TO-3 BTEX and TPH

Method TO-3 uses cryogenic trapping and a gas chromatograph with a flame ionization detector (FID) to measure volatile organic compounds collected in Summa Canisters or Tedlar Bags. This method is suitable for a wide range of hydrocarbons and other volatile compounds having boiling points in the range of –10 to 200C. It was the forerunner to EPA TO-14, but has been used as a method for BTEX, fuel oxygenates, and total petroleum hydrocarbons (TPH) reported as gasoline or diesel.

The EAS modifications to this method include the following; target list and QC criteria. The LCS compounds are in bold in Table 13.1b.

Table 13.1a
Summary of QC Criteria for TO-3 BTEX Oxygenates

Parameter	EAS TO-3 Modified	TO-3 Method
Initial Calibration	5 points relative response factors See Table 13.1b	4 points with a linear regression Weekly
Calibration Check Sample (CCS)	Run after Initial Calibration Curve See Table 13.1b	Not Specified
Continuing Calibration Verification (CCV)	Daily (24 hours) See Table 13.1b	Prior to Sample Analysis and every 4-6 hours
Method Blank	Target analytes less than LOQ	Not Specified
Laboratory Control Spike	With daily batch See Table 13.1b	Not Specified
Duplicate-Either Lab Control Dup Sample Dup	With daily batch <30%	Not Specified
Holding Times - Canister Tedlar Bag	30 Days 3 Days	Not Specified
Canister Certification	Certification <0.2 ppbv by full scan GC/MS	

Table 13.1b
TO-3 BTEX Oxygenates Compound List

Analyte	MDL ppbV	LOQ ppbV	Criteria		
			ICAL CCV %D	LCS CCV %R	Duplicate %RPD
Benzene	1	1	<30	**75-125**	**<30**
Toluene	1	1	<30	**75-125**	**<30**
Ethyl Benzene	1	1	<30		<30
m & p Xylene	1	1	<30	**75-125**	**<30**
o -Xylene	1	1	<30	**75-125**	**<30**
TPH (gasoline)	10	10			<30
TPH (Diesel)	10	10			<30

TO-3 Detailed Hydrocarbon Analysis (DHA) PAMS Compounds

Method TO-3 DHA uses cryogenic trapping and a gas chromatograph with a flame ionization detector (FID) to measure hydrocarbons collected in Summa Canisters. EAS performs a modified version of the method which follows the protocol contained in the EPA Guidance Document "Technical Assistance Documents for Sampling and Analysis of Ozone Precursors". The method is used to determine 90 individual hydrocarbons, including the 55 PAMS compounds in air and gas samples. The FID is calibrated using propane and hexane and the response of individual hydrocarbons are calculated against these compounds in ppbC according to the procedure described in the guidance document. This method can be used for forensic hydrocarbon analysis and PIANO analysis of air and gas samples.

Table 13.1c
Summary of QC Criteria for TO-3 Modified for DHA and PAMS Hydrocarbon Analysis

Parameter	EAS TO-3 DHA Modified	TO-3 Method
Initial Calibration	Five points relative response factors run on Hexane. See Table 13.1d	4 points with a linear regression Weekly
Calibration Check Sample (CCS)	Run after Initial Calibration Curve – 55 PAMS See Table 13.1d	Not Specified
Continuing Calibration Verification (CCV)	Hexane Daily (24 hours) See Table 13.1d	Prior to Sample Analysis and every 4-6 hours
Method Blank	Target analytes less than LOQ	Not Specified
Laboratory Control Spike	With daily batch See Table 13.1d	Not Specified
Duplicate-Either Lab Control Dup Sample Dup	With daily batch See Table 13.1d	Not Specified
Canister Holding Times	30 days	Not Specified
Canister Certification	Certification <0.2 ppbv by full scan GC/MS	

Laboratory Control Spike is made up of a short list of hydrocarbon compounds. They appear in Table 13.1d in bold.

Table 13.1d
Method TO-3 DHA Compound List

The following compounds can be reported as part of the TO-3 DHA analysis. All of the compounds are calibrated against hexane according to the EPA guidance document.

Analyte	MDL ppbV	LOQ ppbV	Criteria			
			ICAL %RSD	CCV %D	LCS %D	Duplicate %RPD
Ethene	0.5	1.5				<20%
Acetylene	0.5	1.5				<20%
Ethane	0.5	1.5				<20%
Propene	0.5	1.5				<20%
Propane	0.5	1.5				<20%
i-Butane	0.5	1.5				<20%
Methanol	0.5	1.5				<20%
1-Butene	0.5	1.5				<20%
1,3-Butadiene	0.5	1.5				<20%
n-Butane	0.5	1.5				<20%
t-2-Butene	0.5	1.5				<20%
c-2-Butene	0.5	1.5				<20%
Ethanol	0.5	1.5				<20%
3-Methyl-1-butene	0.5	1.5				<20%
Acetone	0.5	1.5				<20%
i-Pentane	0.5	1.5				<20%
1-Pentene	0.5	1.5				<20%
Isopropanol	0.5	1.5				<20%
2-Methyl-1-butene	0.5	1.5				<20%
n-Pentane	0.5	1.5				<20%
Isoprene	0.5	1.5				<20%
t-2-Pentene	0.5	1.5				<20%
c-2-Pentene	0.5	1.5				<20%
Tert butyl alcohol	0.5	1.5				<20%
2-Methyl-2-butene	0.5	1.5				<20%
2,2-Dimethylbutane	0.5	1.5				<20%
Cyclopentene	0.5	1.5				<20%
n-Propanol	0.5	1.5				<20%
Cyclopentane	0.5	1.5				<20%
Methyl tert butyl ether	0.5	1.5				<20%
2,3-Dimethylbutane	0.5	1.5				<20%
2-Methylpentane	0.5	1.5				<20%
3-Methylpentane	0.5	1.5				<20%
1-Hexene	0.5	1.5				<20%

Analyte	MDL ppbV	LOQ ppbV	Criteria			
			ICAL %RSD	CCV %D	LCS %D	Duplicate %RPD
n-Hexane	0.5	1.5	<30	<30		<20%
Diisopropyl ether	0.5	1.5				<20%
3-Methylcyclopentene	0.5	1.5				<20%
Ethyl tert butyl ether	0.5	1.5				<20%
Methylcyclopentane	0.5	1.5				<20%
2,4-Dimethylpentane	0.5	1.5				<20%
Benzene	0.5	1.5			75-125	<20%
Cyclohexane	0.5	1.5				<20%
2-Methylhexane	0.5	1.5				<20%
2,3-Dimethylpentane	0.5	1.5				<20%
3-Methylhexane	0.5	1.5				<20%
2-Methyl-1hexene	0.5	1.5				<20%
Tert amyl methyl ether	0.5	1.5				<20%
2,2,4-Trimethylpentane	0.5	1.5			75-125	<20%
n-Heptane	0.5	1.5				<20%
Methylcyclohexane	0.5	1.5				<20%
2,5-Dimethylhexane	0.5	1.5				<20%
2,4-Dimethylhexane	0.5	1.5				<20%
2,3,4-Trimethylpentane	0.5	1.5				<20%
Toluene	0.5	1.5			75-125	<20%
2,3-Dimethylhexane	0.5	1.5				<20%
2-Methylheptane	0.5	1.5				<20%
4-Methylheptane	0.5	1.5				<20%
3-Ethyl-3-methylpentane	0.5	1.5				<20%
3-Methylheptane	0.5	1.5				<20%
2-Methyl-1-heptene	0.5	1.5				<20%
n-Octane	0.5	1.5				<20%
Ethylbenzene	0.5	1.5				<20%
m,p-xylene	0.5	1.5			75-125	<20%
Styrene	0.5	1.5				<20%
o-xylene	0.5	1.5			75-125	<20%
1-Nonene	0.5	1.5				<20%
n-Nonane	0.5	1.5				<20%
i-Propylbenzene	0.5	1.5				<20%
n-propylbenzene	0.5	1.5				<20%
a-Pinene	0.5	1.5				<20%
3-Ethyltoluene	0.5	1.5				<20%
4-Ethyltoluene	0.5	1.5				<20%

Analyte	MDL ppbV	LOQ ppbV	Criteria			
			ICAL %RSD	CCV %D	LCS %D	Duplicate %RPD
1,3,5-Trimethylbenzene	0.5	1.5			75-125	<20%
2-Ethyltoluene	0.5	1.5				<20%
b-Pinene	0.5	1.5				<20%
1,2,4-Trimethylbenzene	0.5	1.5				<20%
n-Decane	0.5	1.5				<20%
1,2,3-Trimethylbenzene	0.5	1.5				<20%
Indan	0.5	1.5				<20%
d-Limonene	0.5	1.5				<20%
1,3-Diethylbenzene	0.5	1.5				<20%
1,4-Diethylbenzene	0.5	1.5				<20%
n-Butylbenzene	0.5	1.5				<20%
1,4-Dimethyl-2-ethylbenzene	0.5	1.5				<20%
1,3-Dimethyl-4-ethylbenzene	0.5	1.5				<20%
1,2-Dimethyl-4-ethylbenzene	0.5	1.5				<20%
Undecane	0.5	1.5				<20%
1,2,4,5-Tetramethylbenzene	0.5	1.5				<20%
1,2,3,5-Tetramethylbenzene	0.5	1.5				<20%
Napthalene	0.5	1.5				<20%
Dodecane	0.5	1.5				<20%

Table 13.1e
Method TO-3 DHA Optional Parameter List

In addition to the standard target compounds listed above the following optional parameters can be reported along with the individual compounds.

Analyte	MDL ppbV	LOQ ppbV	Criteria		
			ICAL/ CCV %D	LCS %R	Duplicate %RPD
Total Petroleum Hydrocarbons:	5	10			<30
Total Non-Methane Hydrocarbons	5	10			<30
Total Volatile Organic Compounds	5	10			<30
TPH (gasoline)	5	10			<30
TPH (diesel)	5	10			<30
Sample: Composition	5	10			<30
Paraffins					
Isoparaffins					
Aromatics					
Napthlenes					
Olefins					
Carbon Ranges:					
C2 (ethane)	5	10			
C3 (propane)	5	10			
C4 (Butane)	5	10			
C5 (Pentane)	5	10			
C6 (Hexane)	5	10			
C7 (Heptane)	5	10			
C8 (Octane)	5	10			
C9 (Nonane)	5	10			
C10 (Decane)	5	10			
C11+ (Undecane)	5	10			