Organic Gas Speciation Profile for E10 Winter-Grade Gasoline Fuel (OG694)

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1 Introduction

In the current CARB emission inventory, E10 gasoline fuel profile OG692 (summer-grade) is assigned to categories of spillage during vehicle refueling at gasoline dispensing facilities (Appendix 1). Due to the lack of a winter-grade fuel profile, the summer-grade profile OG692 is applied to both summer and winter seasons of 2010 and later years when E10 is in use.

This document describes the development of a new speciation profile OG694 for winter-grade E10 gasoline. The profile was generated based on fuel analysis of eight winter-grade E10 samples collected during the CARB Light Duty Vehicle Surveillance Program Series 19 (VSP19). The new profile OG694 will replace the current OG692 for the spillage categories (Appendix 1) for winters of 2010 and later years.

2 Methodology

In April 2013 and March 2014, eight total fuel samples were extracted from the tanks of eight candidate VSP19 light-duty gasoline vehicles, respectively. The vehicles accepted into this program were selected from the in-use fleet within a radius of 50 miles from the Haggen-Smit Laboratory in El Monte, CA [1]. Detailed hydrocarbon analyses (DHA) of fuel samples were performed at Southwest Research Instituted (San Antonio, TX) and oxygenate analyses were conducted in the Fuel Analysis and Method Evaluation Section (FAMES) fuel lab in ARB's Haggen-Smit Laboratory.

In the DHA tests, over two hundred hydrocarbon compounds were detected in the liquid fuel samples using ASTM6729 (*Standard Test Method for Determination of Individual Components in Spark ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography*). Because this method is focused on hydrocarbon analysis, oxygenates in the samples were quantified separately in CARB's fuel lab using ASTM D4815 (*Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography*). Among the species identified in the analyses, three of them are not included in the existing CARB core chemical database – the CEIDARS POLLUTANT table. Thus, new CARB SAROAD codes are generated for these species (Table 1). The speciation profile for each test fuel was obtained by dividing the emission of each species by the total emissions of all measured species. The new profile OG694 was then composited by averaging the eight individual winter-grade E10 speciation profiles.

Table 1. New CARB SAROAD codes to be added to the CEIDARS POLLUTANT table for OG694

CARB SAROAD	*CAS*	*Chemical Name*	*Formula*	*Molecular Weight*
43321	61228-09-9	5-methyl-3-heptyne	C_8H_{14}	110.20
43322	33933-74-3	4-ethyl-3-heptene	C_9H_{18}	126.24
43324	2146-38-5	1-ethylcyclopentene	C_7H_{12}	96.17

3 Results and Discussion

The details of the new profile OG694 are listed in Appendix 2. The most abundant species in OG694 include ethanol (10.8%), isopentane (7.6%), toluene (5.4%) and n-butane (4.2%). The ratio of TOG/THC (total organic gases/total hydrocarbon) calculated from the profile is 1.075. It can be used to convert THC emission mass to actual weight TOG. The ROG/TOG (reactive organic gases/total organic gases) ratio calculated from the profile is 1.000.

The new winter-grade E10 profile (OG694) is compared with the existing summer-grade E10 profile (OG692) in Section 3.1 to see the differences between winter and summer fuels. Additionally, the new E10 winter profile (OG694) is compared with the E6 winter profile (OG682) in Section 3.2 to identify the changes between E10 and E6 fuels.

3.1 E10 *Winter* Fuel Profile vs. E10 *Summer* Fuel Profile (OG694 vs. OG692)

Based on a comparison of carbon number, the E10 winter fuel (OG694) has 4.4% more C4-compounds than the E10 summer fuel (OG692) (Figure 1). The majority of the C4-compounds in the difference is n-butane (3.7%). This is because the winter fuel always contains more n-butane to achieve higher RVP (Reid Vapor Pressure).

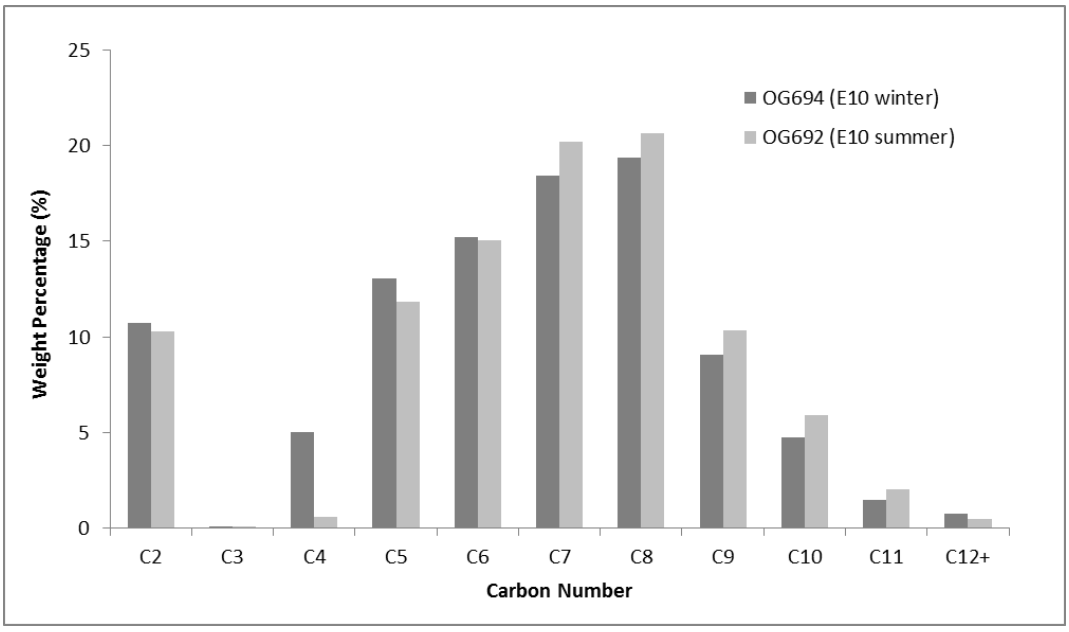

Figure 1. Profile comparison between OG694 (E10 winter) and OG692 (E10 summer) by carbon number

Comparing chemical groups, the winter profile (OG694) and the summer profile (OG692) are close to each other. The differences mainly exist in paraffins and aromatics. Figure 2 shows that the winter fuel (OG694) has 3.8% more paraffins (3.7% is n-butane), but 2.4% less aromatics, compared to the summer fuel (OG692).

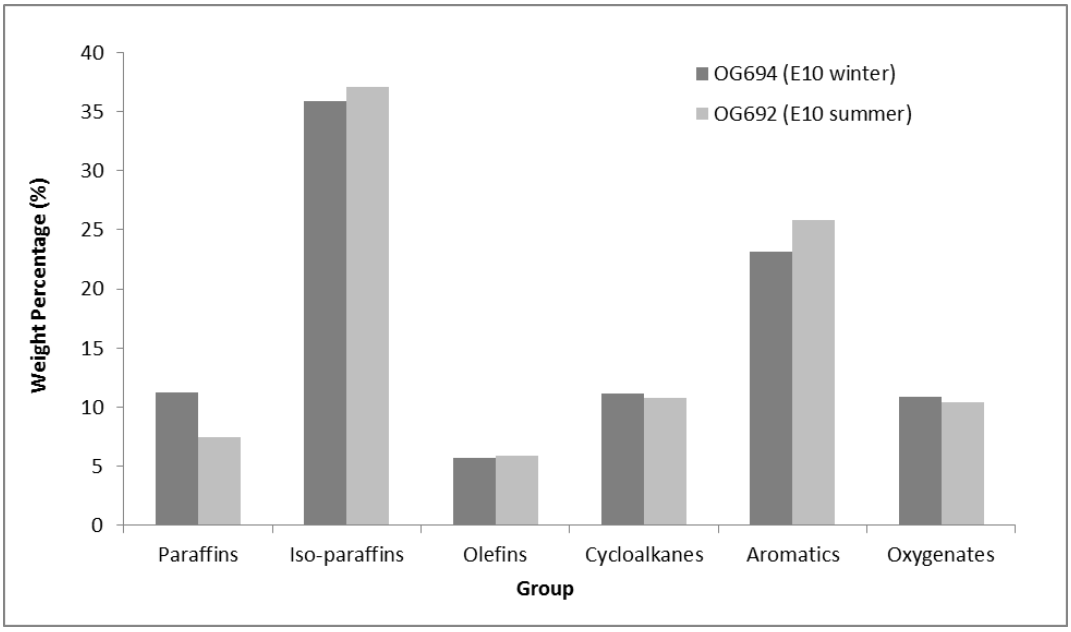

Figure 2. Profile comparison between OG694 (E10 winter) and OG692 (E10 summer) by compound group

3.2 *E10* Winter Fuel Profile vs. *E6* Winter Fuel Profile (OG694 vs. OG682)

Based on carbon number, the E10 winter fuel (OG694) has 4.4% more C2-species than E6 winter fuel (OG682) (Figure 3). This difference is mainly ethanol, which increases from about 6% for E6 fuel to about 10% for E10 fuel. Figure 3 also shows that E10 winter fuel (OG694) has lower contents of C7 to C9-compounds compared to the E6 winter fuel (OG682).

A comparison of compound groups shows that the E10 winter fuel (OG694) has more oxygenates than the E6 winter fuel (OG682) mainly due to ethanol (Figure 4). Figure 4 also indicates that the new E10 profile (OG694) contains about 6.9% less aromatics than the E6 profile (OG682).

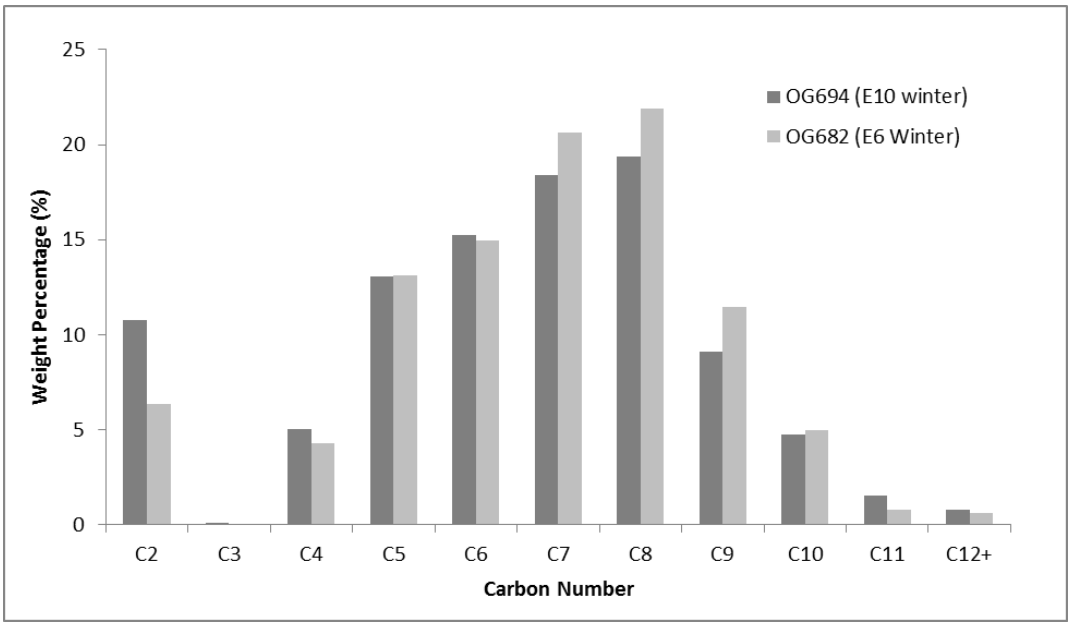

Figure 3. Profile comparison between OG694 (E10 winter) and OG682 (E6 winter) by carbon number

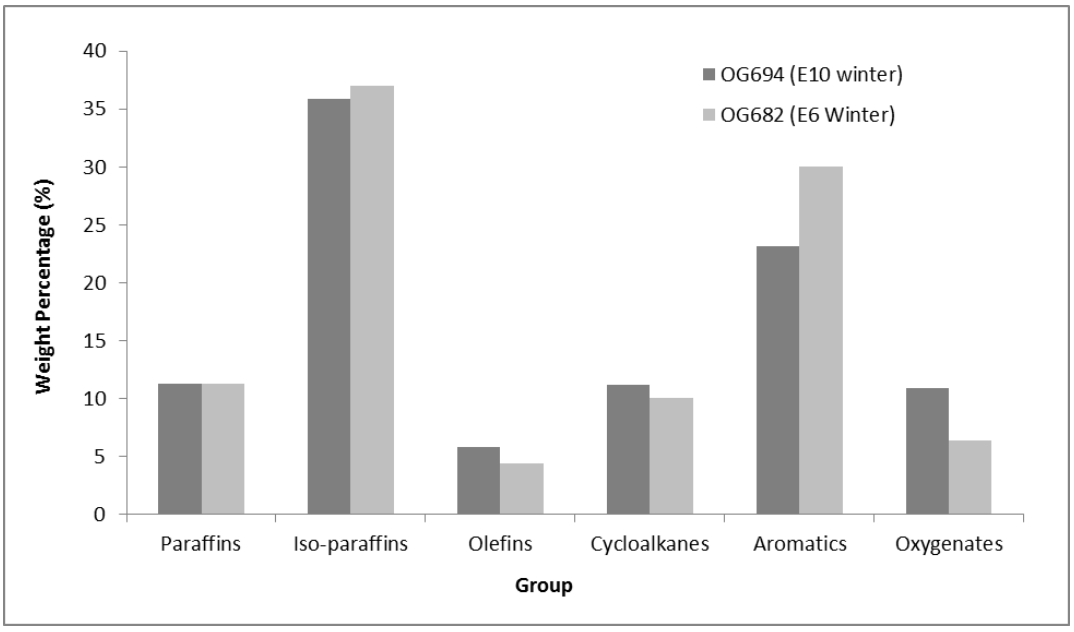

Figure 4. Profile comparison between OG694 (E10 winter) and OG682 (E6 winter) by compound group

4 Estimated Impacts of the Profile Update on the Emission Inventory

The newly-developed profile OG694 will replace the current profile G692 for categories of spillage during vehicle refueling at gasoline dispensing facilities (Appendix 1) for winter of 2010 and later when E10 gasoline is used in California. The winter profile will be used only for the months that the RVP is not regulated. It should be noted that the RVP control period varies for

different air basins [2]. Based on CEPAM [3] data (California 2016 Ozone SIP Emission Inventory, Version 1.00), statewide 2012 annual average TOG emissions for the spillage categories are 4.35 tons/day, which is 0.08% of the grand total statewide TOG emissions. Since the ROG/TOG ratio derived from the new profile OG694 is 1.000, the same as the one for OG692, there will be no impact on ROG emissions with the profile update. The ozone forming potential (OFP) calculated based on the SARPC07 mechanism [4] is 2.87, which is 4.33% lower than the one estimated for the currently-used profile OG692. Using the new OG694 for the winter season will result in 1.97% more benzene emissions but 8.00% less toluene emissions compared to the current estimation with OG692 (Table 2).

Table 2. Impact of OG694 update on emissions and ozone forming potential for gasoline spillage categories (2012)

Statewide Annual Ave. Emissions		*OG692 [Current profile] (tons/day)*	*OG694 [New profile] (tons/day)*	*Change*	
				Emission (tons/day)	*Percentage*
ROG		4.35	4.35	0	0
Ozone forming potential, MIR (g O3/g ORG)		3.00	2.87	-0.13	-4.33%
Toxics	Benzene	3.05E-02	3.11E-02	+6.00E-04	+1.97%
	Toluene	0.25	0.23	-0.02	-8.00%

References:

1. Magbuhat, S., *Supplemental Test Procedures Amendment 2 For Light-Duty Vehicle Surveillance Program Series 19*, 2012, California Air Resources Board.
2. *California Code of Regulations, The California Refomulated Gasoline Regulations, Title 13, , Sections 2250-2273.5*: California Air Resources Board.
3. *CEPAM*, 2014, California Air Resources Board, *Accessed*: October 30, 2014.
4. *Regulation for Reducing Emissions from Consumer Products, California Code of Regulations,* in *Title 17.*

Appendix 1. SCCs/EICs associated with liquid gasoline profile

SCC/EIC	*Names*		
46565	GASOLINE DISP. FACIL	VEHICLE REFUELING	SPILLAGE
40600602	PETROLEUM MARKTNG	MISCELLANEOUS	SPILL LOSS W/O CNTLS
33038011000000	GASOLINE DISP. FACIL	VEHICLE REFUELING	SPILLAGE

Appendix 2. OG speciation profiles for E10 winter liquid gasoline fuel—OG694

Species Name	*SAROAD*	*Weight Percentage (%)*
(2-methylpropyl)benzene	45235	0.031852
1-(1,1-dimethylethyl)-3,5-dimethylbenzene	45256	0.077506
1,1,3-trimethylcyclohexane	91064	0.082827
1,1,3-trimethylcyclopentane	91030	0.163519
1,1,4-trimethylcyclohexane	91057	0.051848
1,2,3,4-tetrahydro-2-methylnaphthalene	43382	0.007783
1,2,3,5-tetramethylbenzene	91104	0.200100
1,2,3-trimethylbenzene	45225	0.405016
1,2,4,5-tetramethylbenzene	91103	0.152523
1,2,4-triethylbenzene	91119	0.022187
1,2,4-trimethylbenzene	45208	1.761372
1,2,4-trimethylcyclohexane	99099	0.043360
1,2-diethylbenzene	98154	0.031336
1,2-dimethyl-3-ethylbenzene	45254	0.074739
1,2-dimethyl-4-ethylbenzene	45252	0.316643
1,2-isodipropylbenzene	91114	0.081059
1,3,5-triethylbenzene	91117	0.020506
1,3,5-trimethylbenzene	45207	0.603280
1,3-cyclopentadiene	90026	0.004119
1,3-diethylbenzene	45113	0.090738
1,3-dimethyl-2-ethylbenzene	45253	0.065238
1,3-dimethyl-4-ethylbenzene	45251	0.173772
1,3-dimethyl-5-ethylbenzene	45257	0.237904
1,3-dipropylbenzene	45237	0.118128
1,4-diethylbenzene	45114	0.141098
1,4-dimethyl-1-cyclohexene	43188	0.004759
1,4-dimethyl-2-ethylbenzene	45250	0.169392
1-butene	43213	0.026095
1-ethyl-2,4,5-trimethylbenzene	43381	0.012798
1-ethyl-4-isopropylbenzene	91102	0.026633
1-ethylcyclopentene	43324	0.083498
1-heptene	98005	0.002121
1-hexene	43245	0.061063
1-methyl-1-ethylcyclohexane	91081	0.107804

1-methyl-2-ethylbenzene	99915	0.362574
1-methyl-2-n-butylbenzene	45243	0.020150
1-methyl-2-n-propylbenzene	98178	0.074781
1-methyl-3-ethylbenzene	99912	1.089442
1-methyl-3-isopropylbenzene	98153	0.012168
1-methyl-3-n-propylbenzene	98152	0.291212
1-methyl-4-(1-methylpropyl)benzene	43189	0.063487
1-methyl-4-ethylbenzene	99914	0.480900
1-methyl-4-isobutylbenzene	99064	0.065090
1-methyl-4-isopropylbenzene	91094	0.007465
1-methyl-4-t-butylbenzene	91100	0.030459
1-methylcyclopentene	92000	0.202153
1-methylnaphthalene	91124	0.059768
1-octene	43265	0.043479
1-pentene	43224	0.168102
2,2,3-trimethylbutane	43160	0.035119
2,2,3-trimethylhexane	91059	0.014091
2,2,3-trimethylpentane	43296	0.062778
2,2,4-trimethylheptane	98174	0.187104
2,2,4-trimethylpentane	43276	2.813663
2,2,5-trimethylhexane	98033	0.754493
2,2-dimethylbutane	43291	0.741718
2,2-dimethylheptane	91056	0.119484
2,2-dimethylhexane	98138	0.032905
2,2-dimethyloctane	98175	0.065045
2,2-dimethylpropane	98130	0.017485
2,3,3-trimethyl-1-butene	91002	0.012049
2,3,3-trimethyl-1-hexene	91054	0.004873
2,3,3-trimethylpentane	43280	0.481009
2,3,4-trimethylpentane	43279	1.060418
2,3,5-trimethylhexane	98141	0.091112
2,3-dimethyl-1-hexene	43190	0.014589
2,3-dimethyl-1-pentene	43384	0.016800
2,3-dimethyl-2-heptene	91079	0.004292
2,3-dimethylbutane	98001	1.222039
2,3-dimethylhexane	98139	0.346342
2,4-dimethylhexane	43277	0.547230
2,4-dimethyloctane	98149	0.080465
2,4-dimethylpentane	43271	1.140517
2,5-dimethylheptane	98143	0.270882
2,5-dimethylhexane	43278	0.472342
2,5-dimethyloctane	98176	0.088722
2,6-dimethylheptane	98157	0.164018
2,6-dimethylnaphthalene	98185	0.022609
2,6-dimethyloctane	98177	0.146884
2,7-dimethyloctane	99095	0.048963
2-ethyl-1-pentene	91022	0.003596
2-methyl-1-butene	43225	0.342122

2-methyl-1-hexene	91020	0.105938
2-methyl-1-octene	91067	0.024347
2-methyl-1-pentene	98040	0.130033
2-methyl-2-butene	43228	0.730329
2-methyl-2-hexene	90028	0.057691
2-methyl-2-octene	91068	0.031295
2-methyl-2-pentene	98004	0.215712
2-methyl-3-ethylpentane	91034	0.119769
2-methyl-cis-3-hexene	91004	0.031201
2-methylheptane	98140	0.863971
2-methylhexane	43275	3.806715
2-methylindan	91108	0.108016
2-methylnaphthalene	91123	0.159965
2-methylnonane	90047	0.026448
2-methyloctane	98146	0.286515
2-methylpentane	43229	3.622953
2-undecene, (e)-	43191	0.009444
3,3-diethylpentane	91072	0.055296
3,3-dimethyl-1-pentene	91000	0.192295
3,3-dimethylhexane	98171	0.040109
3,4-dimethyl-2-pentene	91011	0.042110
3,4-dimethylhexane	98150	0.100539
3,5-dimethylheptane	98144	0.068506
3,6-dimethyloctane	91086	0.015553
3-ethyl-2-pentene	98007	0.020873
3-ethyl-3-hexene	43192	0.012141
3-ethyl-3-methylheptane	43193	0.055851
3-ethyl-3-methylpentane	91036	0.034434
3-ethylheptane	91071	0.066189
3-ethylhexane	91039	0.357385
3-ethylnonane	91097	0.019670
3-ethyloctane	91089	0.034862
3-methyl-1-butene	43223	0.214745
3-methyl-1-hexene	90030	0.009337
3-methyl-5-ethylheptane	91287	0.060121
3-methyl-cis-2-pentene	98163	0.154987
3-methyl-cis-3-hexene	91024	0.025292
3-methylcyclopentene	43272	0.022342
3-methylheptane	43298	0.943835
3-methylhexane	43295	1.749557
3-methylnonane	91090	0.116087
3-methyloctane	98172	0.380660
3-methylpentane	43230	2.236074
3-methyl-trans-2-hexene	91027	0.049331
3-methyl-trans-3-hexene	90032	0.046892
4-ethyl-3-heptene	43322	0.001592
4-ethylheptane	91070	0.017022
4-methyl-1-hexene	91008	0.004473

4-methyl-cis-2-pentene	98170	0.027625
4-methylheptane	43297	0.285821
4-methylindan	91107	0.190463
4-methylnonane	99122	0.114997
4-methyloctane	98173	0.212477
4-methyl-trans-2-hexene	90031	0.045442
4-methyl-trans-2-pentene	43293	0.087692
5-ethyl-1,2,3,4-tetrahydronaphthalene	43385	0.002068
5-methyl-1-hexene	91005	0.088255
5-methyl-3-heptyne	43321	0.000928
5-methylindan	91106	0.171566
5-methylnonane	91088	0.061650
5-undencene	43383	0.012181
benzene	45201	0.715126
butylcyclohexane	90101	0.020000
c10 olefins	43125	0.177265
c11 aromatics	45505	0.183196
c11 cycloalkanes	98071	0.005077
c13 alkyl benzenes	45249	0.001199
c2 alkyl indan	98084	0.020240
c6 olefins	43289	0.007739
c7 cycloalkanes	43115	0.034249
c7 external olefins	43294	0.022443
c8 alkenes	43290	0.175497
c8 cycloalkanes	43116	0.046298
c9 cycloalkanes	43117	0.041787
c9 internal alkenes	98042	0.003253
c9-c12 isoalkanes	99275	0.656292
cis,trans,cis-1,2,4-trimethylcyclohexane	91073	0.029829
cis-1,2-dimethylcyclohexane	91055	0.097064
cis-1,3-dimethylcyclopentane	91018	0.605431
cis-1,trans-2,3-trimethylcyclopentane	91038	0.229197
cis-1-ethyl-2-methylcyclopentane	99093	0.086787
cis-1-ethyl-3-methylcyclopentane	99071	0.238285
cis-2-butene	43217	0.061965
cis-2-hexene	98035	0.096575
cis-2-pentene	43227	0.273702
cis-3-heptene	91025	0.048633
cis-3-nonene	91084	0.003392
cyclohexane	43248	0.992171
cyclohexene	43273	0.026898
cyclopentane	43242	0.394110
cyclopentene	43292	0.117348
dimethylcyclopentene	90065	0.050425
dimethylindans	46750	0.322783
dimethylindene	46752	0.011275
ethanol	43302	10.75125
ethylbenzene	45203	1.104252

ethylcyclohexane	43288	0.373879
ethylcyclopentane	98057	0.385385
indan	98044	0.247844
indene	98048	0.067833
isobutane	43214	0.690390
isobutylcyclohexane	99100	0.006562
isobutylene	43215	0.023396
isopentane	98132	7.554583
isoprene	43243	0.009091
isopropylbenzene	98043	0.059887
isopropylcyclohexane	90120	0.012887
isopropylcyclopentane	43178	0.019611
methylcyclohexane	43261	1.651615
methylcyclopentane	43262	2.536081
methylnonenes	99358	0.025407
m-xylene	45205	3.101961
naphthalene	98046	0.128850
n-butane	43212	4.172262
n-butyl alcohol	43305	0.021967
n-butylbenzene	91098	0.066537
n-decane	43238	0.190774
n-dodecane	43255	0.038895
n-heptane	43232	1.146536
n-hexane	43231	1.805029
n-nonane	43235	0.421318
n-octane	43233	0.665729
n-pentadecane	43260	0.000593
n-pentane	43220	2.709140
n-pentylbenzene	45255	0.048067
n-propanol	43303	0.091579
n-propylbenzene	45209	0.312718
n-tetradecane	43259	0.006129
n-tridecane	43258	0.019994
n-undecane	43241	0.080767
other c12	99035	0.114652
other c9	99032	0.116269
o-xylene	45204	1.740102
pentamethylbenzene	91122	0.023685
propane	43204	0.030475
propylene	43205	0.000122
p-xylene	45206	1.280616
s-pentylbenzene	91111	0.009673
t-butylbenzene	45215	0.051678
t-pentylbenzene	43194	0.089388
toluene	45202	5.375481
trans-1,2-cis-4-trimethylcyclopentane	43312	0.369114
trans-1,2-dimethylcyclopentane	91021	0.701559
trans-1,3-diethylcyclopentane	43195	0.170080

trans-1,3-dimethylcyclohexane	98059	0.612045
trans-1,3-dimethylcyclopentane	91019	0.703661
trans-1,3-pentadiene	90100	0.008725
trans-1-ethyl-3-methylcyclopentane	99085	0.167552
trans-1-ethyl-4-methylcyclohexane	99082	0.043298
trans-1-methyl-2-propylcyclopentane	43183	0.109080
trans-2-butene	43216	0.062144
trans-2-heptene	91026	0.042746
trans-2-hexene	98034	0.215342
trans-2-octene	43263	0.019492
trans-2-pentene	43226	0.499595
trans-3-heptene	98006	0.060363
trans-3-hexene	98136	0.119547
trans-3-nonene	91080	0.069684
trans-3-octene	91049	0.073862
trans-4-octene	43250	0.005935
trimethylindan	46755	0.031719
trimethyloctanes	90096	0.202587
unidentified	99999	1.906129
Total		*100.000000*