RESTEK environmental

Applications note

The Rtx®-5Sil MS Column Provides the Best Resolution for Gasoline Range Organic (GRO) Compounds Listed in Alaska Method AK101AA

The Alaska Department of Environmental Conservation (ADEC) developed a new technique for the gas chromatographic (GC) analysis of gasoline range organic (GRO) compounds in soil, water, and waste water—Method AK101AA. This method quantitates aromatic and aliphatic compounds from C6 (hexane) to C10 (decane), and is capable of a higher level of accuracy over existing GRO methods. Restek's Rtx®-5Sil MS column is ideal for the analysis of GRO compounds, and specifically meets the requirements of Method AK101AA.

The key difference between AK101AA and other GRO methods that use photoionization detection/flame ionization detection (PID/FID) for differentiation of aliphatic and aromatic compounds, is that AK101AA uses the C9 alkyl benzenes (e.g., methyl ethylbenzenes) as target compounds in the calibration mixture. Using specific compound identification reduces error over other GRO methods that rely only on PID ranges for the determination of aromatic compounds. This can help determine the difference between highly degraded gasoline and light components of diesel fuels, such as kerosene and arctic fuel.

Method AK101AA prevents a high bias in reporting of aromatic compounds when they are in the presence of alkenes and alkynes. These are straight-chain unsaturated compounds that can give a false positive on the PID. Because all gasoline compounds respond on the FID, the total quantitation of gasoline is achieved with this detector, and the identification of single compounds are performed with the more selective PID detector. Method AK101AA also disregards analytes eluting before C6 because these pentanes and oxygenates have similar retention and are poorly resolved.

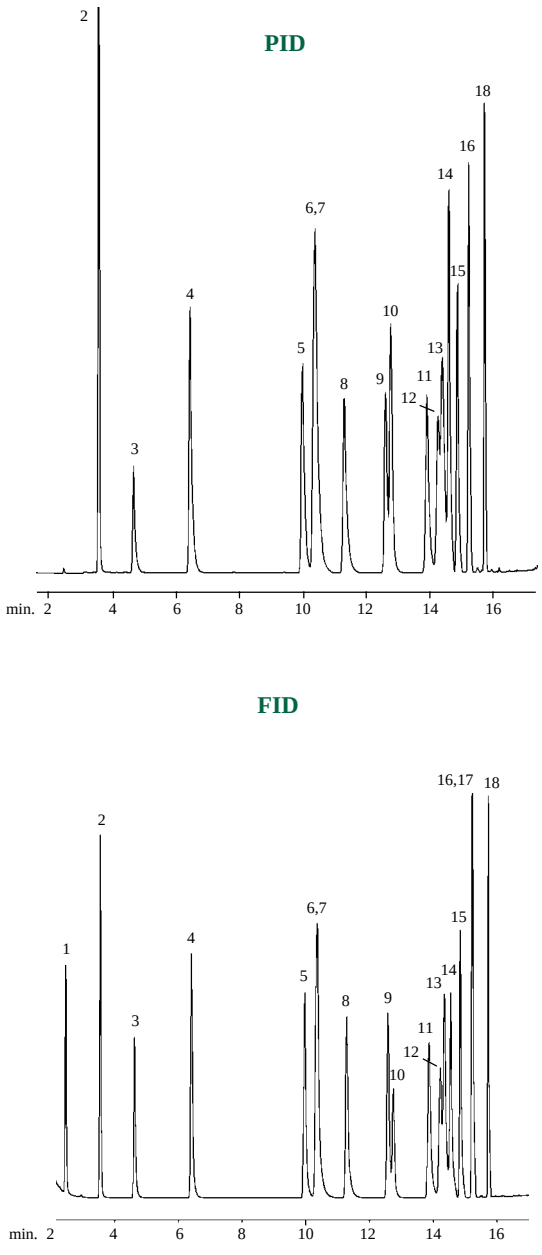
Peak List and Conditions for Figure 1

1. hexane
2. benzene
3. α,α,α-trifluorotoluene (ss)
4. toluene
5. ethylbenzene
6. *m*-xylene
7. *p*-xylene
8. *o*-xylene
9. isopropylbenzene
10. 4-bromo-fluorobenzene (ss)
11. *n*-propylbenzene
12. 1-ethyl-3-methylbenzene
13. 1-ethyl-4-methylbenzene
14. 1,3,5-trimethylbenzene
15. 1-ethyl-2-methylbenzene
16. 1,2,4-trimethylbenzene
17. decane
18. 1,2,3-trimethylbenzene

40m, 0.45mm ID, 1.50µm Rtx®-5Sil MS (cat.# 12798). Injection of 4-bromofluorobenzene (cat.# 30026); α,α,α-trifluorotoluene (cat.# 30048), decane, hexane, and Alaska aliphatic/aromatic GRO mix (cat.# 30461). **GC:** Finnigan 9001; **Column flow:** 9mL/min.; **Concentrator:** Tekmar LSC-3000 Purge & Trap, BTEX trap; **Interface:** direct with Siltek™ transfer line; **Oven temp.:** 40°C (hold 2 min.) to 85°C @ 4°C/min. (hold 1 min.) to 225°C @ 40°C/min. (hold 2 min.); **Det.:** FID (280°C)/PID (200°C); **Make-up flow rate:** 15mL/min.

Figure 1

The Rtx®-5Sil MS column resolves the alkyl benzenes and all the branched aromatic compounds listed in the Alaska GRO Method AK101AA providing more accurate identification and quantitation.

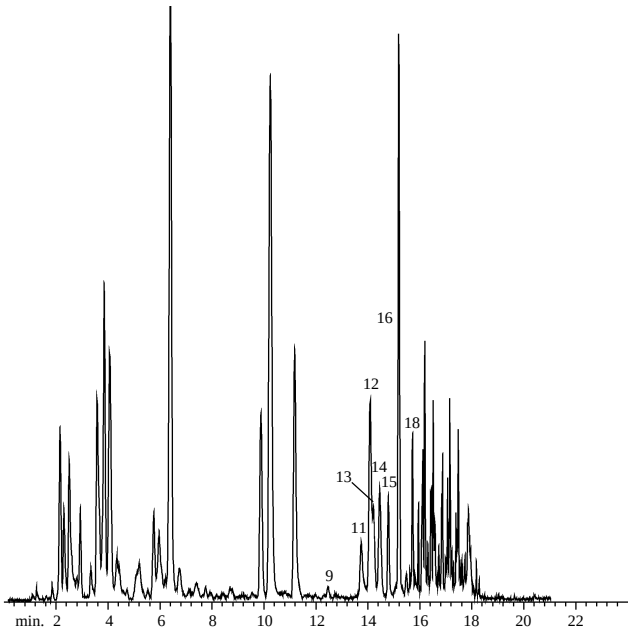


environmental

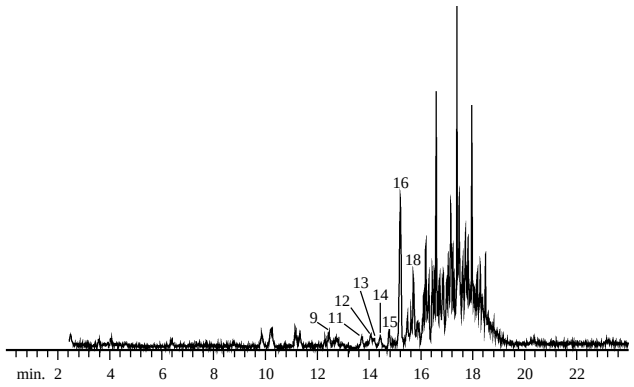
Figure 2

Comparing patterns and elution can help determine unweathered gasoline, kerosene, and diesel fuel.

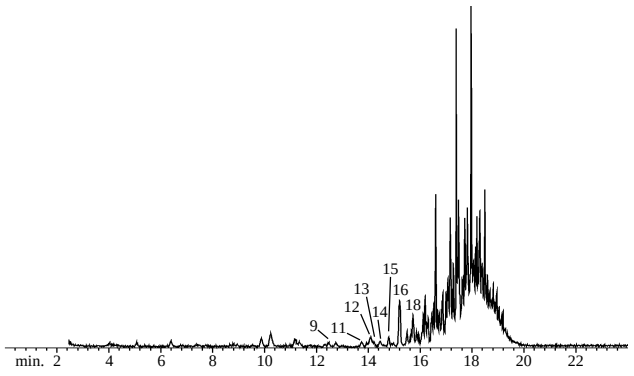
Unweathered gasoline



Unweathered kerosene



Unweathered diesel fuel



The Rtx®-5Sil MS column is capable of resolving all 13 aromatic compounds listed in the method. Columns commonly used for GRO analysis, such as the Rtx®-5 and Rtx®-502.2 columns, cannot adequately resolve the C9 alkyl benzenes. The Rtx®-5Sil MS phase design, column dimensions, and suggested GC conditions are optimized to provide the best possible resolution of the alkyl benzenes and all the branched aromatics listed in the Alaska method (Figure 1). Additionally, the 40m length and a 0.45mm internal diameter (ID) results in faster GC run-times, reduced cost, and lower column bleed. Bleed levels are exceptionally low even at temperatures up to 300°C.

The FID chromatogram in Figure 1 shows the elution of the AK101AA target compounds with the addition of two surrogates and two window markers—α,α,α-trifluorotoluene and 4-bromofluorobenzene, and C6 and C10 , respectively. Two of the eight aromatic C9 compounds—1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene—have longer retention times on the Rtx®-5Sil MS column than the C10 marker, thus these two analytes elute after decane. All the C9 aromatic compounds are included for analyte quantitation on the PID, whereas the FID uses the total gasoline range quantitation, which ends with C10.

Unweathered gasoline, kerosene, and diesel fuel were analyzed under the same conditions to illustrate the differences in their patterns and elution (Figure 2). These three different fractions of petroleum were analyzed using GC/mass spectrometry (MS), with the C9 aromatic compounds labeled. The distribution and concentration of the C9 aromatics is different depending on the following: degree of weathering, type of fuel, and source of the petroleum. It is important to run both weathered and unweathered fuels using PID/FID and your conditions to assist in determining the types of petroleum and degrees of weathering.

Figure 3 shows examples of the C9 aromatic compounds found in gasoline and kerosene, analyzed using GC/MS in selected ion monitoring (SIM) mode and scanning for M/Z 120. These alkylbenzenes are the only compounds that share ions 105 and 120 in this region of the chromatogram. Concentrations of C9 compounds found in kerosene and gasoline differ by an order of magnitude; therefore, the standards were made in two different concentrations to produce a similar signal intensity on the MS system. The area of each C9 aromatic hydrocarbon was compared relative to the total area of all eight of these compounds in

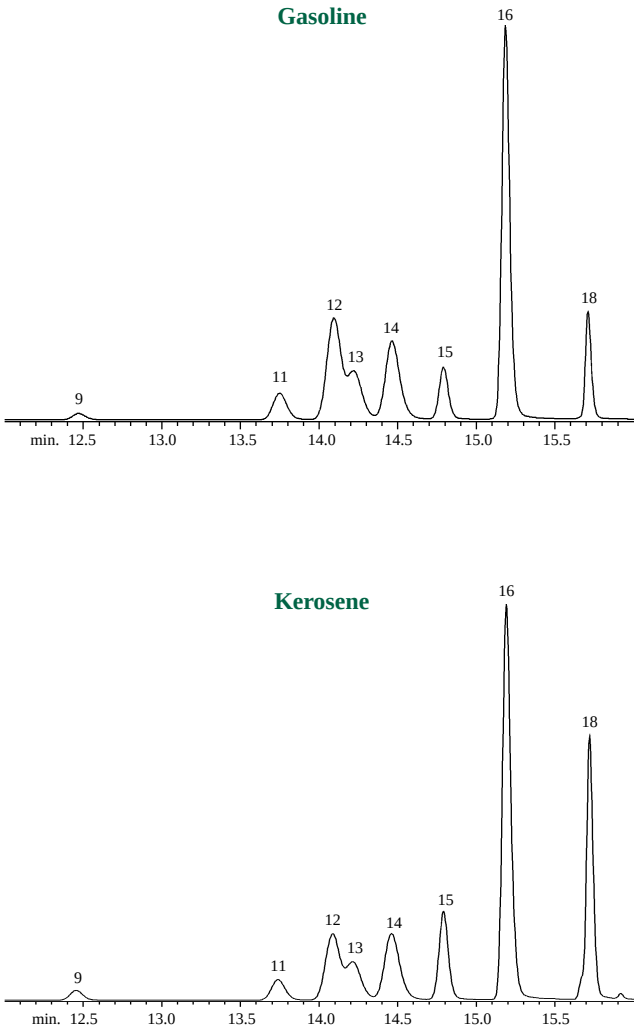
Peak List and Conditions for Figure 2

1. hexane
2. benzene
3. α,α,α-trifluorotoluene (ss)
4. toluene
5. ethylbenzene
6. *m*-xylene
7. *p*-xylene
8. *o*-xylene
9. isopropylbenzene
10. 4-bromo-fluorobenzene (ss)
11. *n*-propylbenzene
12. 1-ethyl-3-methylbenzene
13. 1-ethyl-4-methylbenzene
14. 1,3,5-trimethylbenzene
15. 1-ethyl-2-methylbenzene
16. 1,2,4-trimethylbenzene
17. decane
18. 1,2,3-trimethylbenzene

40m, 0.45mm ID, 1.50µm Rtx®-5Sil MS (cat.# 12798).
Injections of gasoline, kerosene, and diesel.
Column flow: 9mL/min.; **Concentrator:** Tekmar LSC-3000 Purge & Trap, BTEX trap; **Interface:** direct with Siltek™ transfer line; **Oven temp.:** 40°C (hold 2 min.) to 85°C @ 4°C/min. (hold 1 min.) to 225°C @ 40°C/min. (hold 2 min.); **Det.:** GC/MS TIC.

Figure 3

Distribution of C9 for varying types of petroleum are different, which can aid in fuel identification and quantitation.



Peak List and Conditions for Figure 3

1. hexane
2. benzene
3. α,α,α-trifluorotoluene (ss)
4. toluene
5. ethylbenzene
6. *m*-xylene
7. *p*-xylene
8. *o*-xylene
9. isopropylbenzene
10. 4-bromo-fluorobenzene (ss)
11. *n*-propylbenzene
12. 1-ethyl-3-methylbenzene
13. 1-ethyl-4-methylbenzene
14. 1,3,5-trimethylbenzene
15. 1-ethyl-2-methylbenzene
16. 1,2,4-trimethylbenzene
17. decane
18. 1,2,3-trimethylbenzene

40m, 0.45mm ID, 1.50µm Rtx®-5Sil MS (cat.# 12798). Injections of gasoline and kerosene. **Column flow:** 9mL/min.; **Concentrator:** Tekmar LSC-3000 Purge & Trap, BTEX trap; **Interface:** direct with Siltek™ transfer line; **Oven temp.:** 40°C (hold 2 min.) to 85°C @ 4°C/min. (hold 1 min.) to 225°C @ 40°C/min. (hold 2 min.); **Det.:** GC/MS SIM mode for ion 120 only.

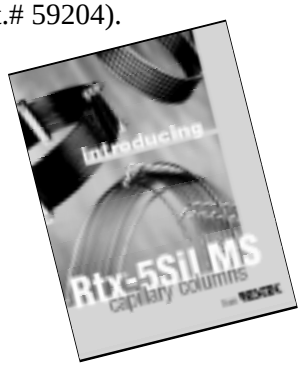
each chromatogram. 1-ethyl-2-methylbenzene and 1,2,3-trimethylbenzene distributions are different for gasoline and kerosene using our standards. Other slight differences were noted between 1-ethyl-3-methylbenzene and 1,3,5-trimethylbenzene requiring separation of the ethyl-methylbenzene isomers. It is important to stress that results may vary due to different fuel sources and the degree of weathering; the point is that the distribution of C9 for varying types of petroleum are different, and these differences can aid in fuel identification and quantitation.

The standards for Method AK101AA consist of a mixture of 13 aromatic compounds. Restek offers this mixture complete with quality assurance (QA) documentation and a Certificate of Analysis, which can be used for audits as well as for internal QA needs. Our Alaska GRO standards are made in the correct concentrations, ensuring accurate identification and quantitation of environmental samples.

Use of the Rtx®-5Sil MS column and the analytical method outlined in Method AK101AA will achieve the best possible resolution of the alkyl benzenes and all the listed branched aromatics.

for more info

Request the *Rtx®-5Sil MS Capillary Columns* flyer (lit. cat.# 59204).



Product Listing

Rtx®-5Sil MS Columns

ID	df (µm)	Stable to	30m	40m	60m
0.45mm	1.50	300/320°C	—	12798	—

Siltek™ Guard Columns

nominal ID	nominal OD	5-meter	10-meter
0.25mm	0.37 ± 0.04mm	10026	10036
0.32mm	0.45 ± 0.04mm	10027	10037
0.53mm	0.69 ± 0.04mm	10028	10038

Alaska UST Method AK101AA

benzene
ethylbenzene
1-ethyl-2-methylbenzene
1-ethyl-3-methylbenzene
1-ethyl-4-methylbenzene
isopropylbenzene
n-propylbenzene
toluene
1,2,3-trimethylbenzene
1,2,4-trimethylbenzene
1,3,5-trimethylbenzene
o-xylene
m-xylene
p-xylene

1,000µg/mL ea. in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30461	30461-510	
w/data pack	30461-500	30461-520	30561

4-bromofluorobenzene

2,000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30026	30026-510	
w/data pack	30026-500	30026-520	30126

10,000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30082	30082-510	
w/data pack	30082-500	30082-520	30182

α,α,α-trifluorotoluene

2,000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30048	30048-510	
w/data pack	30048-500	30048-520	30148

10,000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30083	30083-510	
w/data pack	30083-500	30083-520	30183

Unleaded Gasoline Composite

From samples of regular- and premium-grade unleaded gasoline from three sources, blended to form a composite sample.

2,500µg/mL ea. in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30081	30081-510	
w/data pack	30081-500	30081-520	30181

50,000µg/mL ea. in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30205	30205-510	
w/data pack	30205-500	30205-520	30305

50,000µg/mL ea. in P&T methanol, 5mL/ampul.

	each	5-pack	10-pack
	30206	30206-510	
w/data pack	30206-500	30206-520	30306

Suitable for Matrix Spikes and Laboratory Control Samples

WA VPH Marker Standard

decane (C10)
dodecane (C12)
hexane (C6)
1-methylnaphthalene
naphthalene
octane (C8)
pentane (C5)
toluene
1,2,3-trimethylbenzene

1,000µg/mL ea. in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30450	30450-510	
w/data pack	30450-500	30450-520	30550

WA VPH Standard

benzene
decane (C10)
dodecane (C12)
ethylbenzene
hexane (C6)
1-methylnaphthalene
methyl-*tert*-butyl ether
naphthalene
octane (C8)
pentane (C5)
toluene
1,2,3-trimethylbenzene
m-xylene
o-xylene
p-xylene

1,000µg/mL ea. in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30451	30451-510	
w/data pack	30451-500	30451-520	30551