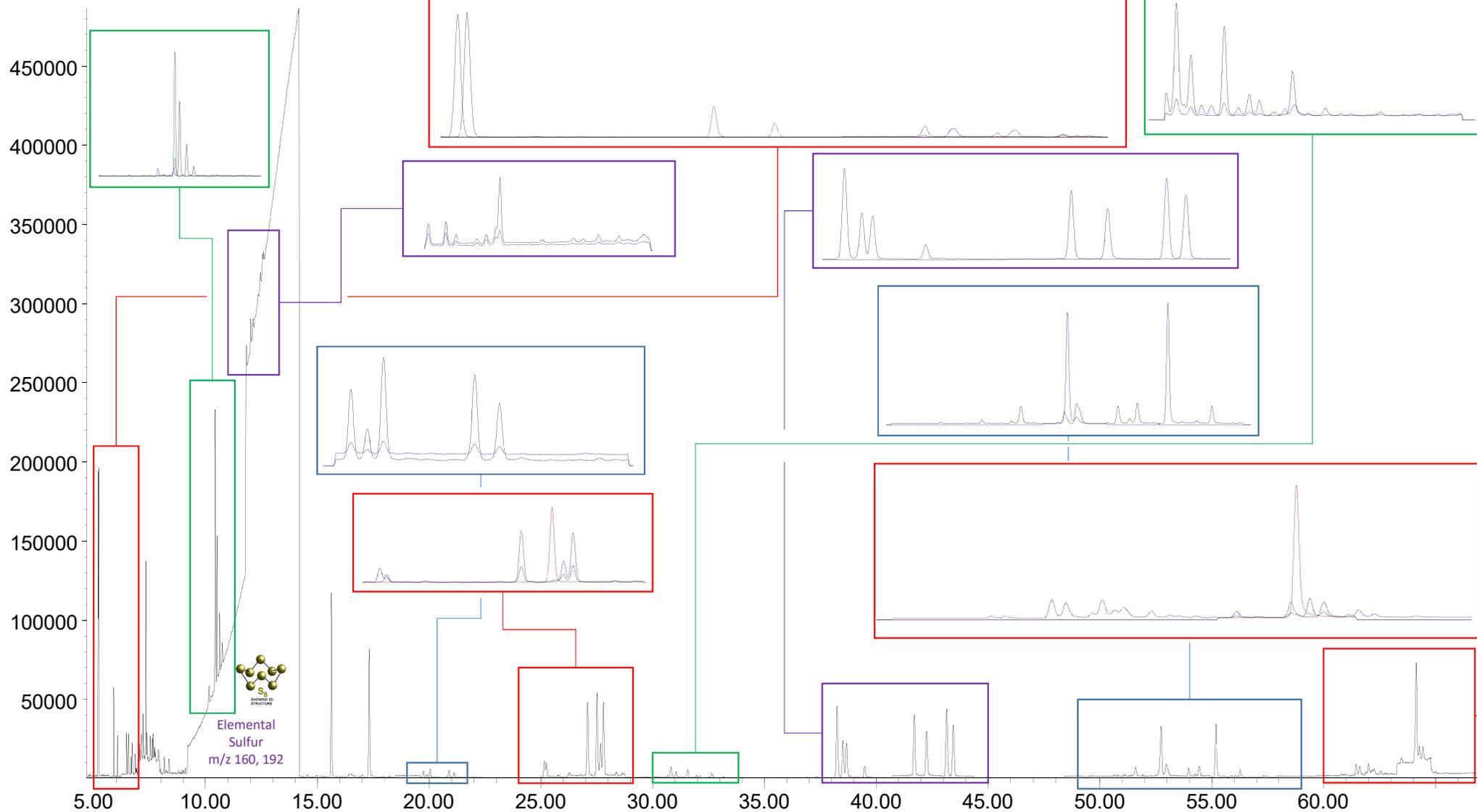


Name	Amount (µg/g)	SRM (µg/g)	Recovery
indeno[123-cd]pyrene	0.090	0.1596	57%
dibenz[ac]anthracene dibenz[ah]anthracene	0.67	0.10507	638%
dibenz[al]pyrene	0.068	0.03591	189%
coronene	0.90	0.8911	101%

m/z = 278.10
m/z = 276.10



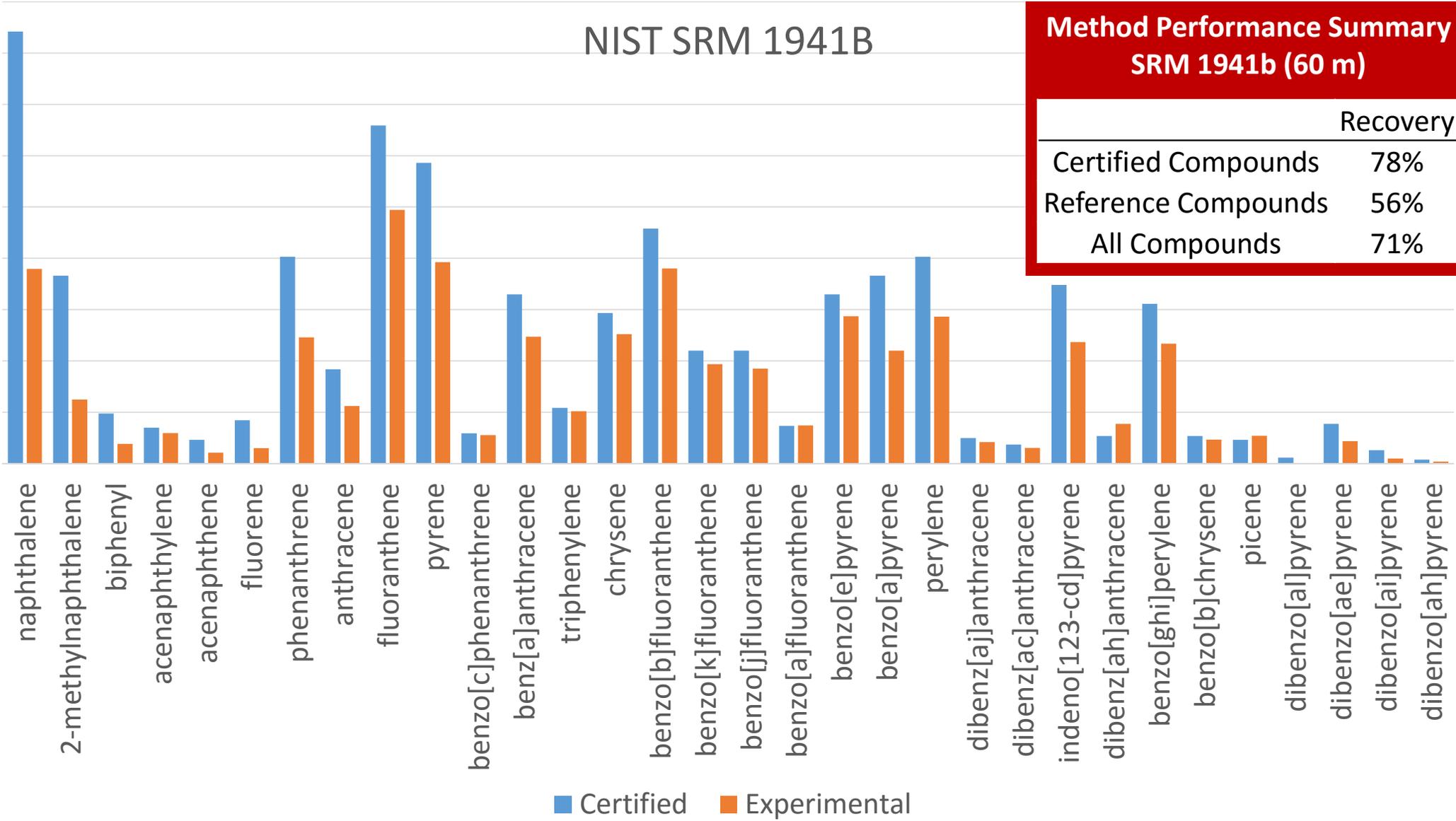
GC_EV1395 1941b on 60m Rxi-PAH



NIST SRM 1941B

Method Performance Summary
SRM 1941b (60 m)

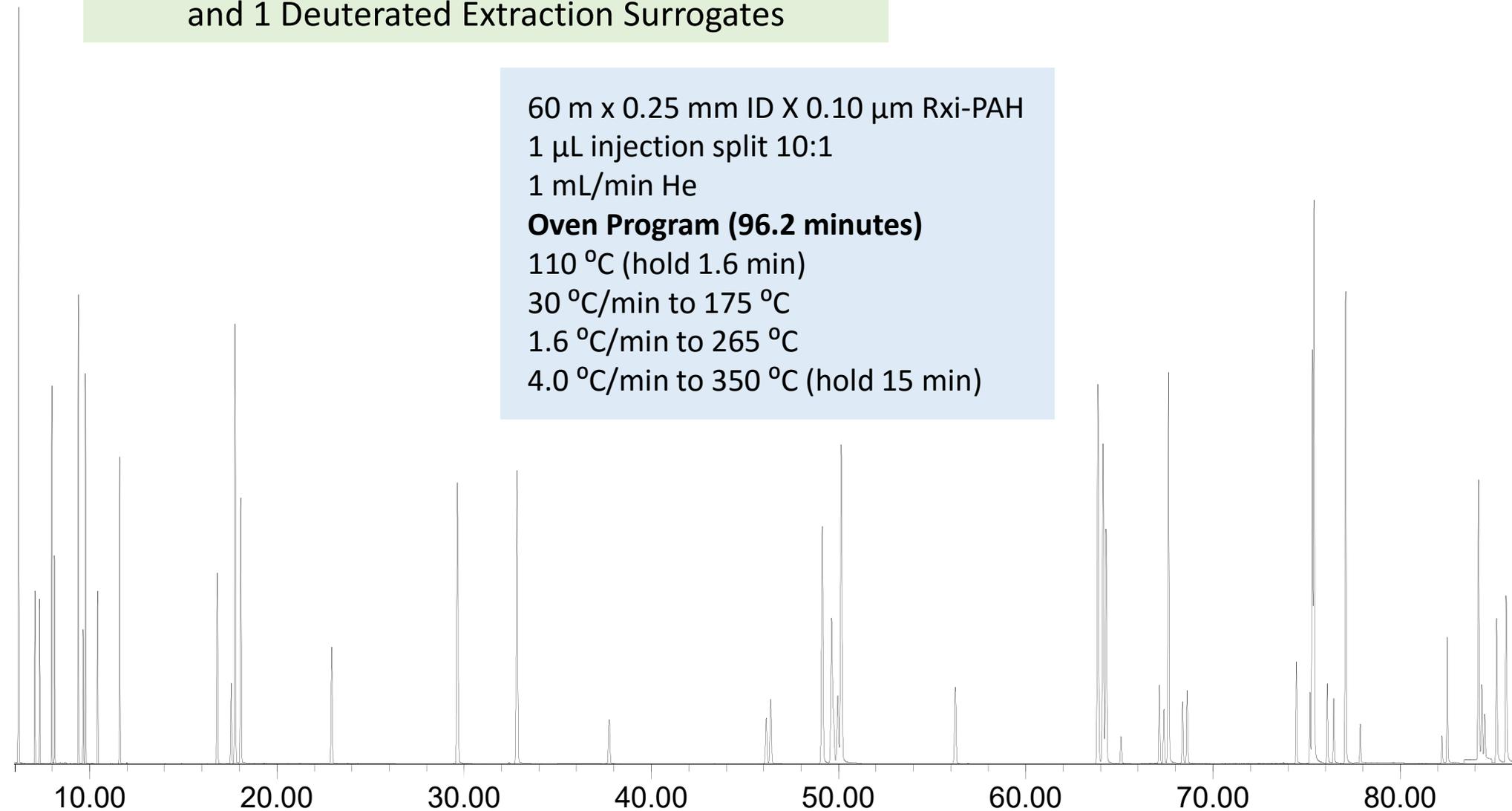
	Recovery
Certified Compounds	78%
Reference Compounds	56%
All Compounds	71%



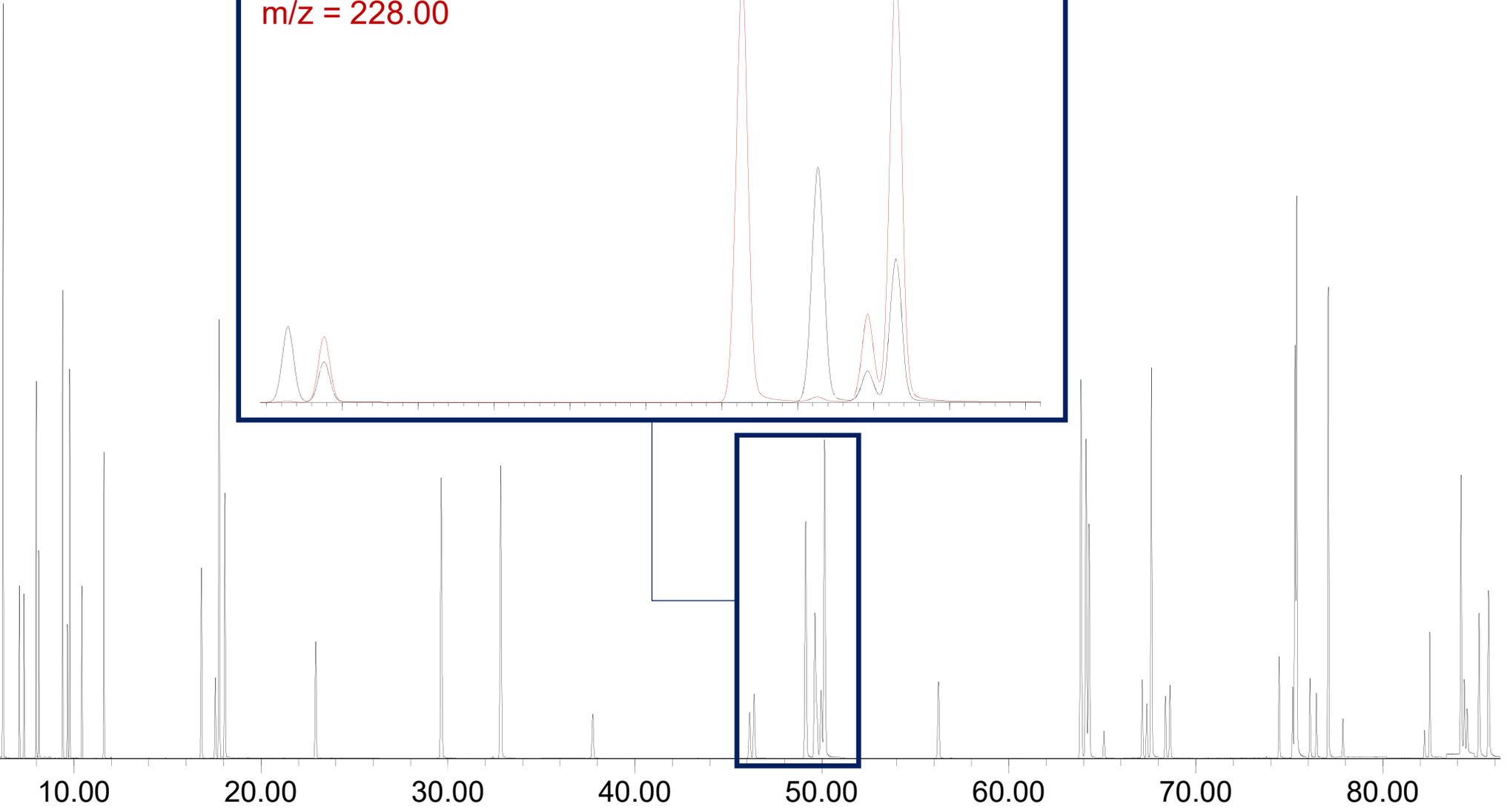
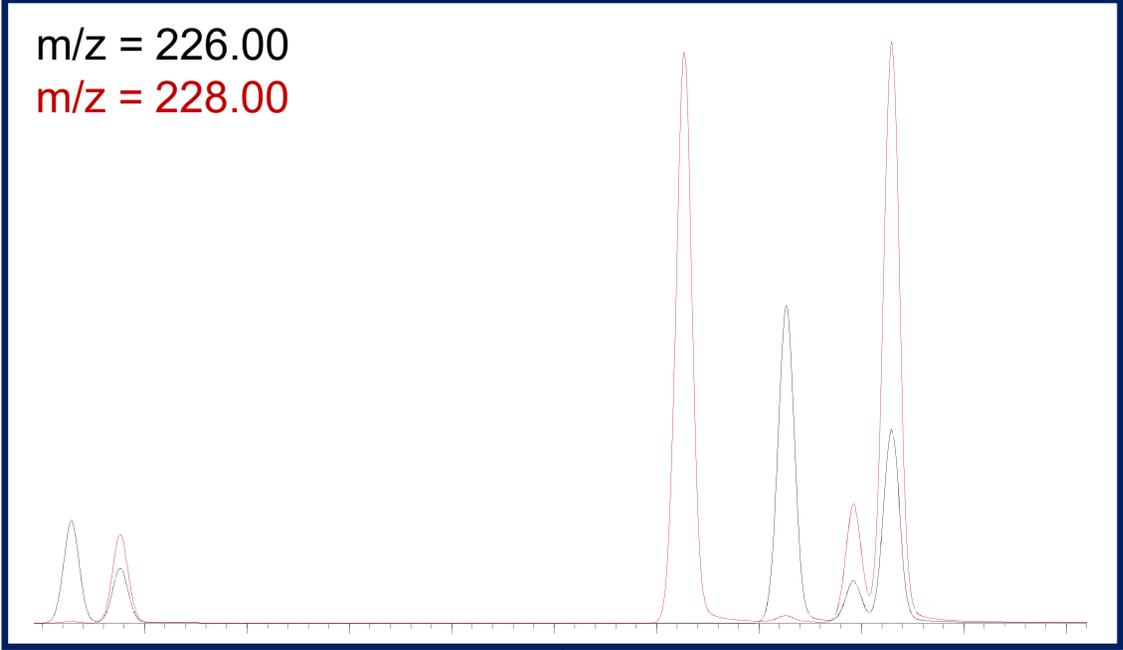
45 Native PAHs + 6 Deuterated Internal Standards
and 1 Deuterated Extraction Surrogates

PAHs on the Rxi-PAH

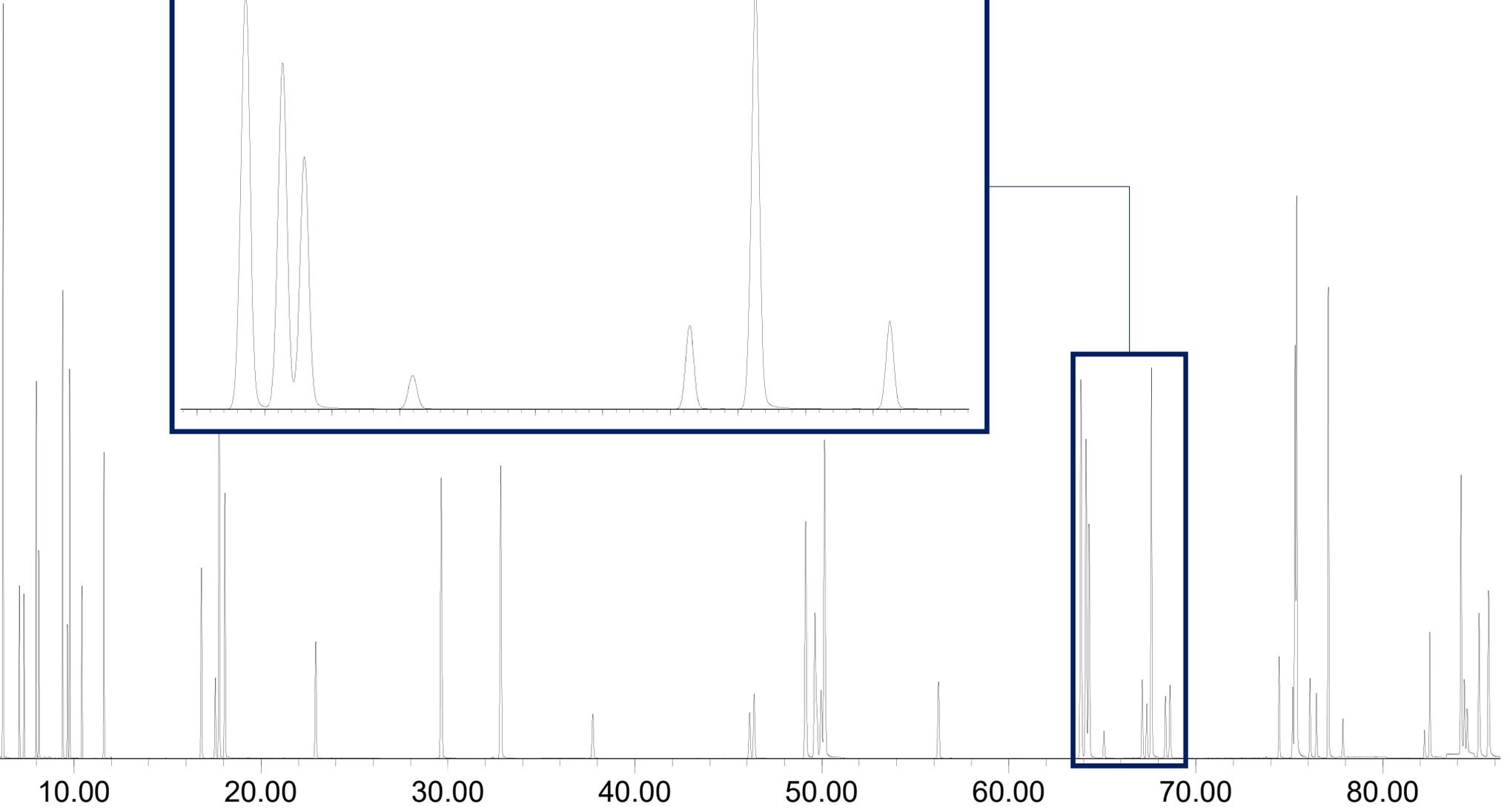
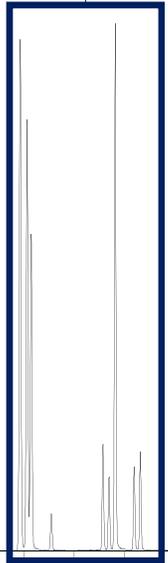
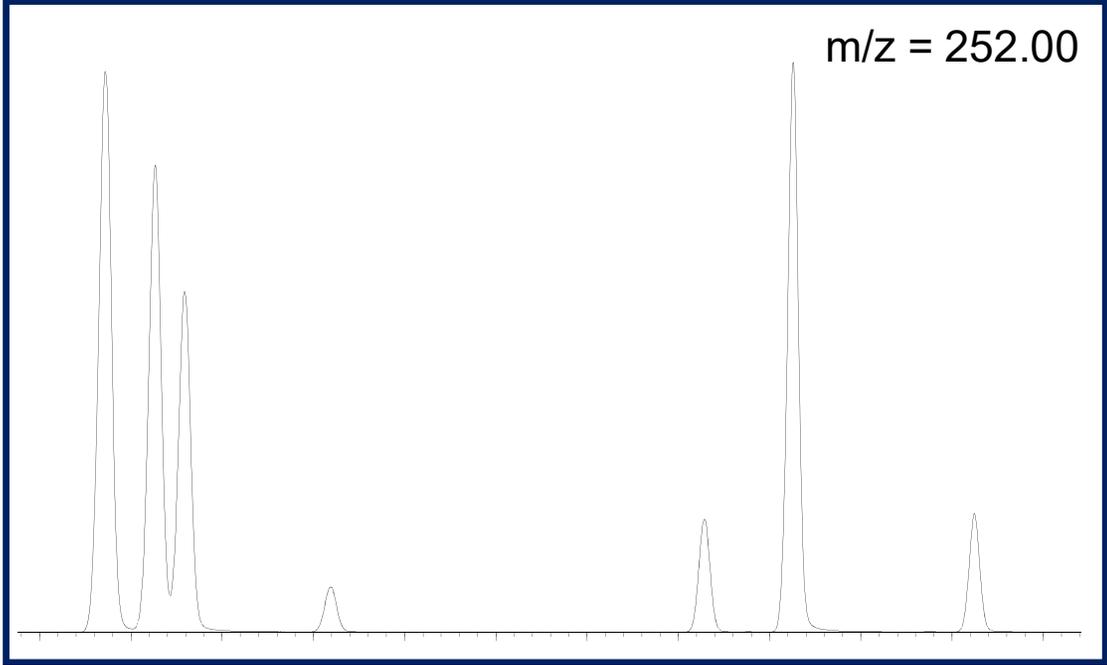
60 m x 0.25 mm ID X 0.10 μ m Rxi-PAH
1 μ L injection split 10:1
1 mL/min He
Oven Program (96.2 minutes)
110 $^{\circ}$ C (hold 1.6 min)
30 $^{\circ}$ C/min to 175 $^{\circ}$ C
1.6 $^{\circ}$ C/min to 265 $^{\circ}$ C
4.0 $^{\circ}$ C/min to 350 $^{\circ}$ C (hold 15 min)



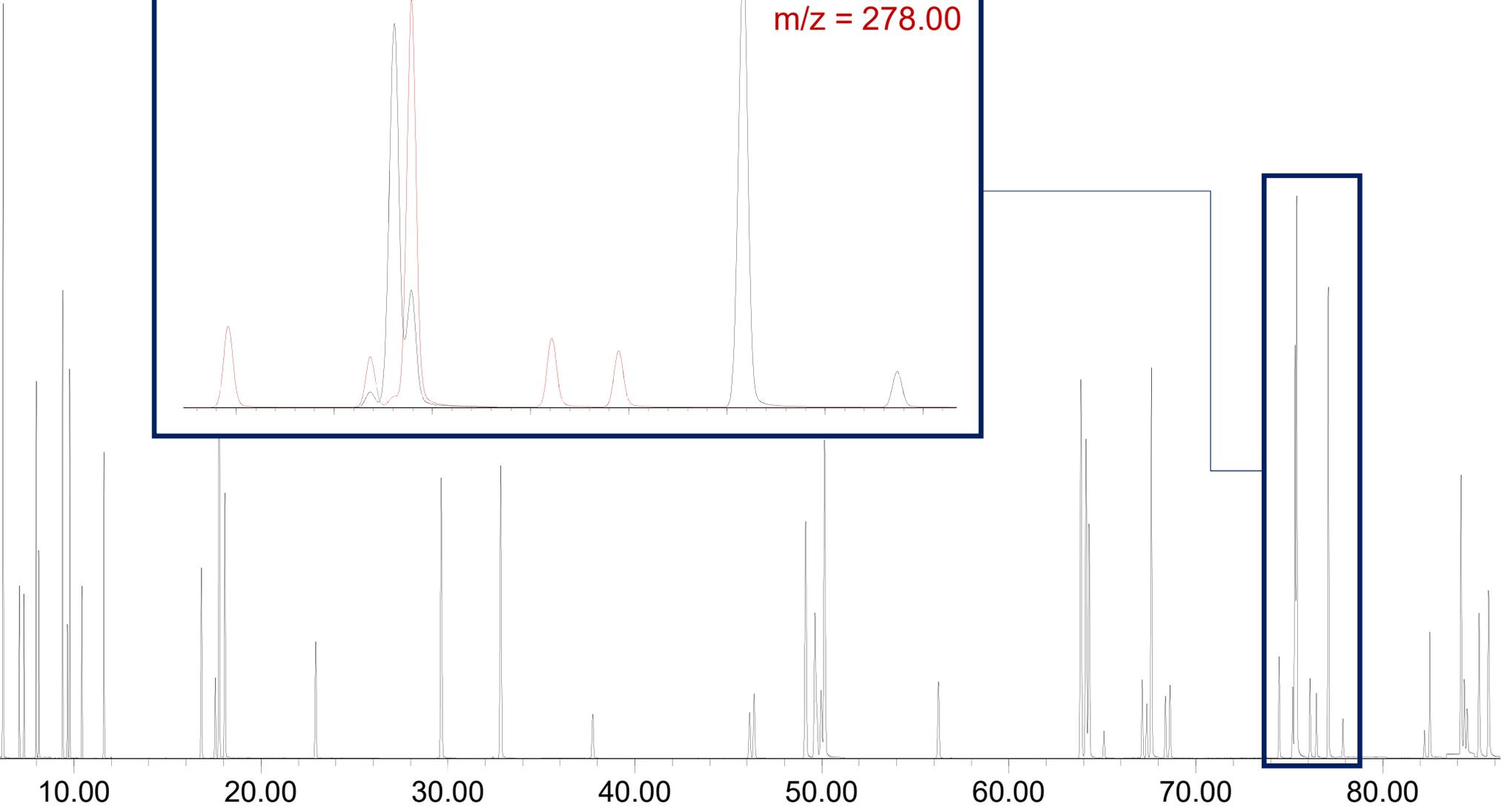
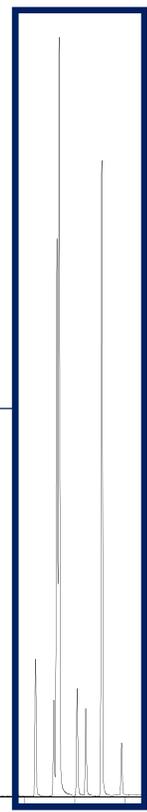
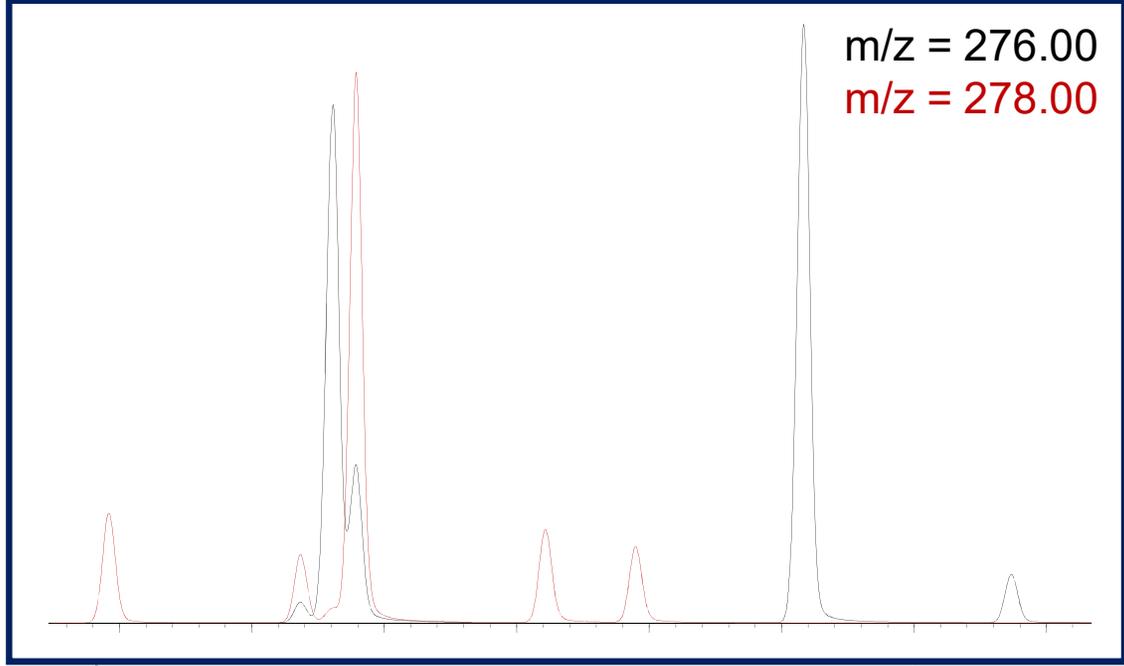
PAHs on the Rxi-PAH



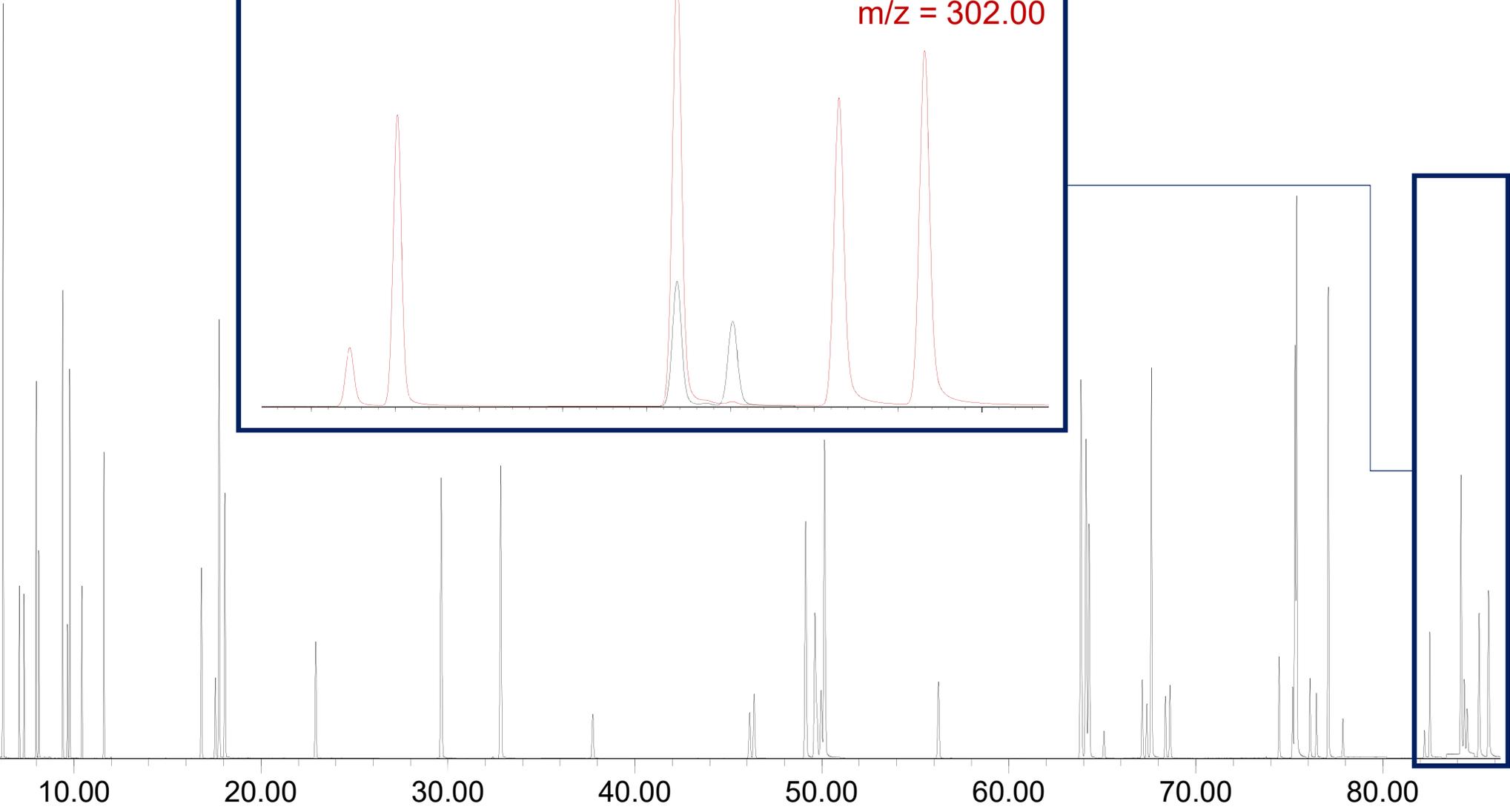
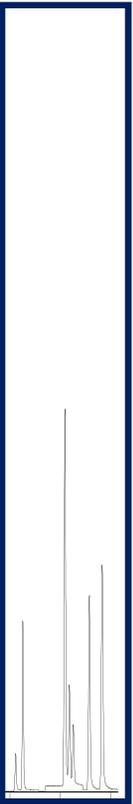
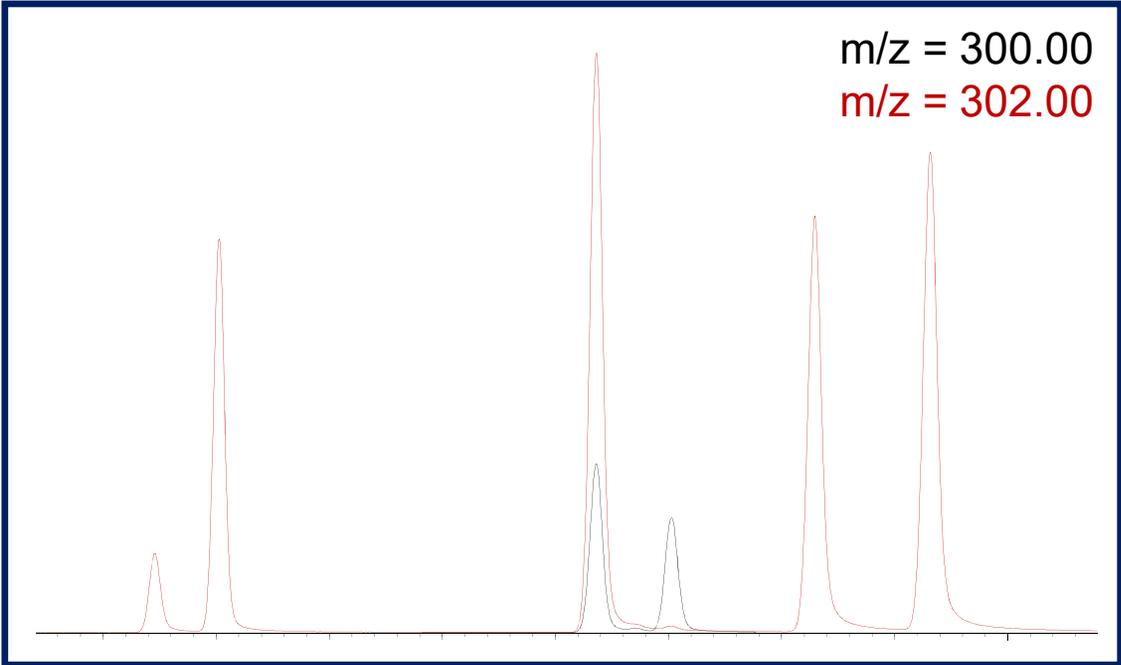
Benzofluoranthenes on the Rxi-PAH



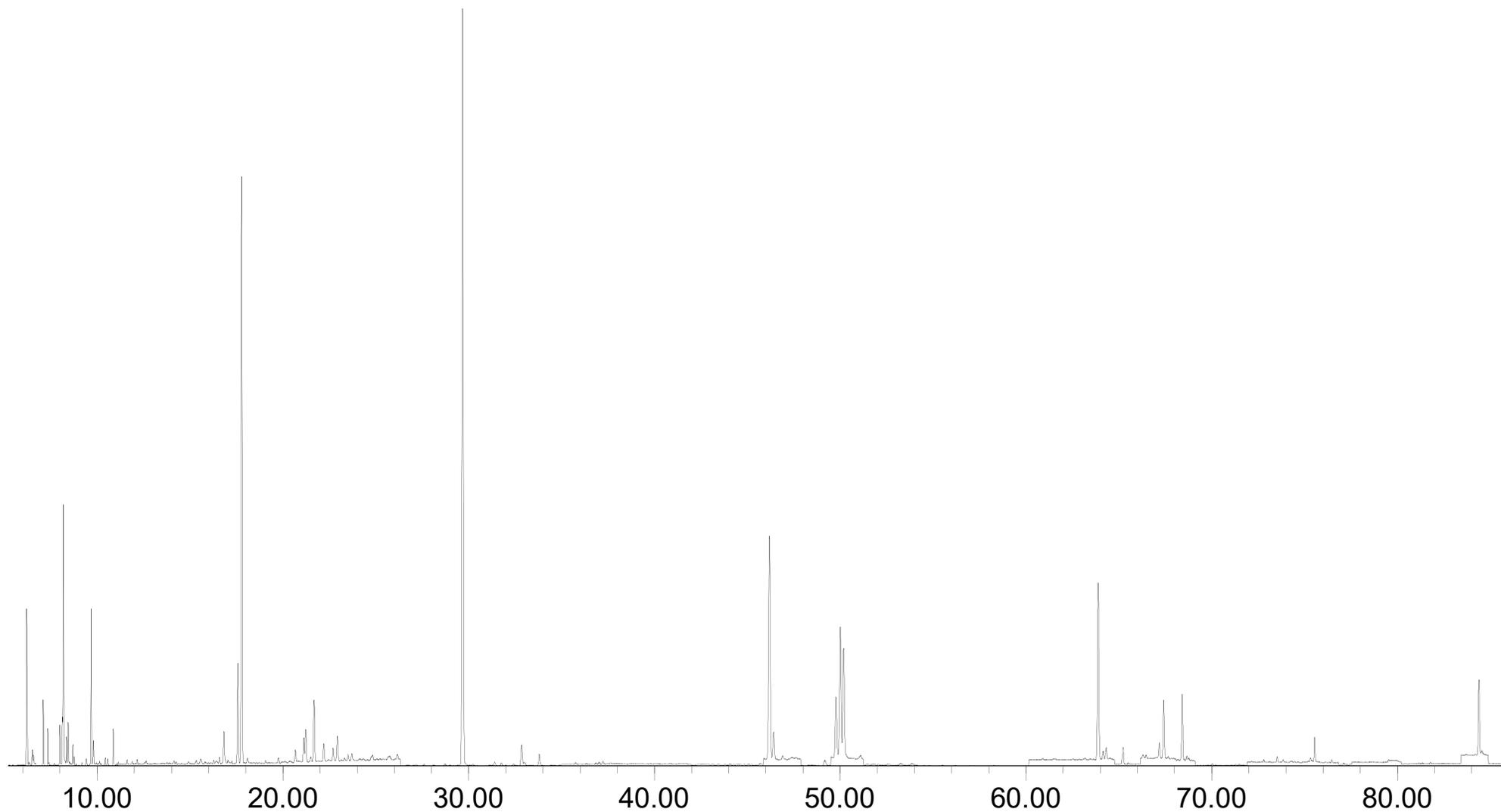
Dibenzo Anthracenes on the Rxi-PAH



Dibenzopyrenes on the Rxi-PAH



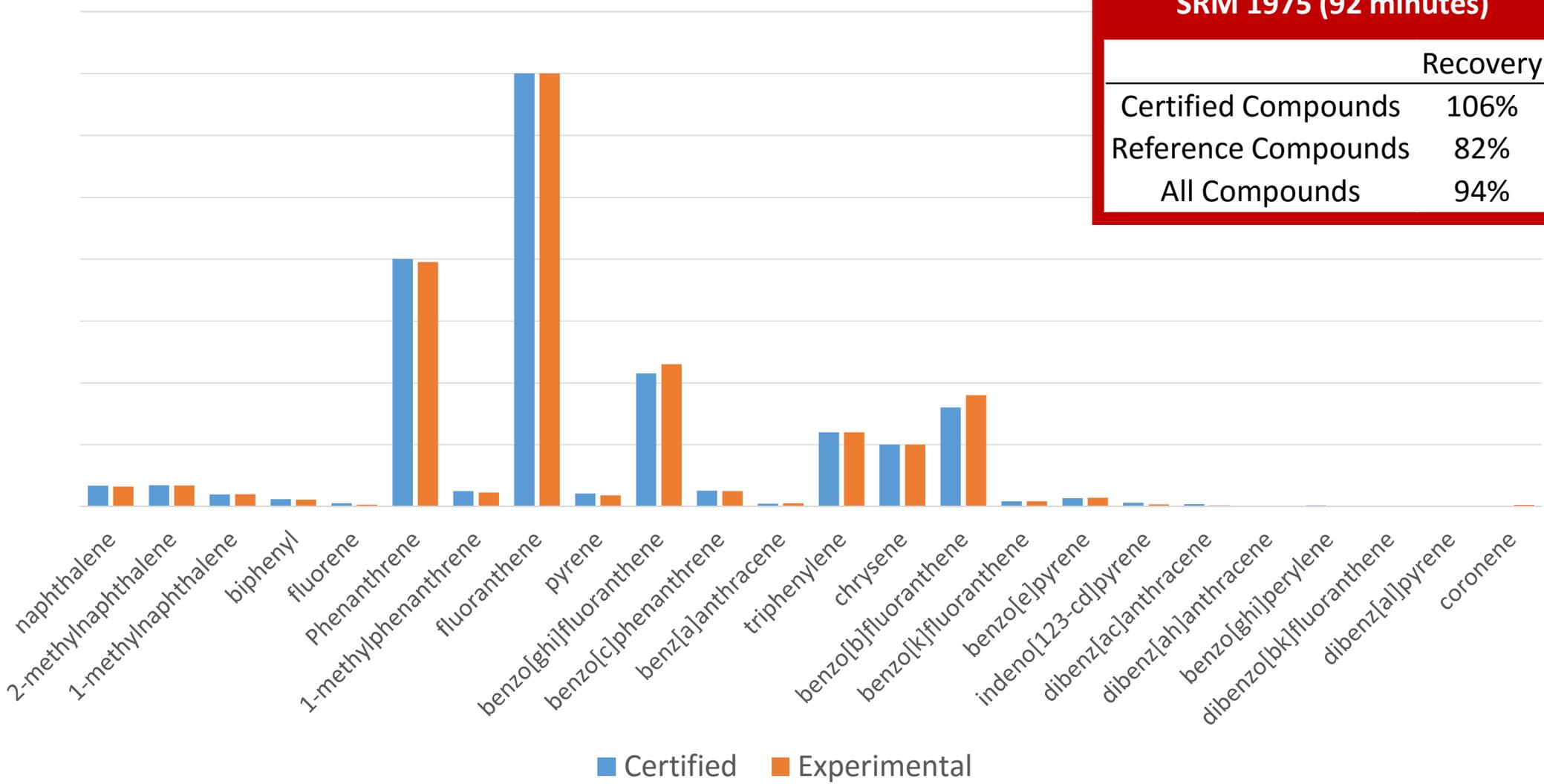
TIC: NIST SRM 1975 GC-MS SIM



NIST SRM 1975

Method Performance Summary
SRM 1975 (92 minutes)

	Recovery
Certified Compounds	106%
Reference Compounds	82%
All Compounds	94%





National Institute of Standards & Technology

Certificate of Analysis

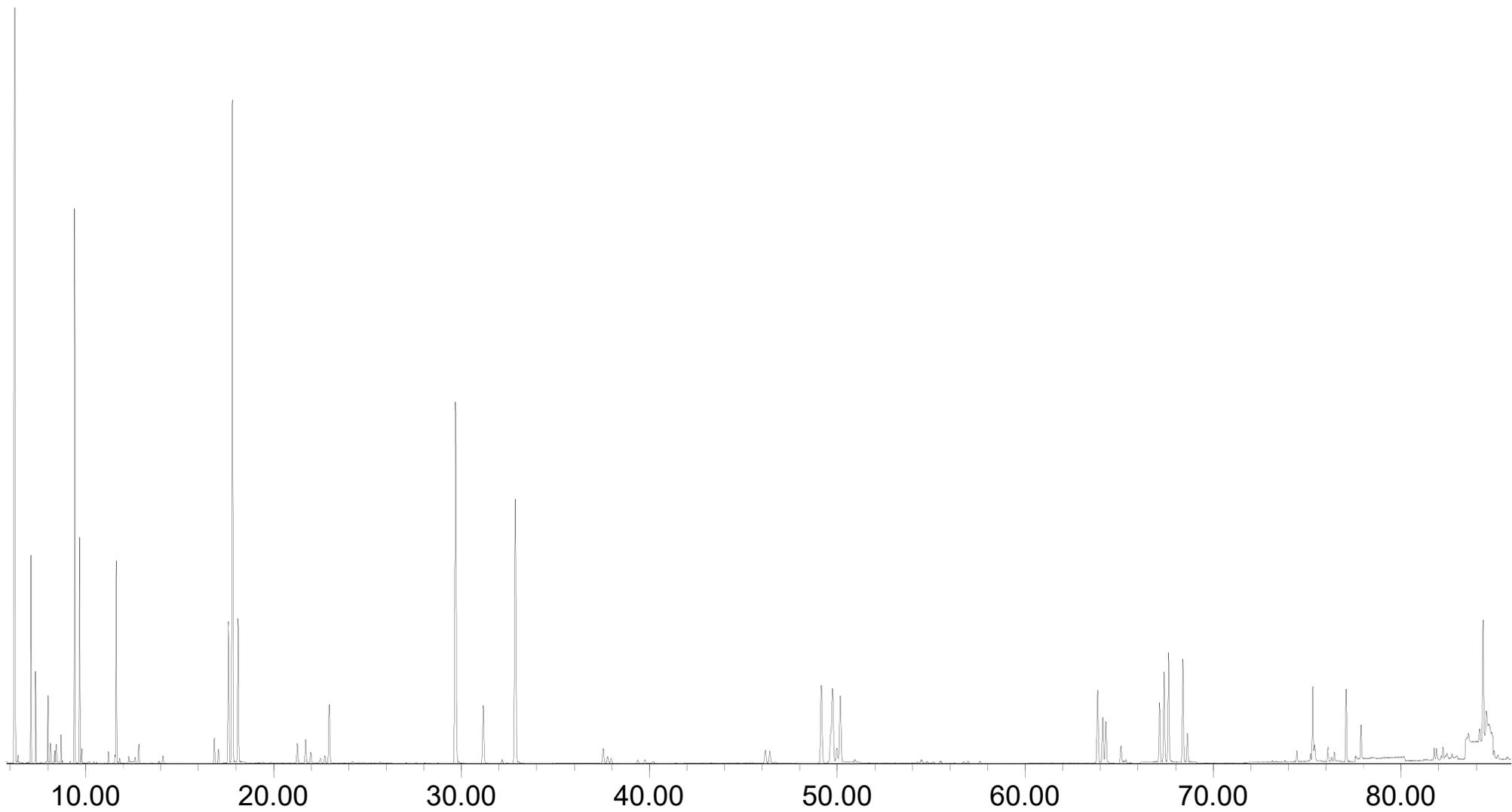
Standard Reference Material[®] 1597a

Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar

This Standard Reference Material (SRM) is intended for use in the evaluation and validation of analytical methods for the determination of a natural, combustion-related mixture of polycyclic aromatic hydrocarbons (PAHs). SRM 1597a is isolated from a coal tar sample and dissolved in toluene. It is suitable for direct analysis (i.e., without sample cleanup or concentration) in the determination of PAHs using analytical techniques such as gas chromatography (GC), liquid chromatography (LC), or gas chromatography/mass spectrometry (GC/MS). This SRM may also be used to evaluate procedures for measurement of mutagenic activity of combustion-related mixtures of PAHs and related compounds. A unit of SRM 1597a consists of one 5 mL ampoule, containing 1.3 mL of material.

Certified Mass Fraction Values: Certified values for concentrations, expressed as mass fractions, for 34 PAHs are provided in Table 1. The certified values are based on the agreement of results obtained at NIST from two or more chemically independent analytical techniques [1,2]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

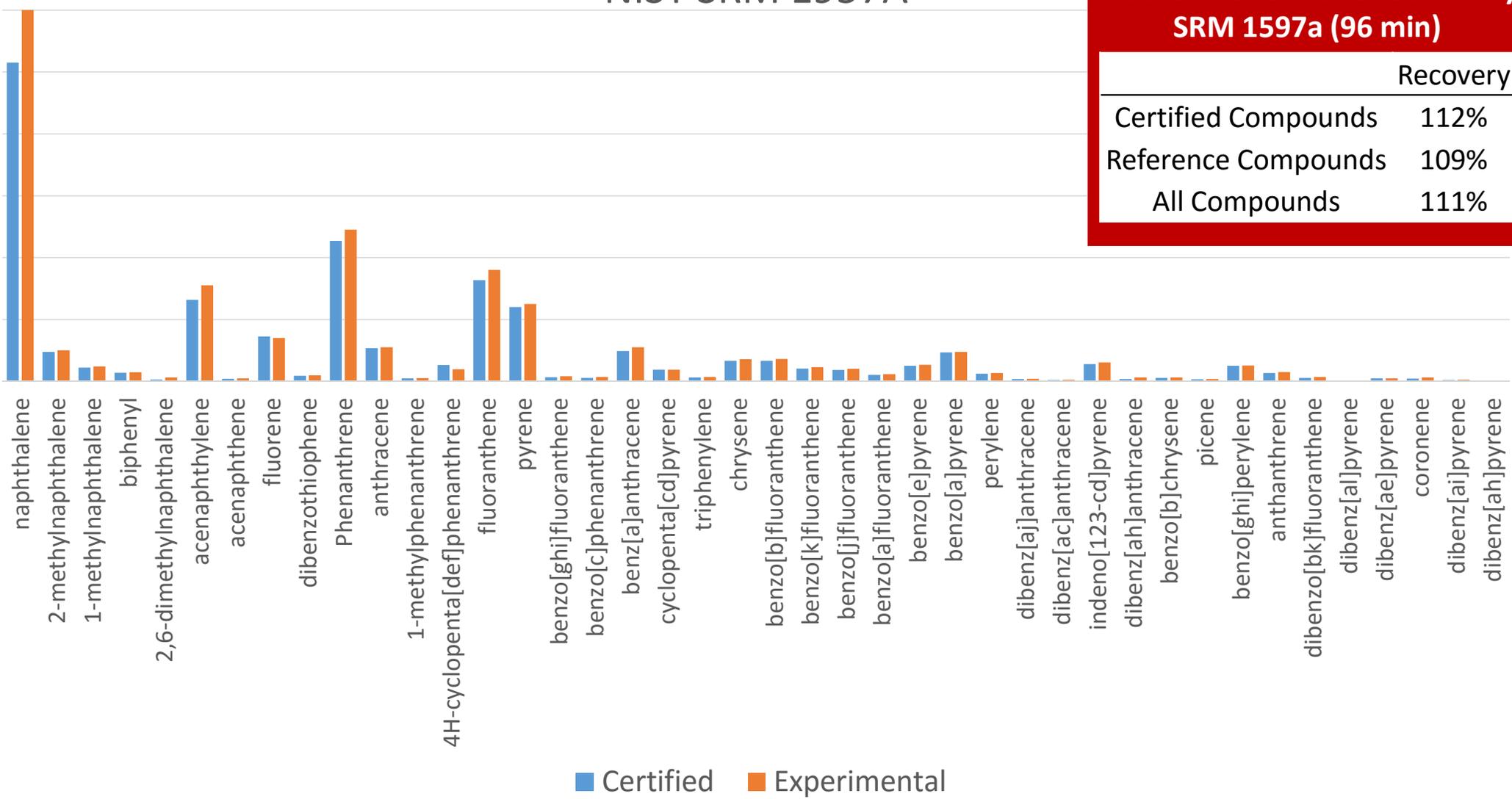
TIC: NIST SRM 1597a (diluted 50:1) GC-MS SIM



NIST SRM 1957A

Method Performance Summary SRM 1597a (96 min)

	Recovery
Certified Compounds	112%
Reference Compounds	109%
All Compounds	111%



Questions?