

# Extended Dynamic Range, High Precision Analysis of Polynuclear Aromatic Hydrocarbon Compounds by GC-MS

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## Overview

**Purpose:** Development of an analytical method for extended low range analysis of PAH's with excellent precision for high molecular weight compounds extracted from matrix.

**Methods:** Using the automated "calibration dilution" function of the Thermo Scientific TriPlus RSH autosampler, standards were produced in a dilution range of 10.0 – 0.01 ng/μL for 16 PAH compounds. The Thermo Scientific ISQ single quadrupole GC-MS was operated in SIM mode to measure samples and standards. Samples extracted from soil matrix at 0.01 ng/μL were analyzed for precision and accuracy.

**Results:** R<sup>2</sup> linearity values of ≥ 0.996 for all 16 compounds. System calibration was maintained while providing internal standards accuracy RSD of ≤10% throughout the analysis. Analysis of matrix extracted samples at 0.01 ng/μL demonstrated the selectivity of the instrument with precision results of ≤ 5 for 16 PAH compounds.

## Introduction

**Polynuclear Aromatic Hydrocarbons (PAH)** are naturally occurring organic pollutants of crude and refined petroleum and coal. Combustion of these materials for energy has increased concerns of human and environmental exposure to these compounds<sup>1</sup>. Additionally, the persisting and carcinogenic nature of some PAH compounds pose a potential hazard to human and environmental health. The potential cost of cleanup and the human health issues resulting from exposure support the monitoring of these compounds at low concentrations in the environment. Sensitive detection and quantitation methods for assessing PAH levels are critical tools in averting the lasting consequences of PAH contamination.

A method was developed to demonstrate the performance of the TriPlus™ RSH autosampler, Thermo Scientific TRACE 1310 gas chromatograph, and ISQ™ single quadrupole GC-MS when analyzing environmental samples for PAH content. The methodology includes a linear range of 10.0 - 0.01 ng/μL for 16 PAH compounds with single digit precision and accuracy for all compounds.

## Methods

### Sample Preparation

Standards included Restek™ SV Calibration Mix #5 - Catalogue #31011 (06-800-950) composed of a single vial containing a solution of methylene chloride spiked with 16 PAH compounds each at 2,000 ng/μL concentration and Restek SV internal standard mix - Catalogue #31206 (06-707-3737) containing a solution of methylene chloride spiked with five PAH internal standard compounds each at 2,000 ng/μL concentration.

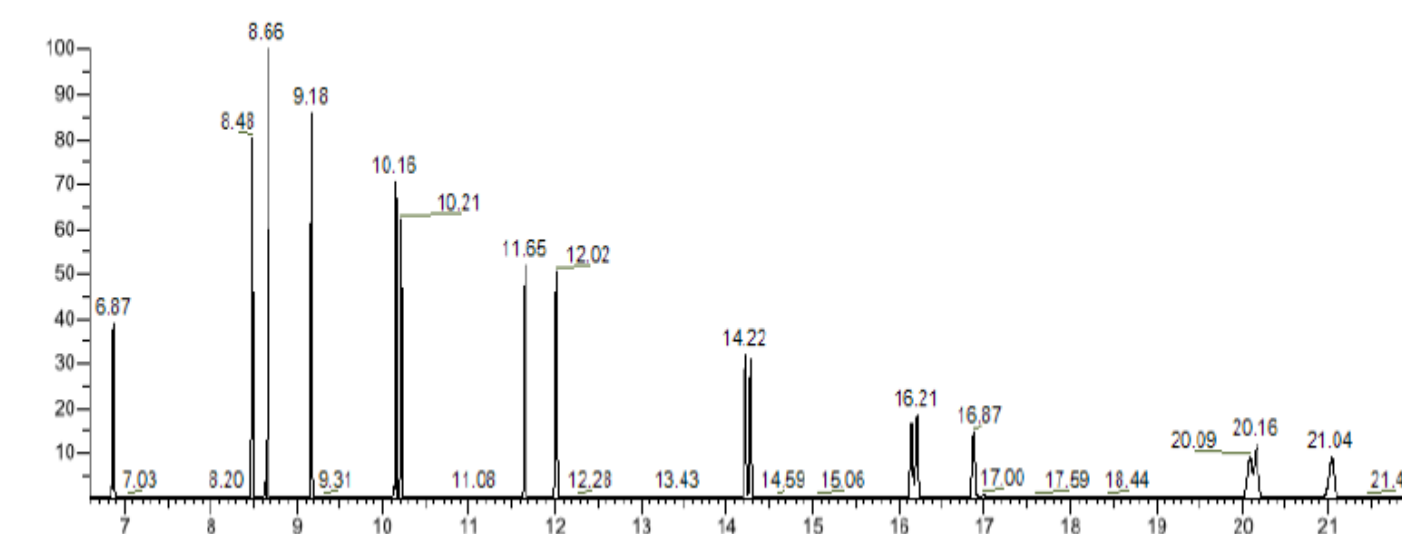
Active stock standard mix was prepared at 10 ng/μL, and internal standards stock was prepared at 50 ng/μL. Standard preparation was completed using the automated calibration dilution function of the TriPlus RSH autosampler. Concentrations of calibration standards are listed in Table 1.

**TABLE 1. Concentrations of calibration standards prepared by the automated calibration dilution function of the TriPlus RSH autosampler - final range of 10 ng/μL to 0.01 ng/μL.**

Dilution Series - 10ng/μL - 0.01ng/μL		
Sample dilution level	10.00	ng/μL
1/2	5.00	ng/μL
1/5	2.00	ng/μL
1/10	1.00	ng/μL
1/20	0.50	ng/μL
1/50	0.20	ng/μL
1/100	0.10	ng/μL
1/200	0.05	ng/μL
1/500	0.02	ng/μL
1/1000	0.01	ng/μL

10 ng/μL calibration standards were analyzed in full scan to establish retention times of analytes and determine SIM method setup parameters.

**FIGURE 1. Full scan chromatogram of 16 PAH active compounds and 5 PAH internal standard compounds.**



### Sample Introduction Data Analysis

A TriPlus RSH autosampler and a TRACE™ 1310 gas chromatograph, equipped with a split/splitless injection port module with surge capability, provided sample introduction into the ISQ mass spectrometer (Table 2).

**TABLE 2. Analysis parameters for TRACE 1310 gas chromatograph and ISQ single quadrupole GC-MS**

TriPlus RSH parameters		Trace 1310 GC Inlet Parameters	
Prep Cycle:	Calibration Dilution	Mode:	Splitless/Surge
Injection Volume (μL):	1.0	Inlet (°C):	300.0
		Carrier Flow He (mL/min):	2.0
		Column 1:	TG-5SiIMS 30m x 0.25mm x 0.50μm
Trace 1310 Oven Temperature Program		ISQ Single Quad Mass Spec Parameters	
Temperature 1 (°C):	250.0	Transfer line (°C):	310
Hold Time (min):	2.0	Mode:	SIM
Rate (°C/min):	25.0	Ion Source Temp (°C):	350.0
Temperature 2 (°C):	250.0	Ionization Mode:	EI
Rate (°C/min):	5.0	Emission Current:	40μA
Temperature 3 (°C):	265.0	Detector Gain:	1.00E+05
Rate (°C/min):	25.0		
Temperature 4 (°C):	300.0		
Hold Time (min):	25.0		

A 30 m × 0.25 mm I.D. × 0.50 μm Thermo Scientific TraceGOLD TG-5SiIMS analytical column was used to enhance separation of the target PAH compounds. The ISQ mass spectrometer system was operated in selected ion monitoring mode (SIM), collecting three ions for each target and deuterated internal standard (Table 3).

Thermo Scientific TraceFinder software provided automated acquisition and processing of all data, including quantitation and ion ratio confirmation calculations. The method was assessed for specificity, linearity, precision, recovery and interference

**TABLE 3. Retention times and ions monitored for the PAH compounds and their deuterated internal standards**

Compound	Retention Time (min)	Quan Ion (m/z)	Qual Ion (m/z)
Naphthalene D8	6.85	136.0	68, 108
Naphthalene	6.87	128.0	129, 127
Acenaphthylene	8.48	152.0	153, 151
Acenaphthene D10	8.62	164.0	162, 160
Acenaphthene	8.66	154.0	153, 152
Fluorene	9.18	166.0	165, 167
Phenanthrene D10	10.13	188.0	94, 80
Phenanthrene	10.16	178.0	179, 176
Anthracene	10.21	178.0	176, 179
Fluoranthene	11.65	202.0	203, 101
Pyrene	12.01	202.0	200, 203
Benz[a]anthracene	14.22	228.0	226, 229
Chrysene D12	14.23	240.0	120, 236
Chrysene	14.28	228.0	226, 229
Benzo(b)fluoranthene	16.15	252.0	253, 125
Benzo(k)fluoranthene	16.20	252.0	253, 125
Benzo(a)pyrene	16.87	252.0	253, 125
Perylene D12	17.00	264.0	260, 265
Indeno(1,2,3-cd)pyrene	20.08	276.0	138, 277
Dibenzo(a,h)anthracene	20.16	278.0	279, 139
Benzo(ghi)perylene	21.02	276.0	277, 138

## Results

### Linearity

• Analysis range from 10 - 0.01 ng/μL for 16 PAH compounds (Table 4).

**TABLE 4. Resulting R<sup>2</sup> values for 16 PAH compounds analyzed from 10.0 - 0.01 ng/μL**

Compound	R <sup>2</sup>
Naphthalene	0.9992
Acenaphthylene	0.9977
Acenaphthene	0.9993
Fluorene	0.9988
Phenanthrene	0.9991
Anthracene	0.9984
Fluoranthene	0.9980
Pyrene	0.9981
Benz[a]anthracene	0.9964
Chrysene	0.9997
Benzo(b)fluoranthene	0.9988
Benzo(k)fluoranthene	0.9992
Benzo(a)pyrene	0.9980
Indeno(1,2,3-cd)pyrene	0.9975
Dibenzo(a,h)anthracene	0.9981
Benzo(ghi)perylene	0.9984

### Internal Standard Precision

**TABLE 5. % RSD for internal standards of all injections analyzed**

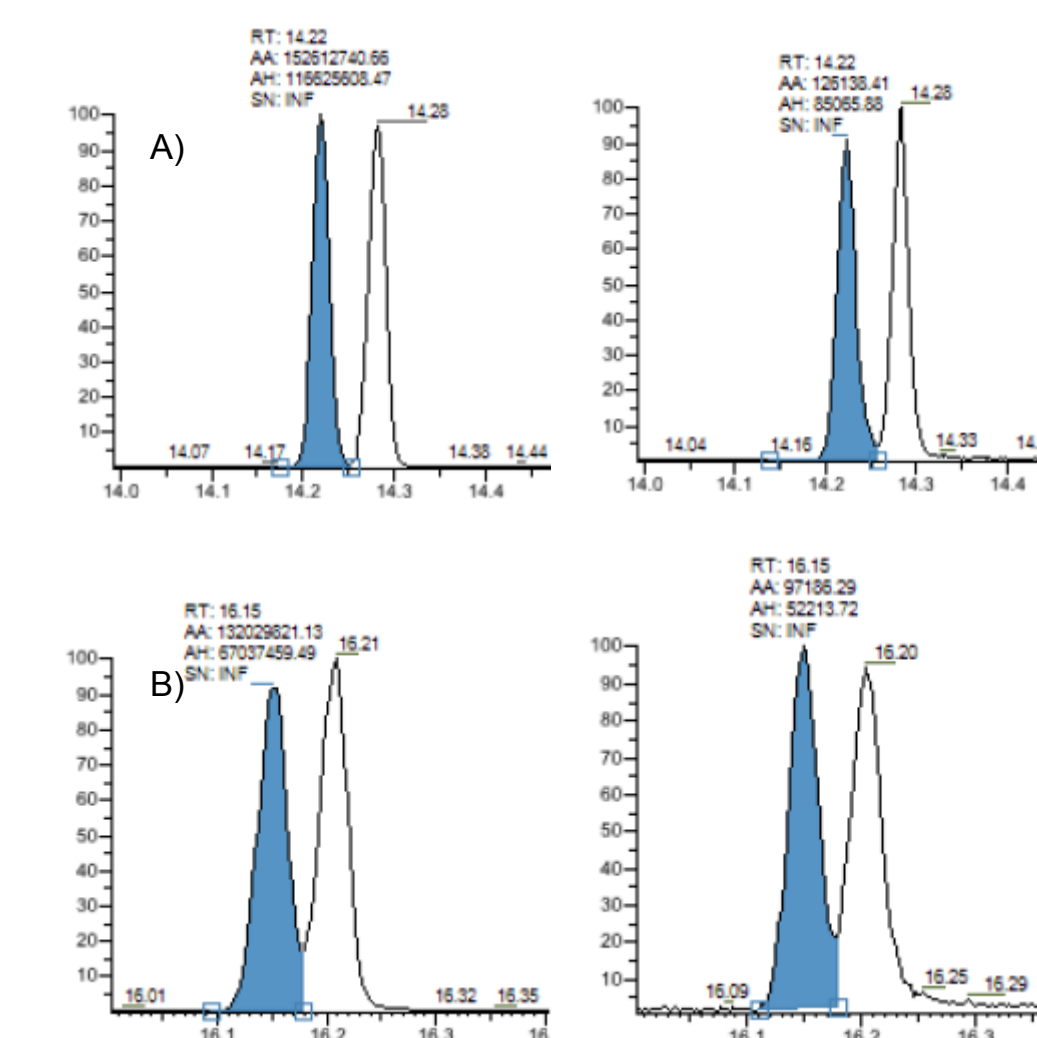
Compound	%RSD
Naphthalene D8	5.88
Acenaphthene D10	4.88
Phenanthrene D10	4.92
Chrysene D12	6.08
Perylene D12	6.28

### Accuracy

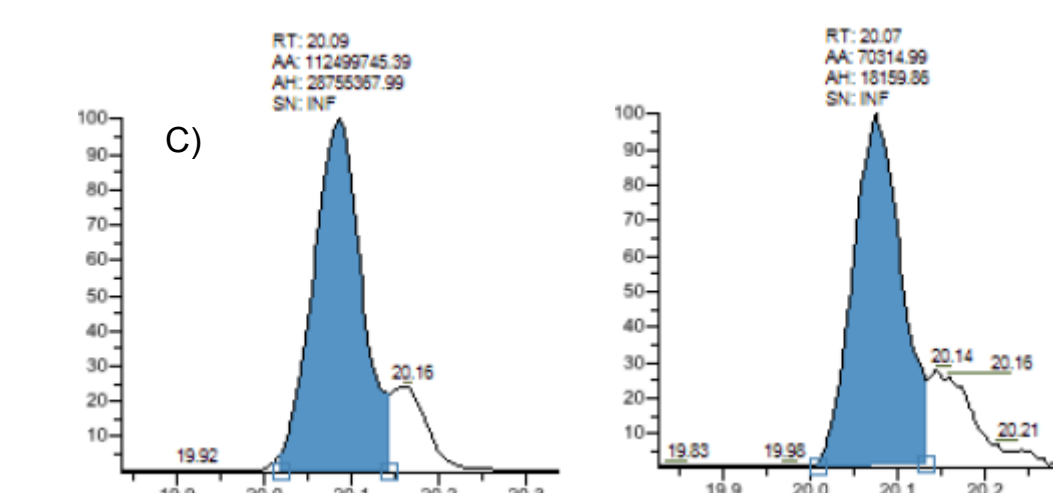
**TABLE 6. Target concentrations vs. measured concentrations for three calibration levels (0.01, 0.1 and 10) of standards**

Compound	Target Conc. (ng/μL)	Measured Conc. (ng/μL)
Chrysene	0.010	0.012
	0.100	0.093
	10.000	10.046
Benzo(b)fluoranthene	0.010	0.014
	0.100	0.086
	10.000	10.880
Benzo(k)fluoranthene	0.010	0.013
	0.100	0.090
	10.000	10.073
Benzo(a)pyrene	0.010	0.015
	0.100	0.085
	10.000	10.113
Indeno(1,2,3-cd)pyrene	0.010	0.015
	0.100	0.081
	10.000	10.129
Dibenzo(a,h)anthracene	0.010	0.015
	0.100	0.083
	10.000	10.109
Benzo(ghi)perylene	0.010	0.014
	0.100	0.086
	10.000	10.101

**FIGURE 2. Integrated peaks for high molecular weight compounds at 10 and 0.01 ng/μL (left to right). A) Benz(a)anthracene B) Benzo(b)fluoranthene C) Indeno(1,2,3-cd)pyrene**



**FIGURE 3. Continued - C) Indeno(1,2,3-cd)pyrene**



### Sample Precision

• N=10 of soil extracted matrix sample at 0.01ng/μL demonstrated RSD ≤ 5.0 % for 16 PAH compounds.

**TABLE 7. RSD of select high molecular weight compounds in replicate injections of sample at 0.01 ng/μL (n= 10).**

Compound	Area % RSD	Concentration % RSD
Chrysene	1.8	4.5
benzo(b)fluoranthene	2.5	0.0
benzo(k)fluoranthene	2.1	2.4
benzo(a)pyrene	5.0	0.0
indeno(1,2,3-cd)pyrene	2.5	0.0
dibenzo(a,h)anthracene	3.9	1.8
Benzo(ghi)perylene	2.4	0.0

## Conclusion

The methodology mentioned here offers excellent performance for the analysis of PAH content in environmental samples.

- The TriPlus RSH autosampler offers added utility of accurate dilution series preparation which saves time and cost during method development.
- System performance is maintained with ≤10% RSD for all internal standard measurements while achieving the required levels of calibration.
- Precise sample analysis with RSD of ≤ 5 % for 0.01 ng/μL matrix extracted samples and a linear range of 10 - 0.01ng/μL is well-suited for a variable range of PAH analyte concentrations.

## References

1. Khan, Z.; Troquet, J.; Vachelard, C.; Sample Preparation and Analytical Techniques for Determination of Poly Aromatic Hydrocarbons in Soil. *Int. J. Environ. Sci. Tech.* 2005, 2, 275-286.

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