City of Fort Collins Well Workover Emission Rate Characterization

Prepared for:

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List of Acronyms and Abbreviations

BTEX……Benzene, Toluene, Ethylbenzene, and Xylenes
CSU……Colorado State University
COGCC……Colorado Oil and Gas Conservation Commission
D-J Basin……Denver-Julesburg Basin
EPA……Environmental Protection Agency
ER……Emission Rate
FID……Flame Ionization Detector
GC……Gas Chromatography
g s^{-1}……Grams per Second
LOD……Limit of Detection
Max……Maximum
Min……Minimum
O&NG……Oil and Natural Gas
PI……Principle Investigator
ppbv……Parts Per Billion by Volume
VOCs……Volatile Organic Compounds
WAS……Whole Air Sample

1. Introduction

Advances in technologies available for unconventional extraction of oil and natural gas (O&NG) have provided opportunities to access previously impractical reserves. One contributor to increased production involves applying new stimulation techniques to older wells, well workovers. Well workover includes the process of repairing or stimulating an existing well to restore or enhance its production of O&NG to increase the economic value of the well by faster delivery of O&NG (Bissoli et al., 2016). The techniques used in a well workover are similar to those of hydraulic fracturing but generally of a shorter duration. Well workover activities may be accompanied by an increase in the emissions of atmospheric pollutants such as methane and volatile organic compounds (VOCs), which can be important due to their impacts on air quality (e.g., through tropospheric ozone production), their effects on human health, and their role as greenhouse gases. Measurements of emission rates of methane and VOCs from well workover operations are not readily available and are needed to produce more accurate national emission estimates (Allen et al., 2013). A complete data set on the emission rates of methane and VOCs from such operations are essential in presenting a complete picture of impacts of emissions from O&NG on local and regional air quality, especially as instances of well workover are increasing across the U.S. (Nysveen and Wei, 2016).

The City of Fort Collins is a part of Larimer County, Colorado. Larimer County partially overlaps the central/western part of the Niobrara shale play, which is located in the Denver-Julesburg (D-J) basin. In April of 2017, Prospect Energy llc. conducted a well workover operation on the Hearthfire #1 well, located in the City of Fort Collins. The wellbore for this well was initially completed on 8/25/1985 and the first production rate recorded by the Colorado Oil and Gas Association was in January 1999. The first reported production was on 3/25/1997 and its major production is oil (COGCC, 2018).

On April 28th and May 1st of 2017, staff members from Colorado State University's (CSU's) Department of Atmospheric Science conducted tracer ratio method (TRM) measurements to quantify the emission rates (ERs) of methane and 43 VOCs from the well workover operations conducted on Hearthfire #1. The results from these measurements are presented here, and the emission rates of some VOCs are compared to similar studies conducted by CSU on other well operations (hydraulic fracturing, flowback, and production) in Garfield County, CO (Collett et al., 2016a) and the North Front Range, CO (Collett et al, 2016b).

1.1. Site Specifications

The site for this study was the wellpad and surrounding area for the Hearthfire #1 well, operated by Prospect Energy, llc., located at 40.63826, -105.053377 (Figure 1.1).

Figure 1.1. Map of measurement site for the project. The white diamond shows the location of the wellpad. (Map was produced using Google Earth).

CSU staff were responsible for site setup, measurements, analyzing collected VOC canister samples, and subsequent data analysis and validation. Measurements were made on site on April 28th and May 1st of 2017. Overall 16 hours of methane data and 10 3-minute time-integrated canisters for VOC analysis were collected during the two day measurement period.

2. Measurement Methods

2.1. Tracer Ratio Method

The TRM determines emission rates of compounds of interest independent of meteorology and local terrain. A passive tracer gas is released, co-located with the source of emissions. The known emission rate (ER) of the tracer gas is multiplied by the ratio of the downwind concentrations of the emitted gas to the tracer gas (both in excess of background) to determine the ER of the gas of interest. The TRM has been used as a technique for estimating the ERs of gases from a variety of sources (e.g., Lamb et al., 1986 and 1995; Lassey et al., 1997; Rumburg et al., 2008; Scholtens et al., 2004). In this study, acetylene (also known as ethyne, C_2H_2) was used as the tracer gas. Acetylene was chosen because of its chemical stability, long lifetime in the atmosphere (~2 weeks), ease of detection at high time resolution and low concentrations, and absence as a major emission from oil and gas operations.

The following equation was used to calculate the ERs of methane, and VOCs,

$$Q_{VOC} = Q_{C_2H_2} * \frac{[VOC]}{[C_2H_2]}$$

where, Q_{VOC} is the ER of the desired species, $Q_{C_2H_2}$ is the (known) release rate of acetylene, and $[VOC]$ and $[C_2H_2]$ are the background-corrected concentrations of the emitted gas (methane or VOCs) and the tracer gas (acetylene), respectively. In this study, the instantaneous and time integrated concentrations were used during data analysis for methane and VOCs, respectively. The basic assumptions of TRM are:

- The ER of the tracer is accurately known.
- The concentrations measured downwind are accurate.
- The two gaseous species disperse in a similar manner.
- The tracer is co-located with the emission source being characterized.
- Neither the tracer, nor the target VOC (or methane) are altered by deposition or chemical reaction between the release and detection points.

The uncertainties associated with TRM and the specific setup used for this study have been discussed in detail by Collett et al. (2016a and 2016b).

2.2. Measurement Techniques

The measurement techniques used were the same as those used for previous projects conducted by CSU at Garfield County and on the North Front Range, CO (Collett et al., 2016a; Collett et al., 2016b). Briefly, a tracer release system was used to ensure consistent, quantified, and safe release of the tracer (acetylene), near a pre-identified main source of emissions on the wellpad. A mobile plume tracker vehicle, equipped with a Picarro G2203 analyzer and A0931 mobile measurement kit, was deployed downwind of the tracer release system to measure 1Hz concentrations of acetylene and methane. The mobile plume tracker was used to obtain simultaneous information on the spatial and temporal variability of methane and acetylene concentrations to determine the emission ratio of methane and to map the location of the plume. Additionally, two to three remote-triggered canister systems were deployed with or near the mobile plume tracker to collect 3-minute time-integrated whole air samples (WAS) which were later analyzed for VOC concentrations.

Figure 2.1. Map of measurement site showing the path of the mobile plume tracker vehicle in yellow for the duration of measurements.

VOCs in this report are defined as compounds containing carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides, carbonate and ammonium carbonate, and methane. The emission rates of 42 VOCs were quantified. A list of the VOCs (and methane) measured and reported in this study is presented in Table A.1 of Appendix A. Ambient air for the measurement of VOCs was collected using pre-cleaned and evacuated 1.4 L Silonite® coated stainless steel canisters. The canisters were analyzed using a procedure similar to EPA's TO-12 method, using a gas chromatograph (GC) coupled with two flame ionization detectors (FID). The multi-channel GC-FID system was calibrated using dilutions of a 1 ppm Linde Gas certified high pressure standard. Six clean canisters, filled with ultra-high purity nitrogen, were analyzed to calculate the limit of detection (LOD) of the system. The results of calibration tests and LODs for the multi-channel GC-FID system are presented in Table B.1 in Appendix B. A detailed description of this system is presented by Collett et al., 2016a and 2016b.

2.3. Data Analysis

2.3.1. Real-Time Methane and Acetylene

Real-time methane and acetylene data were used to calculate a point-by-point distribution of methane emission rates. Background concentrations of acetylene in the area were relatively low (0-0.5 ppbv) compared to the tracer signal (typically > 50 ppbv). The background concentration of acetylene did not change significantly with time and thus the average of the lowest 5% of values was used for each experiment. To address the variability in the methane background, an interpolated background was used. When the detected acetylene concentrations were at background (i.e. out-of-plume), the methane concentrations were also considered out-of-plume. The background methane concentrations during each of these out-of-plume time periods were quantified. During in-plume time periods, the methane background was assumed to change linearly with time. Once the data had been background corrected (background concentrations subtracted from ambient measurements), TRM was performed on a point-by-point basis. Not all methane and acetylene data collected during the study were included in calculations of final ER distributions. TRM was performed only when all of the following criteria were met:

- Mobile plume tracker was stationary.
- Tracer release system was set to be releasing more than 1 slpm of acetylene.
- Acetylene was above a lower cutoff value of 0.5 ppbv (ensuring we were well within the tracer plume).
- Correlation coefficient, r, of methane and acetylene concentrations was above 0.5 (ensuring co-location of the tracer and site emission plumes).

2.3.2. Canister VOCs

The acetylene concentrations within the canisters were evaluated to assess whether a canister was collected inside or outside of a plume. Canister samples were discarded if the acetylene concentration was less than 2 ppbv. The average C_2H_2 background concentration for the two background samples collected during the study was 0.51 ppbv with a standard deviation of 0.01. In some instances, VOC concentrations were below the GC-FID limit of detection (LOD), in which case the measured value was replaced with LOD/2 for the corresponding analysis system and VOC. The LODs for each system and each VOC are presented in Appendix B. Canister VOC data were then background corrected by subtracting the concentrations measured in the background canisters deployed upwind of the emission location from the VOC concentrations in the canisters collected in the source plume. In cases where the background was equal to or higher than the measured concentration of a VOC, the determined value was replaced with LOD/2 for the corresponding analysis system and VOC. After processing the concentrations of the VOCs found in the downwind canister samples, the ERs of the VOCs were calculated using TRM as described in Section 2.1.

3. Results

3.1. Methane Emission Rates

Sixteen hours of 1Hz methane and acetylene data were collected during this project. After filtering the data based on the criteria listed in section 2.3.1, 1.4 hours of in-plume methane and acetylene data were used to calculate the ERs of methane measured during the well workover activities in this project. The normalized frequency distribution of the emission rates of methane are presented in Figure 3.1. The mean and median methane ER values for this dataset are 0.83 and 0.13 g s^{-1}, respectively. The statistical details of the methane ER range measurements are presented in Table 3.1.

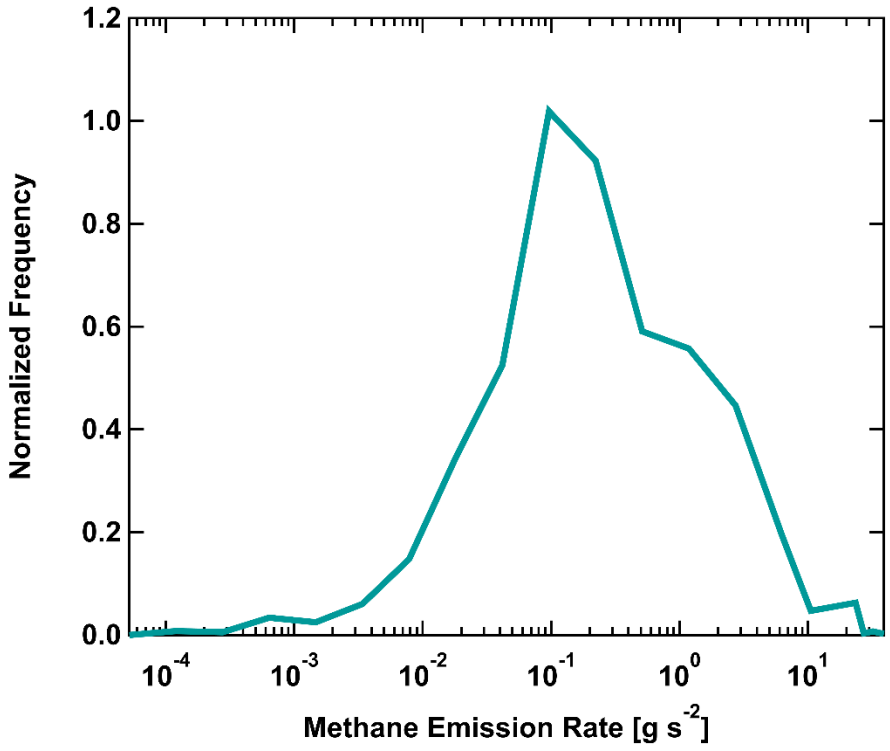

Figure 3.1. Normalized frequency distribution of real-time methane ER data (1.4 hrs.). The x-axis is the emission rate determined from the TRM on a log scale and the y-axis is the normalized frequency distribution.

Table 3.1. Statistical data on the ERs of methane calculated using TRM.

	Methane Emission Rate (g s^{-1})
Average	0.83
Median	0.13
25th Percentile	0.048
75th Percentile	0.57

The median methane emission rates from this study are compared with those from previous CSU-led studies in Garfield County and North Front Range, CO (Collett et al., 2016a and 2016b). Hydraulic fracturing (fracking) and flowback operations were visited and the ERs of methane from these operations were measured and calculated using similar methods as used in this project. Table 3.2 compares the medians ERs of methane from these operations with ERs from the current study.

Table 3.2. Comparison of ERs measured from the well workover in this project to other O&NG well development activities in the North Front Range and Garfield County, CO.

	Median methane emission rates (g s^{-1})
This study	0.13
North Front Range Fracking	0.051
North Front Range Flowback	2.8
Garfield County Fracking/Workover/Flowback	5.1
Garfield County Fracking	2.8
Garfield County Flowback	40

Fracking and flowback operation emissions were measured separately during the North Front Range project. The Garfield County project also examined ERs from fracking and flowback. One site visited during the Garfield County project was a simultaneous operation site where fracking, flowback, and well workover of multiple wells were observed. This is not a direct comparison to the site visited in this project as it contained multiple operations and the pad was located atop a different geological formation, however it does present an interesting point of comparison for the data presented here. The median methane ER from the Hearthfire well workover project was lower than all other studied operations except fracking in North Front Range, CO. Fracking operations are expected to emit less methane as the fracking solution is forced down the borehole at high pressure.

3.2 VOC Emission Rates

Figure 3.2 shows the distribution of 42 VOC emission rates for all canisters collected during this project. Acetylene was one of the VOCs measured but not presented in this graph as it was the tracer released for TRM.

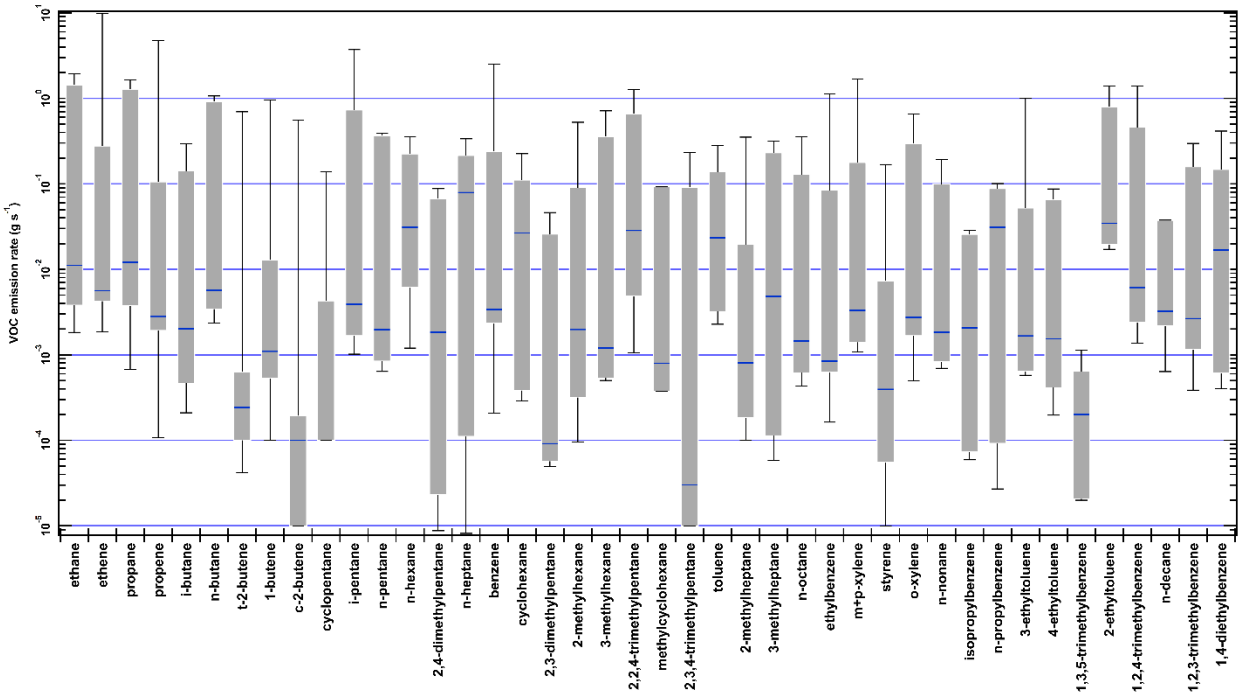

Figure 3.2. ERs of VOCs from well workover operations. The bottom and top of the boxes are the 25th and 75th percentiles, the blue line inside the box represents the median, the bottom and top whiskers are the 5th and 95th percentiles. 10 canisters were collected during 2 days of operations.

Tabulated summaries of well workover ERs for several key VOCs, including average, median, and 25th and 75th percentiles, are presented in Table 3.3. The highest median ERs observed are for light VOCs such as alkanes (ethane and propane) followed by toluene. In general, median ERs of VOCs associated with O&NG operations (e.g., ethane) and those associated with combustion emissions (e.g., 2-ethyltoluene) are higher than other VOCs.

Table 3.3. Average, median, 25th percentile and 75th percentile of the ERs for a subset of VOCs for all canisters collected during Hearthfire #1 well workover operations.

Compound	*Average ($g\ s^{-1}$)*	*Median ($g\ s^{-1}$)*	*25th %-ile ($g\ s^{-1}$)*	*75th %-ile ($g\ s^{-1}$)*
Ethane	0.54	0.011	0.0057	1.14
Propane	0.47	0.012	0.0042	1.23
i-Pentane	0.63	0.004	0.0015	0.63
n-Pentane	0.105	0.001	0.00032	0.17
n-Decane	0.013	0.0032	0.0026	0.017
Ethene	1.16	0.0056	0.0051	0.26
Propene	0.55	0.0028	0.0021	0.079
Benzene	0.34	0.0034	0.0027	0.21
Toluene	0.068	0.023	0.0038	0.081
Ethylbenzene	0.14	0.00085	0.00067	0.37
m+p-Xylene	0.23	0.0033	0.0016	0.15
o-Xylene	0.14	0.0027	0.0026	0.15
2-Ethyltoluene	0.35	0.035	0.021	0.42

The median ERs of benzene, toluene, ethylbenzene, and xylenes (BTEX) from the well workover operation in this project are compared to fracking and flowback operation ERs from Garfield County and the North Front Range, CO in Table 3.4. Again, the processes used in the operations are not the same, the operators and the geological formations are different. However, the data collected by Collett et al., 2016a and 2016b from Garfield County and North Front Range are currently the most relevant regional data for context and comparison with the data collected in this project.

Table 3.4. Comparison of median BTEX ERs from this study with similar measurements in North Front Range and Garfield County, CO.

	This study Well Workover Median (g s^{-1})	*North Front Range Fracking Median (g s^{-1})*	*North Front Range Flowback Median (g s^{-1})*	*Garfield County Fracking Median (g s^{-1})*	*Garfield County Flowback Median (g s^{-1})*
Benzene	0.0034	0.0022	0.069	0.029	0.062
Toluene	0.023	0.0056	0.21	0.12	0.24
Ethylbenzene	0.00085	0.00084	0.0019	0.011	0.017
m+p-Xylene	0.0033	0.0040	0.24	0.24	0.32

The well workover operations had lower BTEX ERs when compared to fracking and flowback operations in Garfield County and flowback operations in North Front Range CO. Benzene, ethylbenzene, and m+p-xylene emission rates were similar between this study and fracking operations in North Front Range, CO, and toluene emission rates were about 4 times higher in this study when compared to North Front Range fracking operations. Toluene can be emitted directly from the mineral deposit down-well or from combustion sources (e.g., vehicular exhaust) on site. It is important to keep the differences of the locations, practices, operators, operation types, and geologic formations in mind during this comparison.

4. Recommendations for Future Research

The growth in unconventional O&NG extraction operations can affect local air quality and thus human health. Better operator practices and equipment can reduce the amount of VOC emissions from these operations. In this study, ERs of methane and 42 VOCs were quantified from the Hearthfire #1 well workover operation. Most VOC ERs measured from this well workover operation were lower than observed during new well completion operations in the North Front Range and Garfield County, CO. Similar future studies can help inform stakeholders regarding emissions of air toxics and other VOCs from workover operations and encourage improvements of technology to lower emissions from unconventional O&NG operations more broadly.

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Appendix A

An overview of the median, average, minimum, and maximum emission rates of methane and VOCs from real-time measurements and canisters collected during the well workover operations.

Table A.1. Median, average, minimum, and maximum of methane and VOC emission rates during the well workover operation.

VOCs	**Median ($g\ s^{-1}$)**	**Average ($g\ s^{-1}$)**	**Min ($g\ s^{-1}$)**	**Max ($g\ s^{-1}$)**
Methane	0.13	0.83	0.0001	38.7
Ethane	0.011	0.54	0.0018	1.93
Ethene	0.0056	1.16	0.0018	10.00
Propane	0.012	0.47	0.0007	1.65
Propene	0.0028	0.55	0.0001	4.7
i-Butane	0.0020	0.065	0.00021	0.30
n-Butane	0.0057	0.32	0.0024	1.06
t-2-Butene	0.00024	0.078	0.000041	0.70
1-Butene	0.0011	0.11	0.0001	0.96
c-2-Butene	0.0001	0.062	0.00001	0.55
Cyclopentane	0.0001	0.017	0.0001	0.14
i-Pentane	0.0039	0.72	0.0010	3.72
n-Pentane	0.0020	0.15	0.0006	0.40
n-Hexane	0.031	0.10	0.0012	0.36
2,4-Dimethylpentane	0.0018	0.023	0.0000087	0.088
n-Heptane	0.079	0.10	0.0000082	0.34
Benzene	0.0034	0.33	0.0002	2.5
Cyclohexane	0.027	0.059	0.0003	0.22
2,3-Dimethylpentane	0.0001	0.010	0.000049	0.046
2-Methylhexane	0.0020	0.10	0.0001	0.52
3-Methylhexane	0.0012	0.14	0.0005	0.71
2,2,4-Trimethylpentane	0.028	0.27	0.0011	1.26
Methylcyclohexane	0.0008	0.031	0.0004	0.092
2,3,4-Trimethylpentane	0.000030	0.046	0.00001	0.23
Toluene	0.023	0.068	0.0023	0.28
2-Methylheptane	0.0008	0.044	0.0001	0.35
3-Methylheptane	0.0048	0.093	0.0001	0.31
n-Octane	0.0015	0.084	0.0004	0.35
Ethylbenzene	0.0008	0.14	0.0002	1.12
m+p-Xylene	0.0033	0.23	0.0011	1.68
Styrene	0.00039	0.021	0.00001	0.17
o-Xylene	0.0027	0.14	0.0005	0.65

Table A.1 Continued

VOCs	**Median ($g\ s^{-1}$)**	**Average ($g\ s^{-1}$)**	**Min ($g\ s^{-1}$)**	**Max ($g\ s^{-1}$)**
n-Nonane	0.0018	0.04	0.0007	0.19
Isopropylbenzene	0.0021	0.011	0.0001	0.029
n-Propylbenzene	0.031	0.041	0.000027	0.10
3-Ethyltoluene	0.0017	0.12	0.0006	1.00
4-Ethyltoluene	0.0015	0.027	0.00020	0.087
1,3,5-Trimethylbenzene	0.0002	0.00033	0.00002	0.0011
2-Ethyltoluene	0.034	0.35	0.017	1.40
1,2,4-Trimethylbenzene	0.0062	0.26	0.0014	1.40
n-Decane	0.0032	0.012	0.0006	0.038
1,2,3-Trimethylbenzene	0.0027	0.064	0.0004	0.30
1,4-Diethylbenzene	0.017	0.096	0.0004	0.41

Appendix B

Calibration statistics for the VOCs measured on the multi-channel system

Table B.1. Calibration statistics for VOCs measured using the multi-channel GC-FID-FID system.

VOC	Calibration r^2	LOD (ppbv)	Slope of the Calibration Curve	Standard range (ppbv)
ethane	0.999	0.105	137	0.4-3362
propane	0.999	0.020	1294	0.4-3203
i-butane	0.999	0.008	1682	0.4-3171
n-butane	0.999	0.010	1691	0.4-3140
cyclopentane	0.999	0.009	2097	0.4-3171
i-pentane	0.999	0.009	2110	0.4-3171
n-pentane	0.998	0.007	2039	0.4-3108
2,4-dimethylpentane	0.992	0.004	4049	0.4-3330
2,3-dimethylpentane	0.998	0.013	1049	0.4-3362
2,2,4-trimethylpentane	0.998	0.018	1196	0.4-3298
2,3,4-trimethylpentane	0.999	0.009	1174	0.4-3299
n-hexane	0.999	0.012	2467	0.4-3267
2-methylhexane	0.999	0.010	1079	0.4-3299
3-methylhexane	0.999	0.014	1064	0.4-3299
n-heptane	0.995	0.009	3164	0.4-3299
2-methylheptane	0.999	0.022	1165	0.4-3299
3-methylheptane	0.999	0.016	1177	0.4-3267
n-octane	0.999	0.016	1115	0.4-3299
n-nonane	0.999	0.010	1165	0.4-3235
n-decane	0.999	0.011	1131	0.4-3299
cyclohexane	0.999	0.015	895	0.4-3330
methylcyclohexane	0.999	0.019	1058	0.4-3299
ethene	0.999	0.053	945	0.4-3362
propene	0.999	0.009	1179	0.4-3203
t-2-butene	0.999	0.018	1662	0.4-3108
1-butene	0.998	0.013	1651	0.4-3104
c-2-butene	0.999	0.022	1756	0.4-3362
benzene	0.999	0.010	903	0.4-3266
1,3,5-trimethylbenzene	0.999	0.012	1091	0.4-3235
1,2,3-trimethylbenzene	0.996	0.012	1074	0.4-3140
1,2,4-trimethylbenzene	0.997	0.0124	1077	0.4-3171
ethylbenzene	0.999	0.019	1066	0.4-3266
1,3-diethylbenzene	0.998	0.027	1136	0.4-3140
1,4-diethylbenzene	0.998	0.013	1133	0.4-3108
isopropylbenzene	0.999	0.011	1171	0.4-3140
n-propylbenzene	0.998	0.012	1157	0.4-3108
toluene	0.998	0.017	1028	0.4-3266
2-ethyltoluene	0.999	0.025	1128	0.4-3140
3-ethyltoluene	0.995	0.014	1084	0.4-3235
styrene	0.996	0.014	1008	0.4-3298
m+p-xylenes	0.995	0.014	1754	0.8-6596
o-xylene	0.999	0.006	1087	0.4-3203