Analysis of Regular-grade Gasoline using Gas Chromatography/Mass Spectrometry

Glenn Murray

Department of Chemistry
Georgia State University, Atlanta, GA
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ABSTRACT

Gasoline is a complex mixture of, primarily, aliphatic and aromatic hydrocarbons used to power internal combustion engines. The aim of this research was to identify the constituents in a regular-grade gasoline sample, using gas chromatography/mass spectrometry (GC-MS). To do this an initial temperature program was developed using a mixture of seven n-alkanes: n-hexane through n-dodecane. A new temperature program was derived from the alkane temperature program, then utilized for the analysis of gasoline. The gasoline sample was diluted in acetone, using dodecane as an internal standard, and in dichloromethane. Thirty-five peaks eluted from the gasoline injection with thirteen peaks tentatively identified via mass spectrum and relative retention time.

The following peaks were tentatively identified with mass spectra peak fragmentation patterns matching those found in the National Institute of Standards and Technology (NIST) mass spectral library. Those provisional identifications are as follows. A peak matching spectrum of n-pentane at 1.45 min, cyclohexane at 2.15 min, toluene at 4.4 min, n-octane or iso-octane (2,4-dimethyl-hexane) at 5.5 min peak eluting at 8.2 ethylbenzene at 8.2 min, Meta and para-xylene coeluting at 8.7 min, o-xylene at 10.0 min, n-nonane 10.75 min, propyl-benzene at 14.7 min, 1,3,5-trimethyl-benzene at 18.2 min, and 1,2,4-dimethyl-benzene (pseudocumene) matched the mass spectrum of a peak eluting at 21.2 min. The compound 2-methyl hexane was weakly identified at 2.5 min.

Therefore, twelve of the 35 peaks labeled were tentatively identified in the regular-grade gasoline sample tested. One compound weakly identified with one being close to an identification, but having fragmentation pattern did not quite match with the NIST spectrum of the suspected compound, reducing confidence in the identification. Twenty-three peaks remain unidentified, including the weak identification.

1.0 INTRODUCTION

Gasoline is a volatile mixture of inflammable fuels primarily used in internal combustion engines. It is composed of a complex mixture of alkanes, alkenes, cycloalkanes, cycloalkenes, aromatics, and additives, such as anti-knock, anti-rust, and fuel-stabilizing compounds. Its constituents vary by refinery as well as a seasonal composition change, made with a lower average vapor pressure during the summer months for preventing fuel system vapor-lock. [1] Current gasoline (USA) can contain up to 10% anhydrous ethanol, acting as an anti-knocking agent. It can contain batch-identifying dyes, such as (Red) alkyl derivatives of azobenzene-4-azo-2-naphthol, (Orange) benzene-azo-2-naphthol,

(Yellow) para-diethyl aminoazobenzene, and (Blue) 1,4-diisopropylaminoanthraquinone. The composition of gasoline hydrocarbons, as a percent of volume, is: 4-8% n-alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; l-4% cycloalkenes; and 20-50% total aromatics, having a boiling range of 50 to 200° C (USA). [2, 3]

Chromatography is a useful tool for determining what is in mixtures of materials and gas chromatography (GC) is very good for measuring volatile mixtures such as gasoline. Capillary GC, in particular, is ideal due to high efficiency separation of complicated mixtures of compounds, primarily by their vapor pressure or boiling point with mass spectrometry (MS) used to confirm the identity of the eluted compound. If a mixture of compounds, with wide range of boiling points is analyzed at a constant temperature, known as an isothermal trial, either the low boiling point constituents will elute quickly with poor resolution, or the high boiling point components will have a high retention time or not elute at all. Temperature programming is a tool in GC to improve the separation and resolution of compounds. By starting at a low temperature and raising the temperature across the run, the separation and resolution of the low boiling fractions improve, and the upper compounds will elute in a reasonable amount of time. [4,5]

Gasoline is a mixture that temperature programming is ideally suited. It has very volatile constituents with boiling points as low as 40° C, on upward to compounds with boiling points close to 200° C. At a low isothermal temperature, the high boiling fraction may never elute, and at a high isothermal temperature there would be little resolution and separation in the low boiling fraction. Temperature programming can provide resolution at the lower boiling points, while both allowing a reasonable total elution time for the high end and ensuring all compounds elute. [6]

2.0 EXPERIMENTAL

2.1 Chemicals

The following chemicals were used for the experiments described in this paper: Dodecane, 99+%, Acros Organics, Fair Lawn, NJ (CAS #112-40-3); Acetone, HPLC grade, Fisher Chemical, Norcross, Ga, (CAS #67-64-1), Dichloromethane, HPLC grade, Fisher Chemical, Norcross, Ga., (CAS #75-09-2), n-hexane 99+%, Acros Organics, Fair Lawn, NJ (CAS# 110-54-3), n-heptane: 99+%, Acros Organics, Fair Lawn, NJ (CAS# 142-82-5), n-octane: 99+%, Acros Organics, Fair Lawn, NJ (CAS# 111-65-9), n-nonane: 99+%, Acros Organics, Fair Lawn, NJ (CAS# 111-84-2), n-decane: 99+%, Acros Organics, Fair Lawn, NJ (CAS# 124-18-5), n-undecane: 99+%, Acros

Organics, Fair Lawn, NJ (CAS# 1120-21-4), n-dodecane: 99+%, Acros Organics, Fair Lawn, NJ (CAS# 112-40-3), meta-xylene, 99+%, Fisher Chemical, Norcross, Ga., (CAS #108-38-3), p-xylene, 99+%, Fisher Chemical, Norcross, Ga., (CAS #106-42-3), and gasoline, regular-grade, purchased in the fall. Given summer gasoline blends have a distinctly different profile, noting time of year this sample was obtained as pertinent information. It was a regular grade gasoline obtained from a QT station (Snellville, GA).

2.2 Equipment

The 8869 gas chromatograph used in this experiment consisting of carrier gas (helium), a split/splitless injector, with 30 m x 0.250 mm x 0.25mm open tubular column coated with a (5%-phenyl)-methylpolysiloxane stationary phase interfaced to electron impact ion source and 5977B single quadrupole MSD manufactured by Agilent Technologies,(Santa Clara, CA). Other items include100-1000 µL micropipette, VWR Brand International (Radnor, PA), and a sonicator.

2.3 Experimental Conditions

The GC-MS conditions were as follows: helium was used as a carrier gas at a flow rate was 1.2 mL/min, the injector was used in the split mode with a split ratio of 1:50; injection volume 1 µL, the column was used in both isothermal and temperature program conditions and was housed in a GC oven. Single ion monitoring (SIM), with 50-250 m/z, was used for the alkane trials, then the range changed to 20 -250 in later trials.

2.4 Procedures

The first mixture was a seven-component standard of mixed alkanes: n-hexane; n-heptane; n-octane; n-nonane; n-decane; n-undecane; and n-dodecane. These were in equal amounts at about 16.7% (v/v) each. 100 µL of this mixture was diluted in 10 mL of acetone (1:100). The solvent detector delay was set to 1.1 minutes, overridden on the first run; the injector temperature was 230° C; A set of three trials for seven component alkane test mixture was performed under isothermal conditions at 90° C. The same alkane test mixture was then run with a temperature program starting at 40° C ramping to 250° C of over 8.5 min, at 25° C/min, then a 250° C hold until the end of the trial. The trial used a solvent detector delay of 1.1 min (overridden on the first run); the injector temperature was 230° C. Three trials were run with the above-mentioned temperature program.

A second mixture was composed of 100 μL regular grade gasoline, with 20 μL of dodecane added as an internal standard, diluted in 10 mL of acetone. That was a 1:100 dilution for the gasoline and 1:500 dilution for the dodecane internal standard. The solvent detector delay was set to 1.1 min (overridden on the first run); the injector temperature was 230° C, and the method was set for 3 pre-injection and 3 post-injection syringe flushes. The temperature program of the column oven was set as follows: 40° C for 4 min; a ramp of 1° C/minute to 60° C; a hold of 10 mins; a ramp at 15° C/min to 240° C, then a final hold for 10 min. The sequence was set to do three automated trials.

A third mixture composed of 100 μL regular grade gasoline diluted in 10 mL of dichloromethane (a 1:100 dilution), with 20 μL meta-xylene internal standard (a 1:500 dilution); a fourth mixture of gasoline/dichloromethane was spiked with 20 μL of para-xylene (1:500), a fifth mixture spiked with 20 μL of meta-xylene and 20 μL of para-xylene (each at 1:500), as internal standards. The vial of the above three mixtures were placed in position 1 through 3 of the sample tray in the GC-MS; the solvent detector delay was set to 1.1 min (overridden on the first run); the injector temperature was 230° C; and the system was set to 3 pre and 3 post-injection syringe flushes. The temperature program was set under the same conditions as mentioned above for the second mixture. The sequence was set to do one trial of each sample.

A sixth mixture was composed of 20 μL m-xylene diluted in 10 mL of dichloromethane (a 1:500 dilution); a seventh mixture with 20 μL of para-xylene in 10 mL of dichloromethane (a 1:500 dilution); a eighth mixture was prepared with 20 μL of meta-xylene and 20 μL of para-xylene in 10 mL dichloromethane (a 1:500 dilution each); a ninth mixture was prepared by dissolving 100 μL of gasoline in 10 mL of dichloromethane (1:100). Finally, for blank analysis a vial of pure dichloromethane was prepared. The abovementioned 6-9 mixtures were set, in vials, in positions 1 through 4 of the sample tray in the GC; the solvent detector delay was set to 1.1 min (overridden on the first run); the inlet temperature was 230° C; and the system was set to 3 pre-injection and 3 post-injection syringe flushes with dichloromethane. The temperature program settings were the same as mentioned above for the analysis of the second mixture.

3.0 RESULTS AND DISCUSSION

3.1 Developing a temperature program for separating alkanes and light hydrocarbons.

Seven n-alkanes, hexane, heptane, octane, nonane, decane, undecane, and dodecane, were used as a guide in developing a temperature program for gasoline separation. Seven n-alkanes, hexane, heptane, octane, nonane, decane, undecane, and dodecane, were used as a guide in developing a temperature program for gasoline separation. Under isothermal trials, at 90°C, n-hexane, n-heptane, and n-octane eluted quickly, at average retention times of 1.250, 1.524, and 1.836 min, with separation factor of 1.2 and 1.2, and resolutions of 1.2 and 1.6 for n-hexane/n-heptane and n-heptane/n-octane respectively. The alkanes of n-nonane, n-decane, n-undecane, and n-dodecane eluted progressively more slowly with average retention times of 2.457, 3.700, 6.158, and 11.025 minutes. Respectively, n-octane/n-nonane, n-nonane/n-decane, n-decane/n-undecane, and n-undecane/n-dodecane had resolutions of 3.1, 5.0, 7.0, and 9.7, with separation factors of 1.3, 1.5, 1.7, and 1.8 (Table 1). There was a pattern of low boiling point constituents eluting quickly, continuing to higher retention times as the component boiling points rise, along with higher resolutions and separation factors.

These trials were followed up with a temperature-programmed set of trials. The isothermal run was at 90°C, and the temperature program was a linear increase from 40° to 250° C, at a 25°C ramp. Figure 1 shows an overlay of chromatograms of a mixture of C6 through C12 n-alkanes, using an isothermal (a) and a temperature-programmed (b) set of conditions. As shown in Table 1, under isothermal trials, the alkanes, from n-hexane/n-heptane through n-undecane/n-dodecane had resolutions of 1.20, 1.56, 3.11, 4.97, 7.03, and 9.72. For the temperature programmed trials, the resolutions were 1.92, 2.85, 3.70, 3.78, 3.24, and 3.11. Comparing the two sets, the n-hexane/n-heptane through n-octane/n-nonane resolutions increases slightly, but the last three resolutions dropped perhaps due to decrease in chromatographic selectivity. The last, n-undecane/n-dodecane dropped by a factor of three. Nevertheless, all peaks in the temperature programmed condition provided baseline resolution with almost half the analysis time. The higher the temperature, the faster a component will elute, so the increasing temperature of the program is causing the lower boiling fractions to speed up so they are eluting in a more regular timing. This affects the resolution by lowering the very high resolutions of the isothermal trials to the more reasonable values seen in the temperature programmed trials.

The isothermal separation factors, for the same set, were 1.2, 1.2, 1.3, 1.5, 1.7, and 1.8, respectively. The temperature programmed separation factors were 1.3, 1.3, 1.2, 1.2, 1.2, and 1.1, respectively. Clearly, the comparisons between the isothermal and temperature programed suggest increases in separation factor slightly, from 1.1 to 1.2 for hexane/heptane, and at the high end dropping significantly from 1.8 down to 1.1 for undecane/dodecane. All separation factors were in a reasonable range. The effects of the separation factors, while not as pronounced as with the resolution, are due to the same effect on elution time by changing the temperature as the higher boiling point constituents progress through the column, resulting in decreasing selectivity.

The data reported in Table 1 demonstrates an improvement in resolution (R_S) and separation factor (α), for the shorter chain alkanes using a temperature program compared to isothermal trials. The same is seen visually in Figure 1a and 1b, though the scales are different. Additionally, and for the same reasons, the efficiency of the column improves with the temperature programming. Comparison of the two groups, in chain length order (n-hexane through n-dodecane) are: *N* values of 385, 929, 1348, 2348, 2415, 2434, 3793, and 5403 for the isothermal trials, and *N* values of 443, 1694, 2763, 7632, 6200, 8409, and 10841 for the temperature program. The standard deviations for all efficiencies were less than 10. While they start at similar efficiencies, the temperature programmed trials are almost twice as efficient at the point n-dodecane elutes.

As shown in Figure 1b, a temperature program starting at 40° C, going up linearly with a ramp of 25° C to 250° C, and holding for 10 min, drops the total analysis time from 11.5 min to 5.5 min, with a pronounced improvement in the R_S and α values for the shorter chain alkanes while still providing baseline *Rs* and acceptable α for longer chain alkanes. With a temperature programming profile having a lower initial temperature, the lower boiling point (b.p) alkanes elute more slowly, increasing the separation. As the temperature rises along the temperature ramp, the alkanes with higher b.p elute faster than they would have at a fixed lower temperature (isothermal conditions). In this case the temperature profile yielded a total elution time of less than half that of the isothermal elution. This temperature programming exercise guided the development of a profile for separating regular-grade gasoline.

3.2 Chromatographic separation of aliphatic and aromatic constituents in regular-grade gasoline

Using the temperature profile information gained in testing the n-alkane mixture, a new profile was developed for the gasoline trials. Gasoline has numerous low b.p. fraction hydrocarbons, such as aliphatics (pentanes, hexanes, heptanes, octanes) and aromatics (toluene, benzene, and xylenes). At elevated temperatures these would elute quickly with a low resolution. It also has higher b.p. hydrocarbons which would elute very slowly, assuming they elute at all. For this reason, a temperature program was created.

The temperature program was as follows: a starting temperature of 40° C was held for 4 min, proceeding with a 1° C ramp up to 60° C, followed by a hold of 10 min. The increasing temperature causes the higher boiling point fractions to elute more quickly. The 10 min hold was followed by a ramp of 15° C/min to 240° C, and another 10 min hold at the final temperature of 240° C.

Gasoline samples were run diluted in two sets, differing by solvent. One set diluted in acetone and one set was diluted in dichloromethane. The results from trials of a specific solvent will be referred to as chromatogram datasets or series. This is to indicate they were run diluted in that solvent and is to relate data and chromatographs from a set of trials with its diluent.

Thirty-five peaks seen in the chromatograms (Figure 2). They were labeled from 1 to 35, as seen in Figure 2a and b. The n-dodecane did not have a peak discernible in trials of samples without an internal standard, so it was not given a numeric designation. Some trials had no peak information reported by the Agilent systems corresponding to some of the 35 specified seen in other trials. In these cases, a blank column in the tables will indicate that there was missing peak information. As an example, in Table S1, trail 1 of peak 4 had no information returned by the Agilent system, so was left blank.

The first sample set run was prepared by adding 100 μL of gasoline in 10 mL of acetone (diluted 1:100), then spiked with 20 μL of dodecane (diluted 1:500). Three trials of this were run, and 35 peaks were specified for examination. A second sample set was prepared by adding 100 μL of gasoline in 10 mL of dichloromethane (diluted 1:100), then 20 μL of a xylene added (diluted 1:500) as an internal sample. The first sample of the set had m-xylene added, the second had p-xylene added, and the third had both m-xylene and p-xylene added, 20 μL each. Figure 2 shows one of the

acetone trial sets (Figure 2a) overlaid with one of the dichloromethane-set trials (Figure 2b), with the peaks of interest numbered. A clear peak for dodecane is seen in Figure 2a with no corresponding peak in the second chromatogram (Figure 2b), which had no added dodecane internal standard. The second chromatogram, in Figure 2b, was from a specimen diluted in dichloromethane and an added m-xylene. This chromatogram shows a large xylene peak, labeled as peak 16. Figure 2a shows a small xylene peak at the same retention time, run from the acetone diluted sample with no added xylene. The labels used in Figure 2 for peak numbering are used across chromatograph datasets obtained from gasoline trials with acetone and dichloromethane.

In the supplemental section, table S1a shows the retention times, peak areas, peak heights, and peak widths for all compound peaks observed in gasoline dissolved in acetone and spiked with dodecane. In addition, the table also identifies the α and R_S for adjacent peaks. If no information was reported for a component with a specific label no data was generated for that peak in that solvent series/dataset. In the table, the R_S and α values used adjacent peaks of the chromatogram, if a peak label had no data. Table S1b shows the retention times, peak areas and heights, and peak widths for gasoline in dichloromethane, with two trials spiked with m-xylene or p-xylene, the last being gasoline without added xylene. The α and R_S for shown for adjacent peaks.

Meta and para-xylene (peak 16) both elute at the same retention time, at approximately 8.7 min, given they are positional isomers and have identical boiling points. Trials of m-xylene in dichloromethane and p-xylene in the same solvent showed they would not resolve and had differences in retention times that were quite close, and when run together came out as one peak. Dodecane eluted at approximately 38.35 min. Dodecane only showed a peak in the dodecane spiked series. The samples with no added dodecane had dodecane levels too low to detect a peak in this region. The dodecane peak in the spiked sample appears between peaks 34 and 35. Dodecane served as a good internal standard as it is not present in gasoline and elutes and separated well from the other gasoline components. Given there was no peak without added dodecane, dodecane was not given a numeric designation (label). Figure S2 gives an overlaid comparison of the gasoline with dodecane (in acetone) chromatogram and the chromatogram of gasoline (in dichloromethane) without added dodecane.

3.3 Constituent identification in the regular-grade gasoline.

Constituent identification was based on two factors, retention time and matching the produced mass spectra to NIST mass spectra, the former a guide to where to look and the latter a more definitive identification. In general, boiling point is a strong driver of elution time, with lower boiling points having shorter retention times. Gasoline will have alkanes from butane up to at least up to undecane, perhaps higher, though the amounts may be below the level of detection.[7] It also contains alkenes of various types. These can include some cycloalkanes and cycloalkenes, such as cyclohexane and cyclohexene. Anti-knock and fuel stabilizer additives may be present as well, such as ethanol, 2-propanol, benzene, toluene, ethylbenzene, pseudocumene, and xylenes. [8]

Ethanol is a component of most gasoline marketed, added as an anti-knock ingredient. Nothing corresponding was found early in the chromatograms with no peak for mass spectra (MS) matching the NIST library mass spectrum for ethanol. Ethanol has a low boiling point, so it could have been masked by the solvent signal, both in the chromatogram and the mass spectra listed in that region. The butanes and hexanes are significant constituents of gasoline, estimated at about 40% by weight, according to a commercial literature.[9]

The first peak, labeled peak 1 in the chromatogram in Figure 2b, had a retention time of about 1.5 min. The mass spectrum of this peak, for this research (Agilent) is shown in Figure 3a. It matches the NIST mass spectrum and fragmentation pattern of n-pentane, with peaks at 72, 57, 43, and 27 m/z shown in Figure 3b. The latter three correspond to the loss of successive methylene groups, with 43 m/z being the largest. Stephenson's rule says the most stable carbocation should predominate in a mass spectrum, and propane carbocation, with the charge on the number 2 carbon, would be quite stable, relative to alkane carbocations[10] and corresponds to the 43 m/z region. The molecular ion peak and base peaks match between the Agilent and NIST library mass spectra.

For the dichloromethane solvent trials the peak labeled 2 has a mass spectrum (Figure 4a) with peaks and a fragmentation pattern matching the NIST mass spectrum (Figure 4b). The major mass spectra peaks occur at 88, 86, 85, 84, 51, 49, and 47 m/z. Loss of a chlorine atom from dichloromethane would produce an ionized fragment in the 49 m/z region, which is the largest peak in both Agilent (this research) and the NIST spectra. Due to the differing atomic weights of the two stable chlorine isotopes (^{35}Cl and ^{37}Cl), more peaks show than would be expected from a single isotope. [11] This chromatographic peak had a retention time of 1.8 min. The peak corresponding to

label 2, for the acetone solvent trials, shows a peak area expected for the solvent. That said, the maximum *m/z* is much higher than the molecular weight of acetone (58), nor does it match the mass spectrum for acetone. The Agilent and the NIST acetone mass spectra are shown in Figure S1 a-b.

Figure 5 shows the mass spectrum of peak 3 and the NIST webbook mass spectrum of cyclohexane. The *m/z* readings of interest are at 84, 69, 56, 41, and 28, common to the *m/z* readings of the Agilent and NIST mass spectra. The molecular ion and base ion peaks match between the Agilent and NIST library mass spectra. While the fragmentation pattern is very similar between the two, the fact this shows up so early in the chromatogram, before compounds with boiling points 20° C lower than cyclohexane, is of concern. This would be a tentative identification.

Figure 6 shows the mass spectrum of peak 6, and the NIST webbook mass spectrum of 2-methylhexane, an isomer of heptane. The *m/z* fragments of interest are at 100, 85/84, and 57/56, with similar fragmentation patterns in both spectra. The base ion peak matched NIST at m/z 43, where the most stable carbocation of 2-dimethylhexane, a 2-propyl cation, is predicted by Stephenson's rule. This compound had a retention time of 2.52 min. The identification is only tentative given a prominent high intensity peak in the Agilent mass spectrum at 71 m/z ($C_5H_{11}^+$) that did show very prominently in the NIST library mass spectrum.

Peak 12, at the approximate retention time of 4.4 min., occurs at a similar retention time as the Pierce and Shaff research, for toluene. Significant mass spectra peaks present at 93, 92, 91, 65, 51, and 39 m/z, in both the Agilent mass spectrum and the toluene mass spectrum from NIST, appear the same. The fragmentation pattern of the two mass spectra appear to match. This is shown in Figure 8 a/b. This is shown in Figure 7.

Peak 14, at the approximate retention time of 5.5 min., has a mass spectrum that has a similar set of peaks and fragmentation pattern of octane as seen on the NIST library mass spectra for n-octane and 2,4-dimethyl-hexane (iso-octane). These are shown in Figure 8 as overlays of the three spectra. These peaks occur at 114, 85, 71, 57, 43, and 29 m/z. The m/z fragments match molecular weights expected if an ethyl group, then two successive methyl groups (85, 71, 57) fragmented off the octane molecule. There was not enough difference in the NIST mass spectra of n-octane and 2,4-dimethyl-hexane to differentiate the compound eluted in this trial, as n-octane or iso-octane. However, considering the difference in boiling point and those of the identified peaks around this peak, n-octane is a stronger candidate. It has a higher boiling point than peak 12, with iso-octane a lower

boiling point. Factoring in the higher retention time, n-octane appears as the more probable identity of this peak.

Peak 15 is a good candidate for ethylbenzene. Figure 9 shows the mass spectra from this research, overlaid with the mass spectra obtained from NIST for ethylbenzene. Mass peaks are present at 106, 91,77, 65, 51, 30, and 27/28 in both mass spectra. Combined with the retention time (~8.2 min) this is a strong candidate for ethylbenzene. The 91 and 77 m/z values would be expected if successive methylene groups had been fragmented off the ethyl group of the benzene. The high intensity peak at m/z = 28 in the Agilent MS spectrum is the only peak whose intensity is different from the reference peak. The molecular weight of 28 would match that of a naked ethylene ionized from the benzene. The molecular ion and base ion peaks match between Agilent and the NIST library spectra with quite similar fragmentation patterns.

Peak 16 is xylene, specifically para or meta xylene. They have extremely close boiling points (138.3 and 139.1° C) so elute at the approximate same retention time (8.7 min), in two trials in gasoline. They also eluted as unresolved peaks when run together in dichloromethane, without gasoline at retention time of about 8.7 mins. Ortho-xylene has a boiling point that is different enough (144.4° C) from meta and para-xylene that its peak and those of its two other isomers resolve. Xylenes are anti-knock fuel additives. The mass spectra for this peak and the NIST mass spectra are found in Figure 10 a-b, and the mass spectra peaks and fragmentation are quite similar, with molecular ion and base ion peaks at the same *m/z*.

Peak 17 was tentatively identified as o-xylene, with a retention time of 10.04 min. There were matching peaks at 106, 105, 91, 77, 65, and 51 m/z, for the Agilent and NIST library mass spectra, seen in Figures 11 a-b. The 91 and 77 m/z values would be expected if successive methyl groups had been fragmented off the xylene. The fragmentation pattern of the two mass spectra appeared to match with molecular ion and base ion peaks at the same m/z. Xylenes function as anti-knock fuel additives. These mass spectra are found in Figures 11a-b.

Peak 18, at retention time of about 10.8, as a mass spectrum that shows a match to the NIST library spectrum for n-nonane. It has overlaid mass spectra from this research and the NIST library, shown in Figure 12a-b. The mass spectrum from NIST is that for n-nonane. The fragmentation pattern and major peaks appear to match, with peaks at 128, 99, 85, 71, 57, 43 and 28 m/z, which correspond to loss of successive methylene groups, with the same molecular ion peak. The only variance is

with the intensity of the peak at 28 m/z. Peaks at 43 and 57 have a significantly higher intensity, as would be expected from the most stable carbocations from n-nonane.

Peak 19, at retention time of about 14.7 min, has a mass spectrum that shows a match to the NIST library mass spectrum for propyl-benzene. They both have MS peaks at 120, 105, 91, and 78, which line up with the loss of 1, 2, and 3 methylene groups. There are further m/z peaks at 65 and 51, which would also line up with the further loss of methylene groups, implying the breaking of the benzene ring. The fragmentation patterns of the two mass spectra seem to match, as do the molecular ion and base ion peaks. The mass spectra for this peak and the NIST mass spectra are found in Figure 13a-b.

Peak 23, at a retention time of about 18.25 min, appears to match 1,3,5-trimethylbenzene, commonly known as mesitylene. Comparing the Agilent and NIST library mass spectra, both have peaks at 120, 105, 91, and 77 m/z, as seen in Figures 6 a-b. These are the approximate molecular weights as 1, 2, then 3 methyl groups fragmenting from mesitylene, leaving a bare benzene molecule. The fragmentation pattern of the two mass spectra appeared to match, as do the molecular ion and base ion peaks. The mass spectra for this peak and the NIST mass spectra are found in Figure 14a-b.

Peak 24 mass spectra are shown in Figure 15, overlaid, with the NIST library entry for 1,2,4-trimethylbenzene (pseudocumene), with common peaks at 120, 105, 91, and 77 *m/z*, with the only questionable peak being at 28 m/z, being much higher intensity on the Agilent mass spectrum. Otherwise, the fragmentation pattern seems to match, as do the molecular ion and base ion peaks. Like mesitylene, these m/z readings tend to correlate with the approximate molecular weights as 1, 2, then 3 methyl groups are progressively stripped from 1,2,4-trimethylbenzene. Pseudocumene, aka 1,2,4-trimethylbenzene, is a fuel stabilizer in gasoline.

No peak was seen corresponding to dodecane, at the retention time seen in the sample with added dodecane. No clear candidate for decane or undecane was found. None of the labeled peaks presented fragmentation patterns or predominant mass spectra peaks matching these alkanes. The data reported in Table S2, includes molecular weights, boiling points, names, alternate names, and potential function if it is a potential fuel additive. It was useful in differentiating between compounds with similar mass spectrums and molecular weights, but with a different boiling point.

4.0 CONCLUSIONS

The purpose of this research was to analyze and identify compounds in regular-grade gasoline. As part of the process, a temperature program was developed to elute the compounds in the gasoline. Using seven alkanes, n-hexane through n-dodecane, three isothermal trials (at 90° C) were run. A temperature program, starting at 40° C, ramping to 250° C using a 25° C/min ramp. The alkane temperature program produced an improved resolution and separation for the initial alkanes used (n-hexane through n-dodecane) with the R_S values for hexane-heptane and heptane-octane changed from 1.20 – 9.72 to 1.92 – 3.11 and the separation (α) values from 1.2 - 1.8 to 1.3 - 1.1. Using this information, a gasoline temperature program was developed, as follows. The temperature of 40° C was held for 4 minutes, ramped at 1° C/minute to 60° C, holding for 10 minutes for 60° C, then ramping at 15° C/minute to 240° C, and holding for 10 minutes, at which time the test terminated.

Thirteen of the thirty-five peaks labeled were tentatively identified compounds in the regular-grade gasoline sample tested, with 22 remaining unidentified. Peaks were tentatively identified as the constituents n-pentane, cyclohexane, 2-methylhexane, toluene, n-octane, ethylbenzene, meta and/or para-xylene, o-xylene, n-nonane, propyl benzene, and two trimethylbenzenes: 1,2,5-trimethylbenzene and 1,2,4-trimethylbenzene (pseudocumene). The solvent peak for dichloromethane was identified. Toluene, xylenes, and ethylbenzene are anti-knock compounds, and pseudocumene is a fuel stabilizer. While several specific alkane isomers were tentatively identified in this research, they could be from other isomers of that alkane. Many mass spectra are similar for alkane isomers.

These results include 12 tentatively identified gasoline constituents, with 23 unidentified peaks. The remaining 23 unidentified peaks require a deeper investigation for identification.

Figures

Figure 1 shows a chromatogram overlay alkanes n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-nonane, and n-dodecane, run with an isothermal temperature profile at 90° Ca and with a programmed temperature profile from 40° C ramping to 250° C at 25° C/min (b).

Figure 2 shows gasoline spiked with dodecane in acetone Figure 2a chromatogram overlaid with gasoline in dichloromethane Figure 2b chromatogram. The 2b chromatogram labels the peaks of interest with number designations used throughout this research and have approximately the same retention time as those chromatograms run in an acetone solvent.

Figure 3 shows the mass spectrum of peak labeled 1 and the NIST webbook mass spectrum of n-pentane. The mass spectrogram of this peak, in Figure 3a, matches the NIST mass spectrum, in figure 3b, and fragmentation pattern of n-pentane, with peaks at 72, 57, 43, and 27 m/z. The latter three correspond to the loss of successive methylene groups, with 43 m/z being the largest.

Figure 4 shows the mass spectrum of peak labeled 2 (4a) in dichloromethane, and the NIST spectrum of dichloromethane (4b). The peaks and fragmentation pattern in these two spectra appear to match.

Figure 5 shows the mass spectrum of peak 3a, and the NIST webbook mass spectrum of cyclohexane. The m/z readings of interest are at 84, 69, 56, 41, and 28, common to the m/z readings of the Agilent and NIST mass spectra.

Figure 6 shows the mass spectrum of peak 5a, and the NIST webbook mass spectrum of 2-methylhexane, an isomer of heptane. The m/z readings of interest are at 100, 85/84, and 57/56, with similar fragmentation patterns in both spectra.

Figure 7 shows the mass spectra from peak 12 of this research, overlaid with two mass spectra obtained from NIST. Mass peaks are present at 92, 91, 65, 51, and 39 in both mass spectra and the fragmentation patterns appear to match. Combined with the retention time (~4.4 min) this is a good candidate for toluene.

Figure 8 shows the overlay of the mass spectrum of peak 14, eluting at about 5.5 min, and two NIST library mass spectra for octanes (n-octane and iso-octane). This mass spectrum seems to match the NIST library spectra for both n-octane and iso-octane (2,4-dimethyl-hexane). There is an apparent match to the fragmentation pattern and the peaks at 114, 85, and 57, but with a peak at 28 that appears too large.

Figure 9 shows the mass spectra from this research, overlaid with the mass spectra obtained from NIST for peak 15. Mass peaks are present at 106, 91,77, 65, 51, 30, and 27/28 m/z in both mass spectra. Combined with the retention time (~8.2 min) this is a strong candidate for ethylbenzene. The 91 and 77 m/z values would be expected if successive methylene groups had been ionized off the ethyl group of the benzene. The strong 28 peak in the Agilent (this research) chromatograph is the only peak intensity that is quite different.

Figure 10 shows the mass spectra from this research, overlaid with the mass spectra obtained from NIST for peak 16. Mass peaks are present at 106, 91,77, 65, and 51m/z in both mass spectra. Combined with the retention time (~8.7 min) this is a strong candidate for meta and/or para-xylene. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 11 shows the mass spectra from this research, overlaid with the mass spectra obtained from NIST for peak 16. Mass peaks are present at 106, 91,77, 65, and 51m/z in both mass spectra. Combined with the retention time (~10 min) this is a strong candidate for ortho-xylene. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 12 shows the mass spectrum from this research's peak 18, having a retention time of about 10.8 min overlaid with the NIST library mass spectrum for n-nonane. The fragmentation pattern and major peaks appear to be a match, with peaks at 128, 99, 85, 71, 57, 43 and 28 m/z, which correspond to loss of successive methylene groups. The only variance seems to be with the intensity of the peak at 28 m/z. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 13 shows the mass spectrum from this research's peak 19, having a retention time of approximately 14.7 min overlaid with the NIST library mass spectrum for propyl-benzene. The fragmentation pattern and major peaks appear to be a match for propyl-benzene, with peaks at 120, 106, 91, and 77 m/z, which correspond to the loss of 1, 2, and 3 carbons with their hydrogens. More peaks line up, including 65 and 51, which would approximate the loss of two more carbons, but benzene groups do not break easily, so this doesn't provide as strong a support as the molecular weights of the first three alkyl carbons. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 14 shows the mass spectrum overlaid from this research's peak 23 and from the NIST library mass spectrum for 1,3,5-trimethylbenzene (mesitylene), with common peaks at 120, 105, 91, and 77 m/z. These are the approximate molecular weights as 1, 2, then 3 methyl groups are stripped from mesitylene. It had a retention time of 18.25 min. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 15 shows the mass spectra overlaid for peak 24, retention time of 21.1, with the NIST library entry for 1,2,4-trimethylbenzene (pseudocumene), with common peaks at 120, 105, 91, and 77 m/z, with the only questionable peak being at 28 m/z, being much higher on the Agilent mass spectrum. Otherwise, the fragmentation pattern seems to match. Both base and molecular ion peaks match between the Agilent and NIST mass spectra.

Figure 1

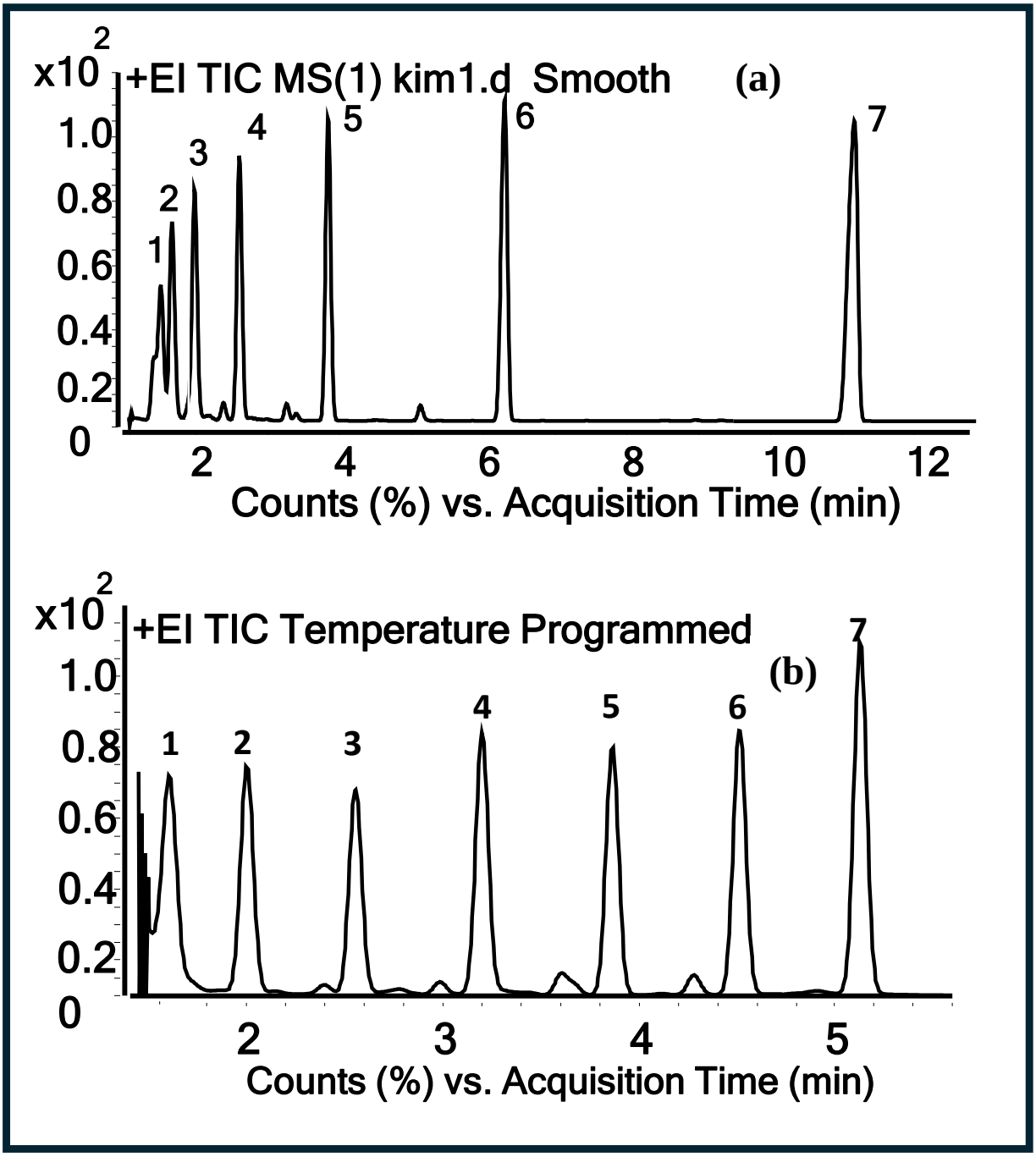
x10 2
+EI TIC MS(1) kim1.d Smooth
(a)
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
2
4
6
8
10
12
Counts (%) vs. Acquisition Time (min)
x10 2
+EI TIC Temperature Programmed
(b)
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
2
3
4
5
Counts (%) vs. Acquisition Time (min)

Figure 2

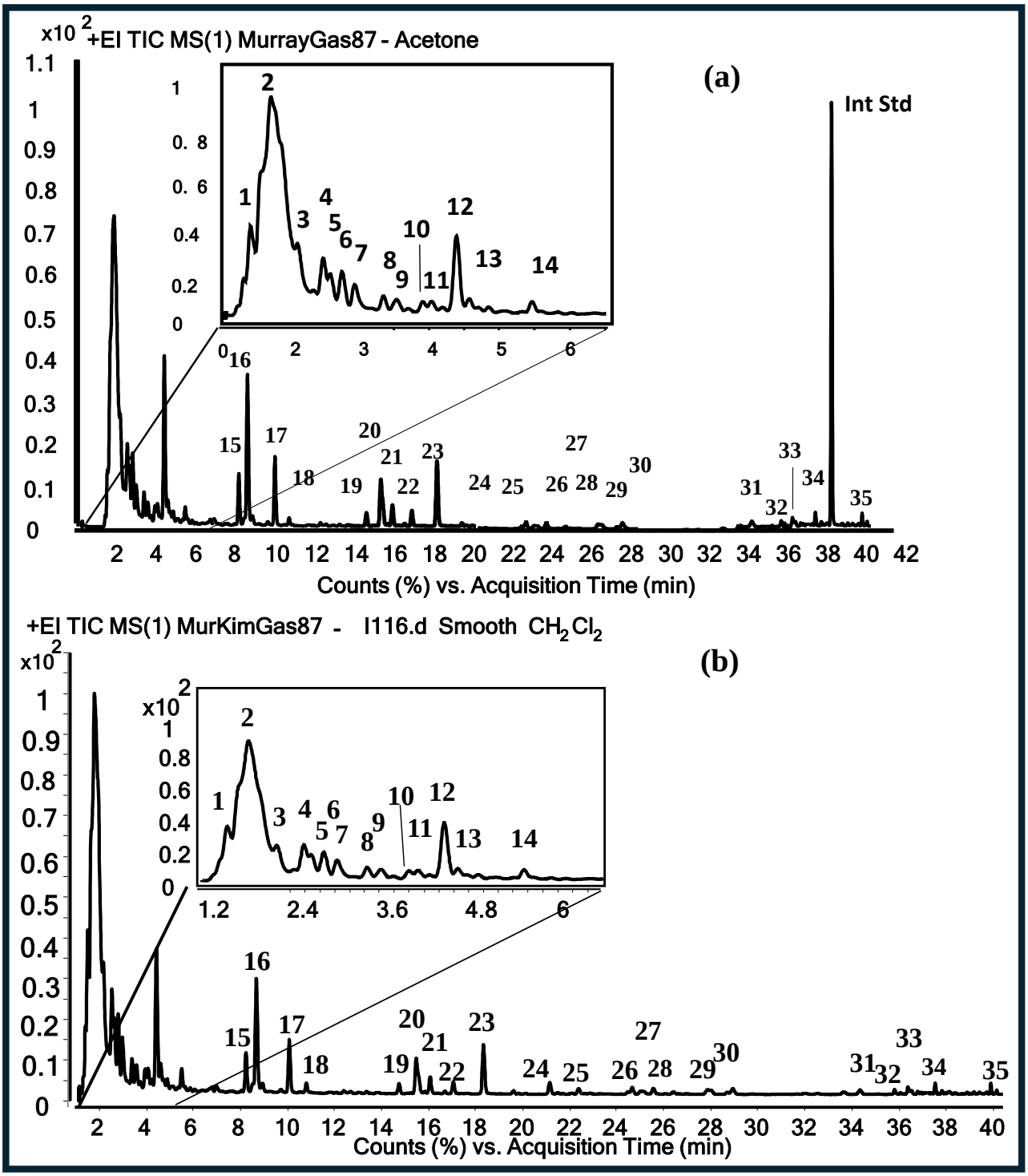
x10 2 +EI TIC MS(1) MurrayGas87 - Acetone
(a)
Int Std
Counts (%) vs. Acquisition Time (min)
+EI TIC MS(1) MurKimGas87 - I116.d Smooth CH2Cl2
(b)
Counts (%) vs. Acquisition Time (min)

Figure 3

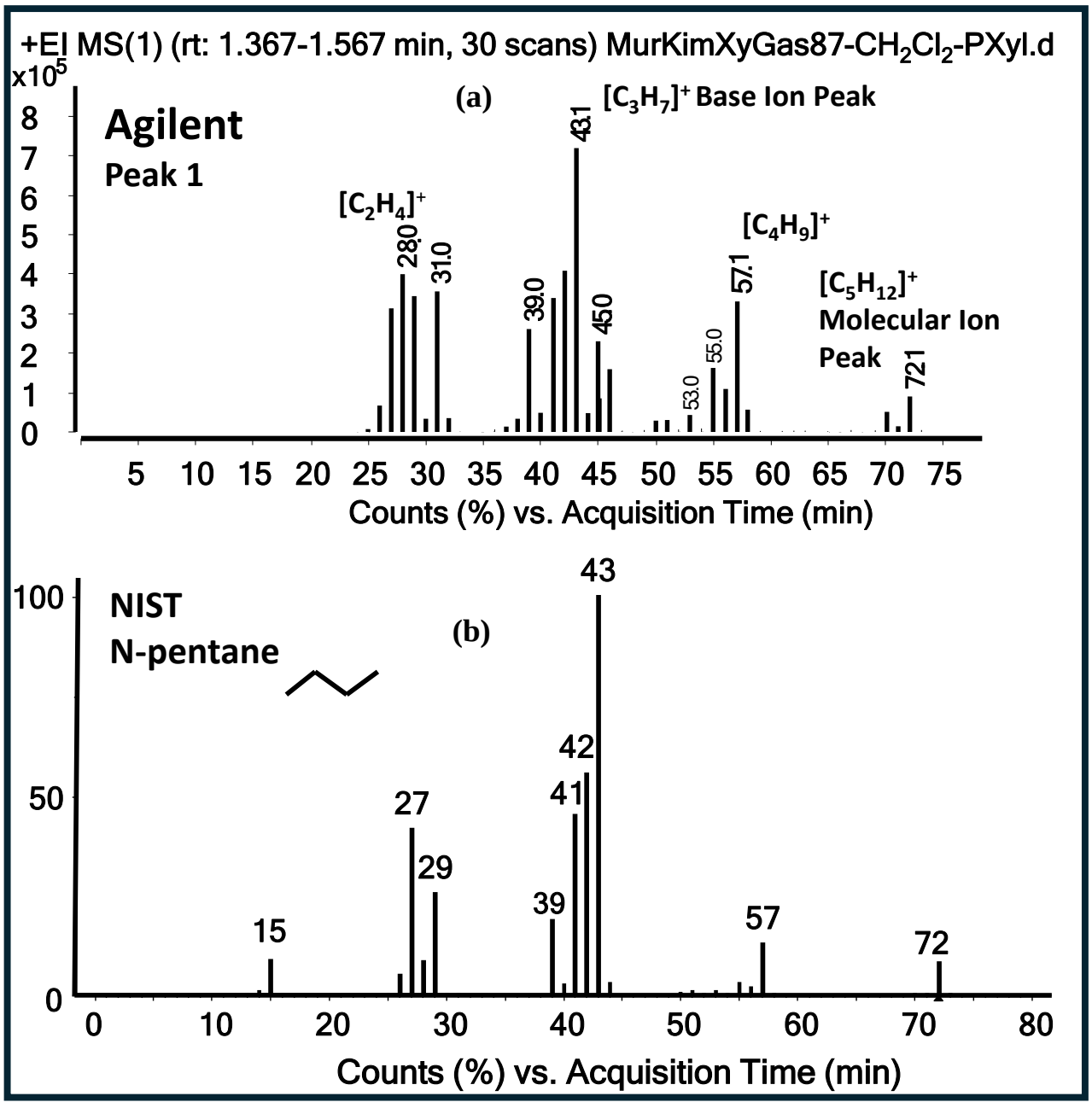
+EI MS(1) (rt: 1.367-1.567 min, 30 scans) MurKimXyGas87-CH2Cl2-PXyl.d
x10^5
(a)
Agilent
Peak 1
[C3H7]+ Base Ion Peak
[C2H4]+
[C4H9]+
[C5H12]+
Molecular Ion
Peak
43.1
28.0
31.0
39.0
45.0
55.0
53.0
57.1
72.1
Counts (%) vs. Acquisition Time (min)
(b)
NIST
N-pentane
43
42
41
27
29
39
15
57
72
Counts (%) vs. Acquisition Time (min)

Figure 4

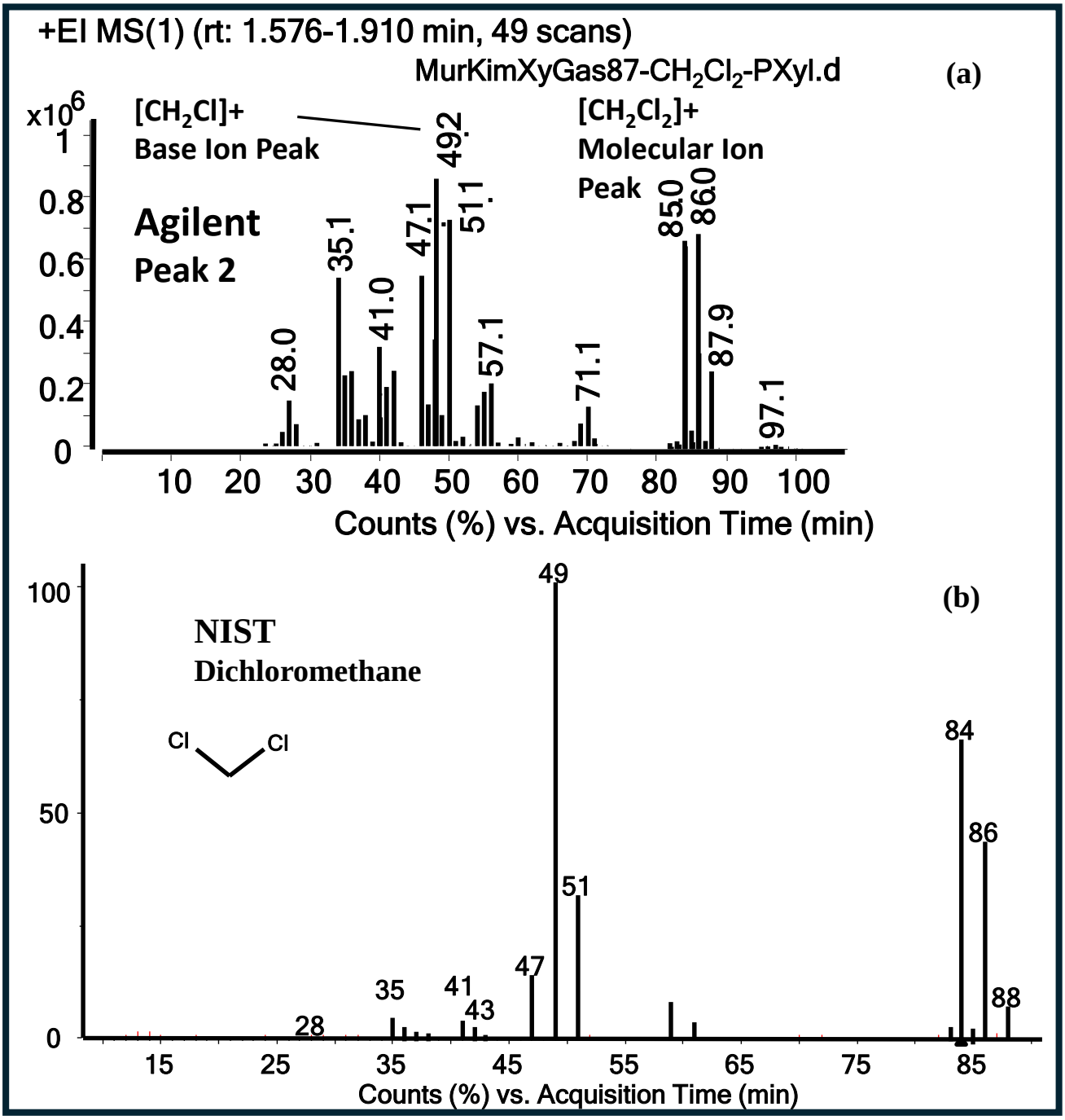
+EI MS(1) (rt: 1.576-1.910 min, 49 scans)
MurKimXyGas87-CH2Cl2-PXyl.d
(a)
x10^6
[CH2Cl]+
Base Ion Peak
[CH2Cl2]+
Molecular Ion
Peak
Agilent
Peak 2
28.0
35.1
41.0
47.1
49.2
51.1
57.1
71.1
85.0
86.0
87.9
97.1
Counts (%) vs. Acquisition Time (min)
(b)
NIST
Dichloromethane
Cl
Cl
49
84
86
51
47
35
41
43
28
88
Counts (%) vs. Acquisition Time (min)

Figure 5

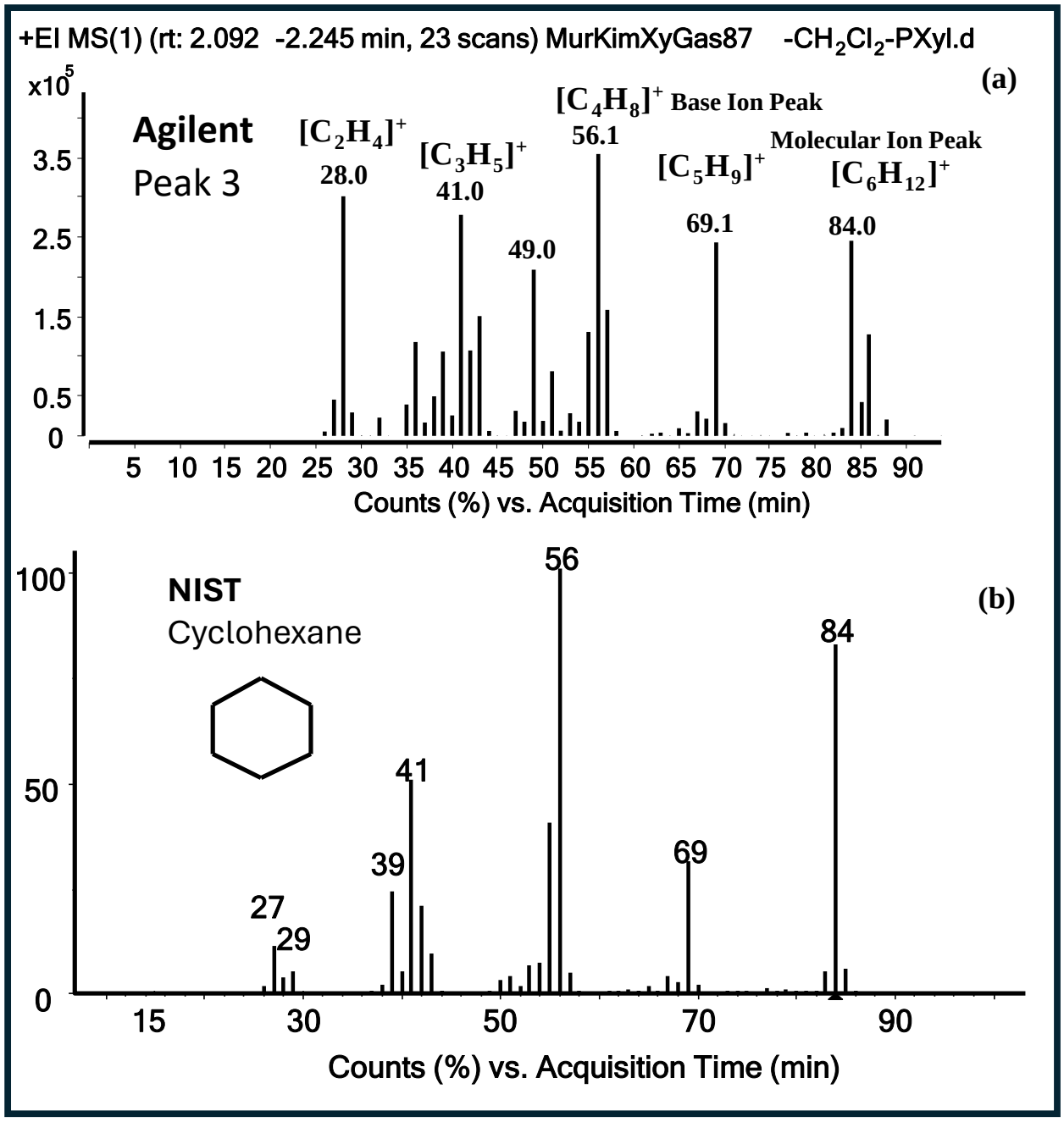
+EI MS(1) (rt: 2.092 -2.245 min, 23 scans) MurKimXyGas87 -CH2Cl2-PXyl.d
(a)
x10^5
Agilent
Peak 3
[C2H4]+
28.0
[C3H5]+
41.0
49.0
[C4H8]+ Base Ion Peak
56.1
[C5H9]+
69.1
Molecular Ion Peak
[C6H12]+
84.0
Counts (%) vs. Acquisition Time (min)
(b)
NIST
Cyclohexane
56
84
41
39
69
27
29
Counts (%) vs. Acquisition Time (min)

Figure 6

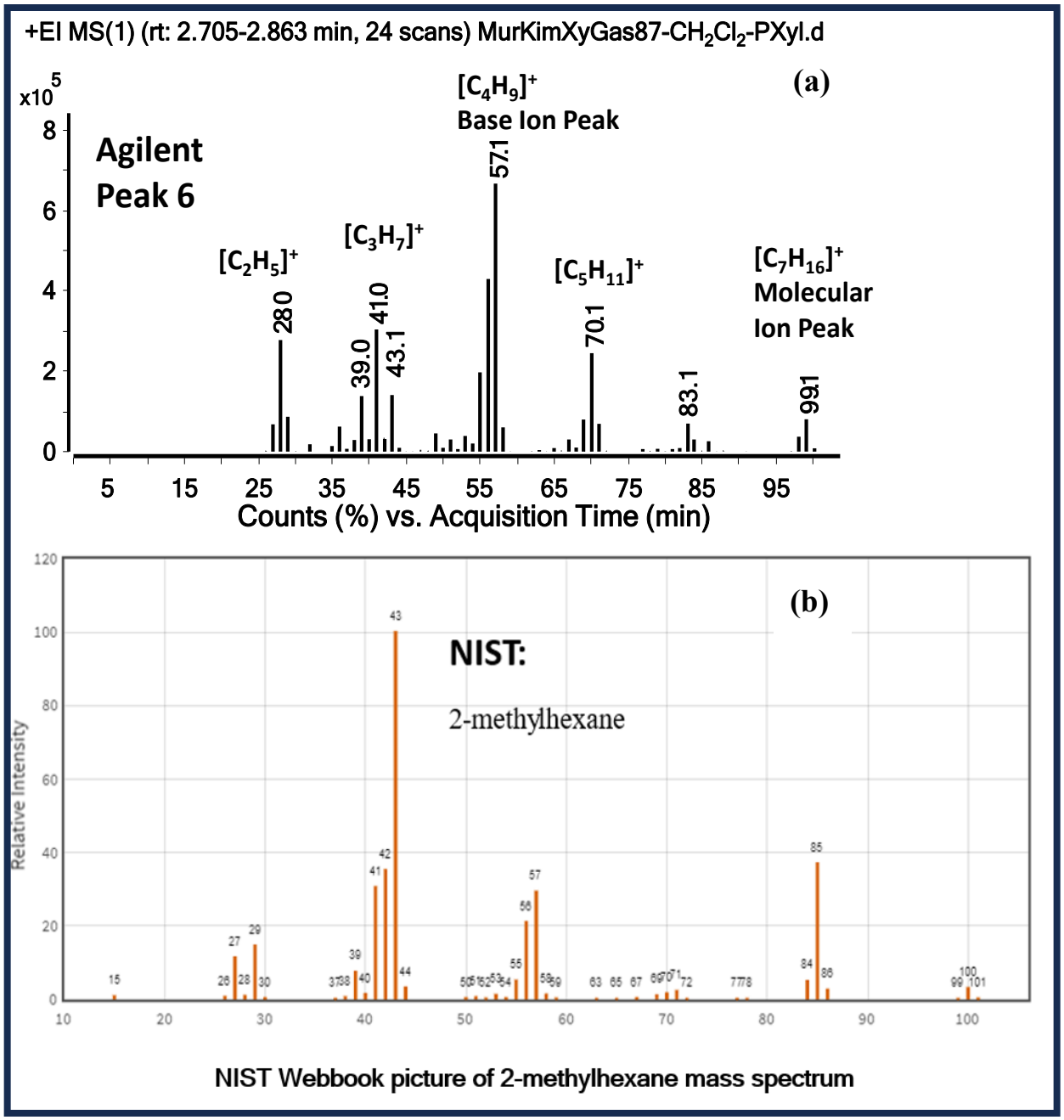
+EI MS(1) (rt: 2.705-2.863 min, 24 scans) MurKimXyGas87-CH2Cl2-PXyl.d
(a)
x10^5
Agilent
Peak 6
[C4H9]+
Base Ion Peak
[C3H7]+
[C2H5]+
[C5H11]+
[C7H16]+
Molecular
Ion Peak
28.0
39.0
41.0
43.1
57.1
70.1
83.1
99.1
Counts (%) vs. Acquisition Time (min)
(b)
NIST:
2-methylhexane
Relative Intensity
NIST Webbook picture of 2-methylhexane mass spectrum

Figure 7

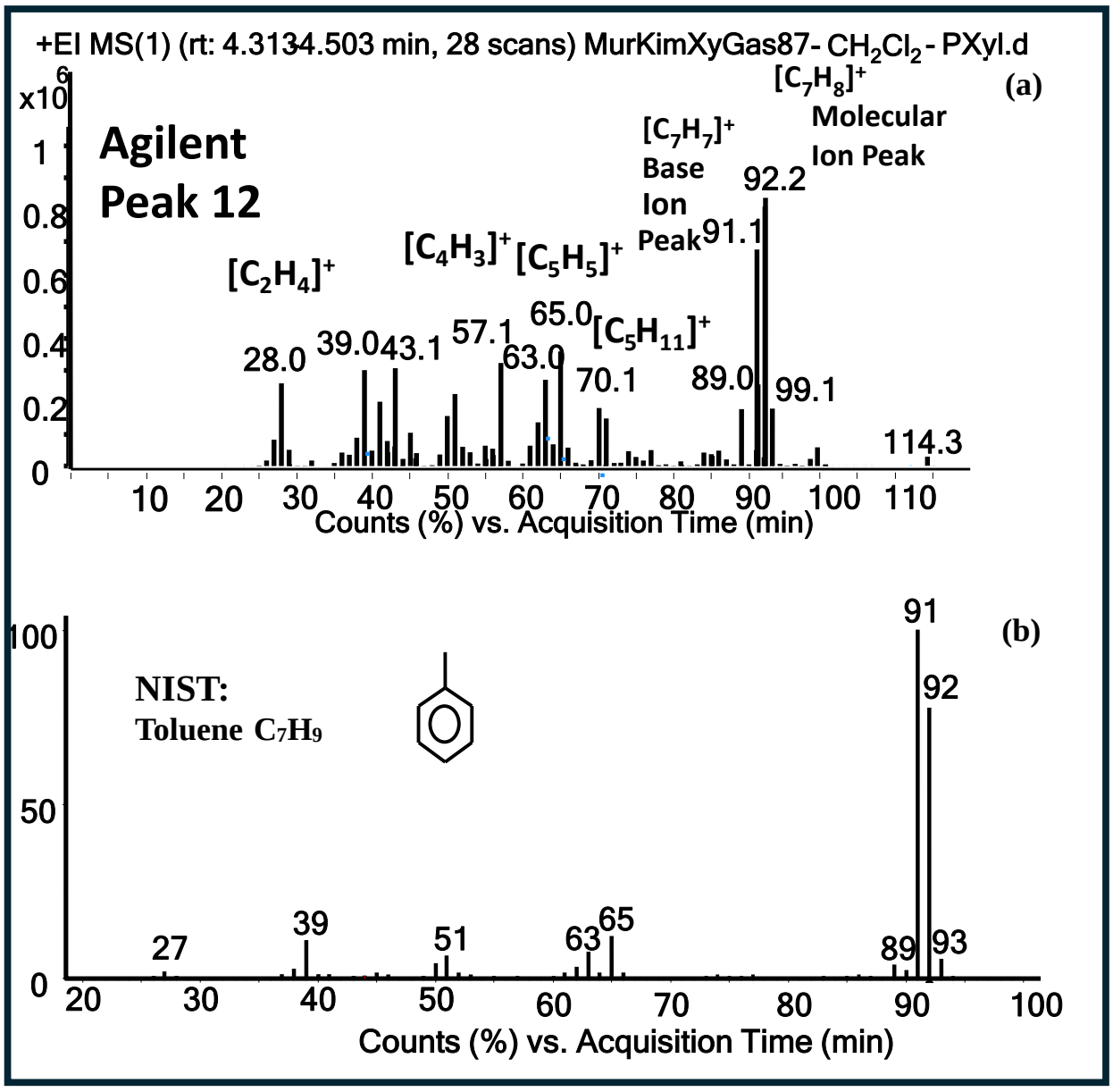
+EI MS(1) (rt: 4.313-4.503 min, 28 scans) MurKimXyGas87- CH2Cl2 - PXyl.d
(a)
Agilent
Peak 12
[C7H8]+
Molecular
Ion Peak
[C7H7]+
Base
Ion
Peak
92.2
91.1
[C4H3]+
[C5H5]+
[C2H4]+
65.0
[C5H11]+
28.0
39.0
43.1
57.1
63.0
70.1
89.0
99.1
114.3
Counts (%) vs. Acquisition Time (min)
(b)
NIST:
Toluene C7H9
91
92
39
27
51
63
65
89
93
Counts (%) vs. Acquisition Time (min)

Figure 8

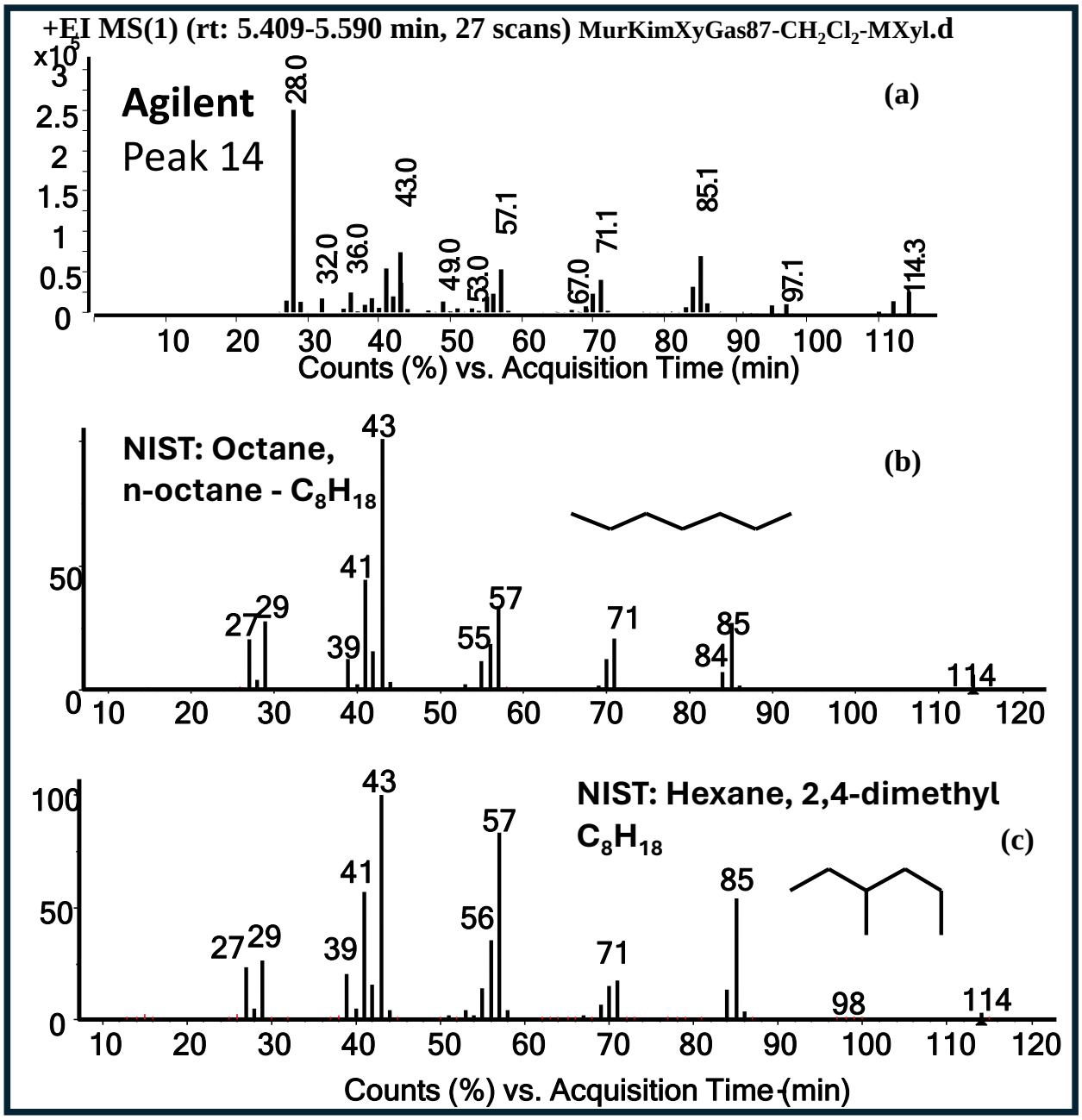
+EI MS(1) (rt: 5.409-5.590 min, 27 scans) MurKimXyGas87-CH2Cl2-MXyl.d
x10 3
Agilent
Peak 14
(a)
28.0
43.0
57.1
71.1
85.1
32.0
36.0
49.0
53.0
67.0
97.1
114.3
Counts (%) vs. Acquisition Time (min)
NIST: Octane,
n-octane - C8H18
(b)
43
41
57
71
85
29
27
39
55
84
114
NIST: Hexane, 2,4-dimethyl
C8H18
(c)
43
57
41
85
56
29
27
39
71
98
114
Counts (%) vs. Acquisition Time (min)

Figure 9

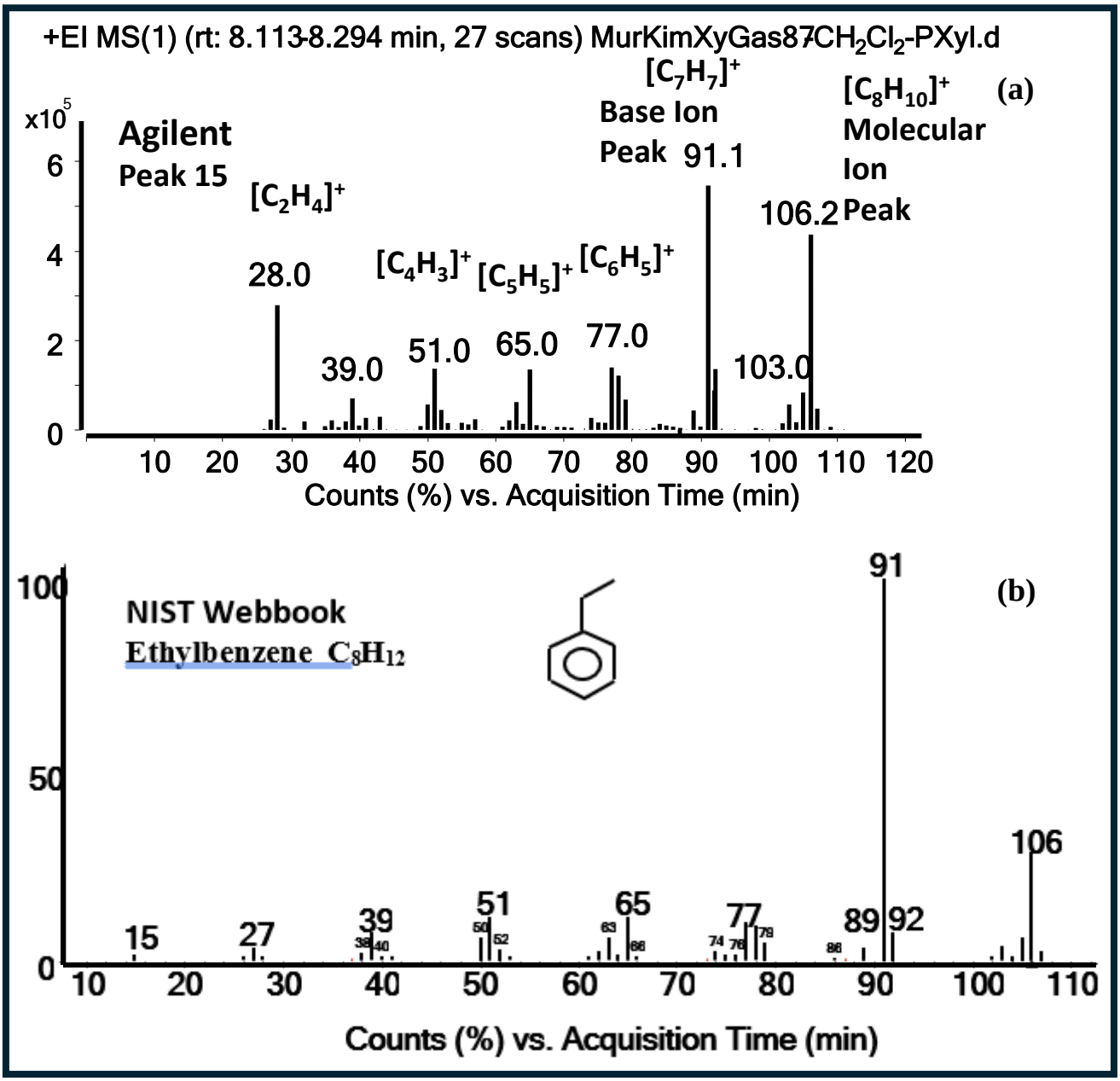
+EI MS(1) (rt: 8.113-8.294 min, 27 scans) MurKimXyGas87-CH2Cl2-PXyl.d
x10^5
Agilent
Peak 15
[C2H4]+
28.0
[C4H3]+
39.0
51.0
[C5H5]+
65.0
[C6H5]+
77.0
[C7H7]+
Base Ion
Peak
91.1
103.0
106.2
[C8H10]+
Molecular
Ion
Peak
(a)
Counts (%) vs. Acquisition Time (min)
NIST Webbook
Ethylbenzene C8H12
(b)
Counts (%) vs. Acquisition Time (min)

Figure 10

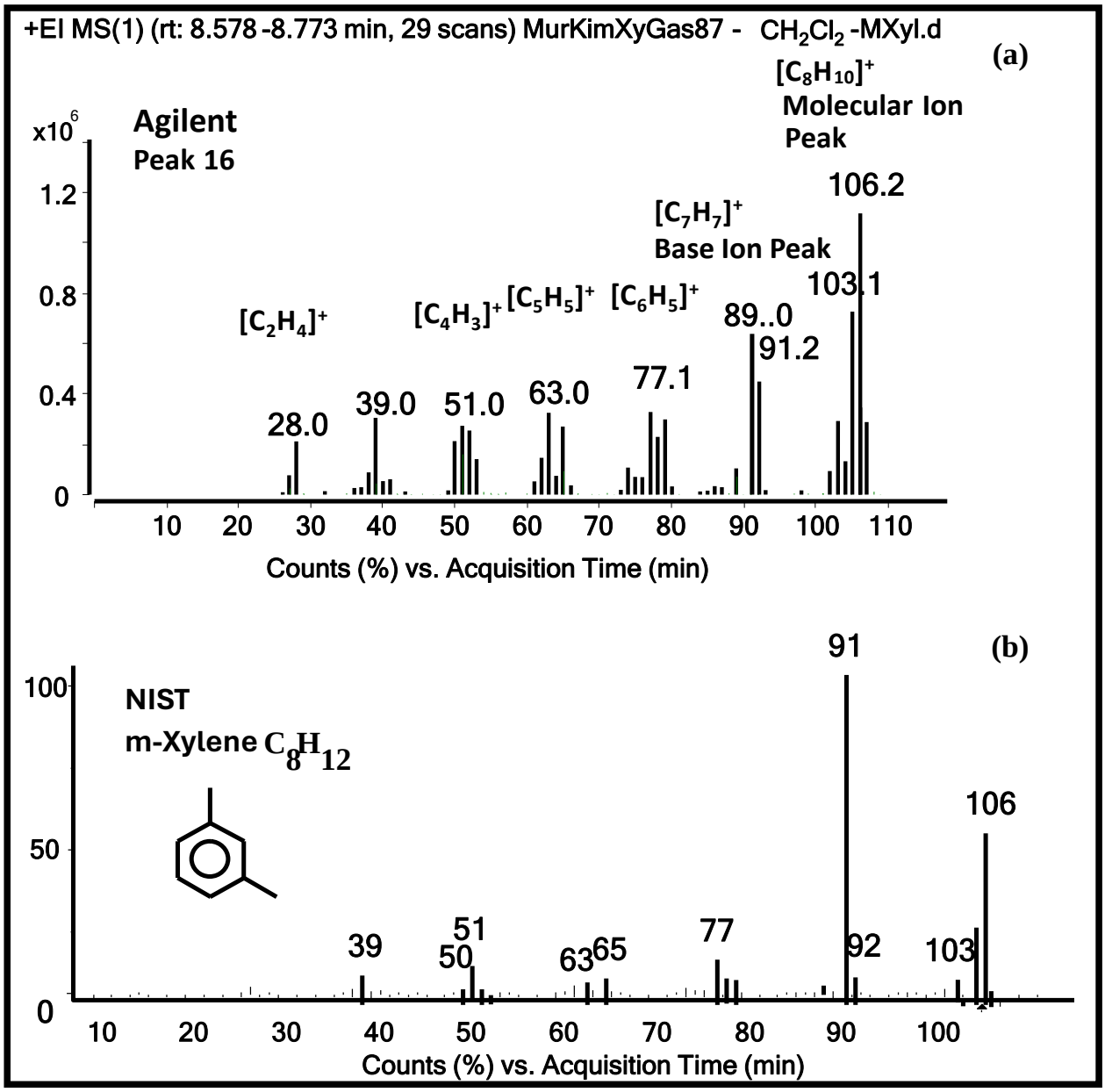
+EI MS(1) (rt: 8.578 -8.773 min, 29 scans) MurKimXyGas87 - CH2Cl2 -MXyl.d
(a)
[C8H10]+
Molecular Ion
Peak
x10^6
Agilent
Peak 16
106.2
[C7H7]+
Base Ion Peak
103.1
[C2H4]+
[C4H3]+
[C5H5]+
[C6H5]+
89..0
91.2
77.1
63.0
28.0
39.0
51.0
Counts (%) vs. Acquisition Time (min)
(b)
91
NIST
m-Xylene C8H12
106
39
51
50
63
65
77
92
103
Counts (%) vs. Acquisition Time (min)

Figure 10

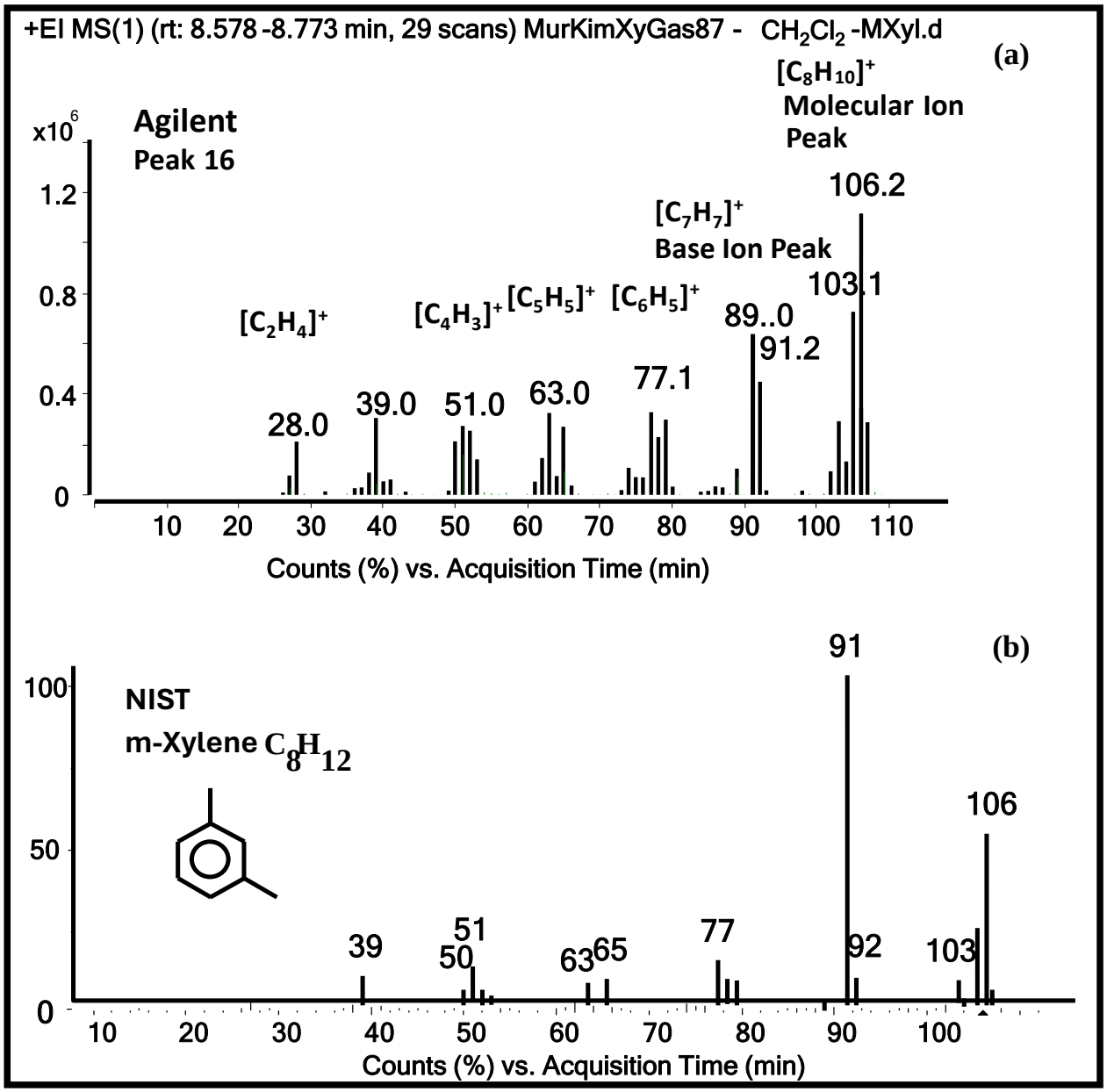
+EI MS(1) (rt: 8.578 -8.773 min, 29 scans) MurKimXyGas87 - CH2Cl2 -MXyl.d
(a)
[C8H10]+
Molecular Ion
Peak
x10^6
Agilent
Peak 16
106.2
[C7H7]+
Base Ion Peak
103.1
[C2H4]+
[C4H3]+
[C5H5]+
[C6H5]+
89..0
91.2
77.1
63.0
39.0
51.0
28.0
Counts (%) vs. Acquisition Time (min)
(b)
91
NIST
m-Xylene C8H12
106
39
51
50
63
65
77
92
103
Counts (%) vs. Acquisition Time (min)

Figure 11

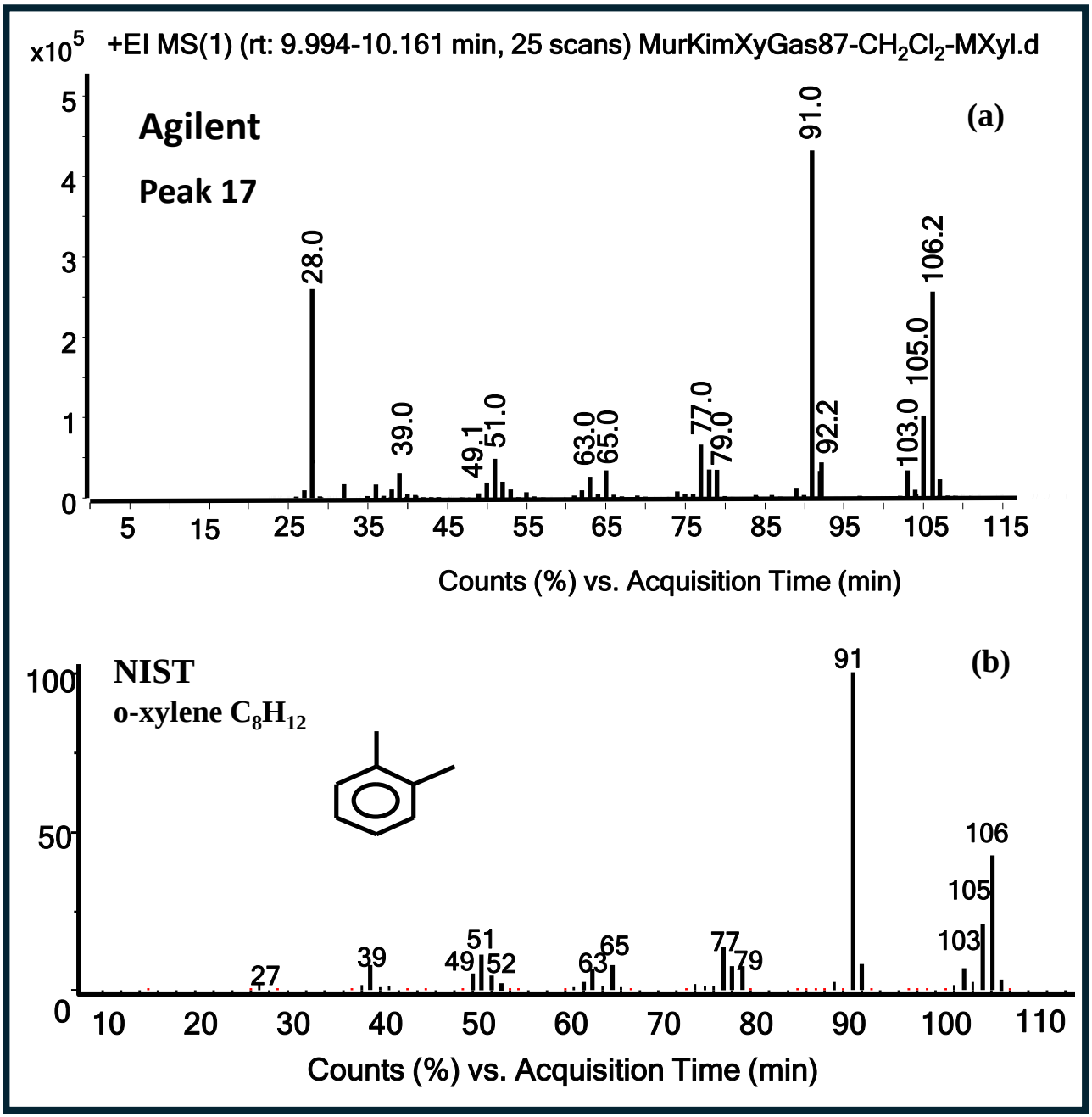
x10^5 +EI MS(1) (rt: 9.994-10.161 min, 25 scans) MurKimXyGas87-CH2Cl2-MXyl.d
Agilent
Peak 17
(a)
91.0
28.0
106.2
105.0
39.0
49.1
51.0
63.0
65.0
77.0
79.0
92.2
103.0
Counts (%) vs. Acquisition Time (min)
NIST
o-xylene C8H12
(b)
91
106
105
103
51
39
49
52
27
63
65
77
79
Counts (%) vs. Acquisition Time (min)

Figure 12

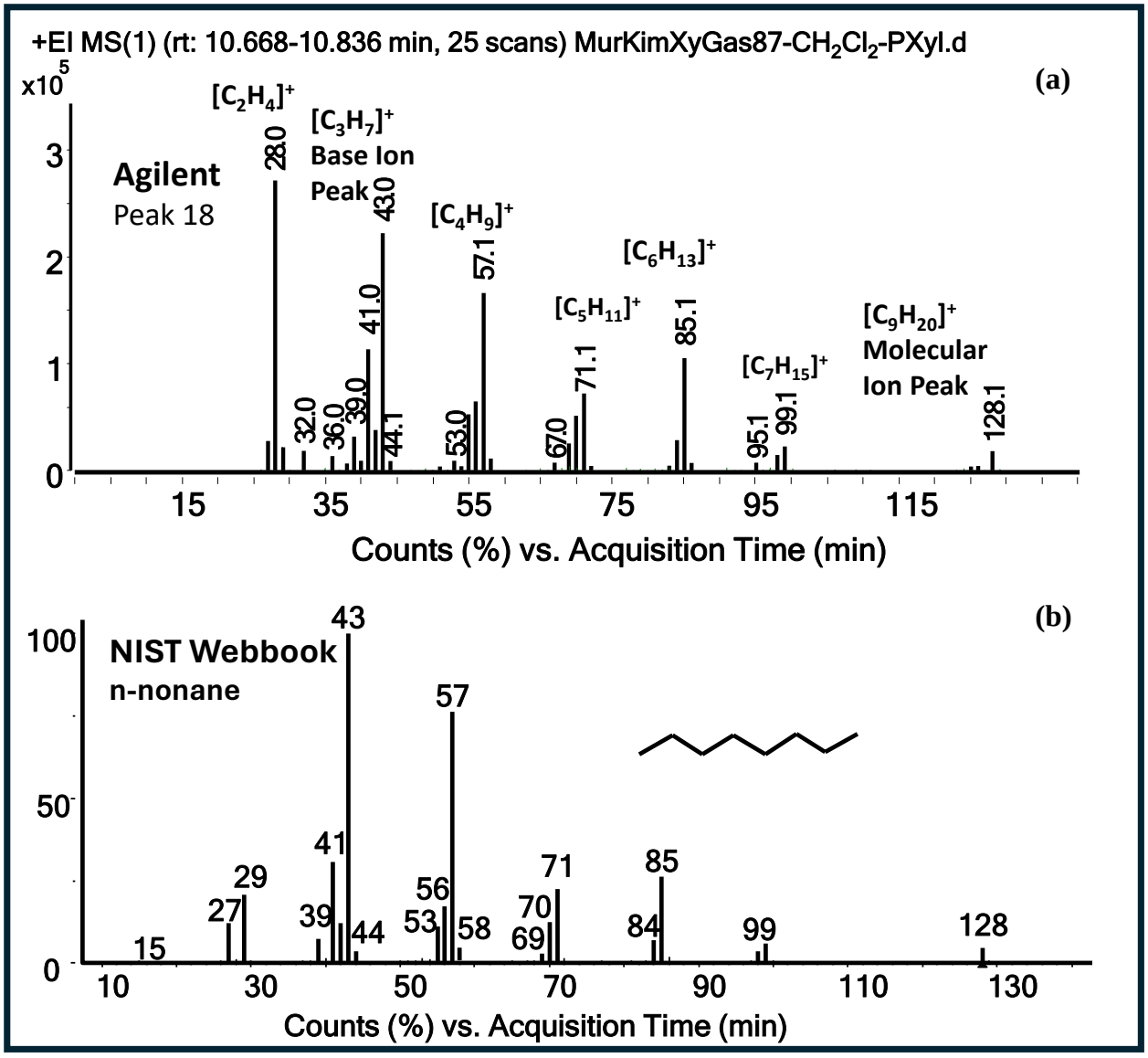
+EI MS(1) (rt: 10.668-10.836 min, 25 scans) MurKimXyGas87-CH2Cl2-PXyl.d
(a)
x10^5
Agilent
Peak 18
[C2H4]+
[C3H7]+
Base Ion
Peak
[C4H9]+
[C6H13]+
[C5H11]+
[C9H20]+
Molecular
Ion Peak
[C7H15]+
28.0
43.0
57.1
41.0
85.1
71.1
32.0
36.0
39.0
44.1
53.0
67.0
95.1
99.1
128.1
Counts (%) vs. Acquisition Time (min)
(b)
NIST Webbook
n-nonane
43
57
41
29
27
39
44
56
53
58
71
70
69
85
84
99
128
15
Counts (%) vs. Acquisition Time (min)

Figure 13

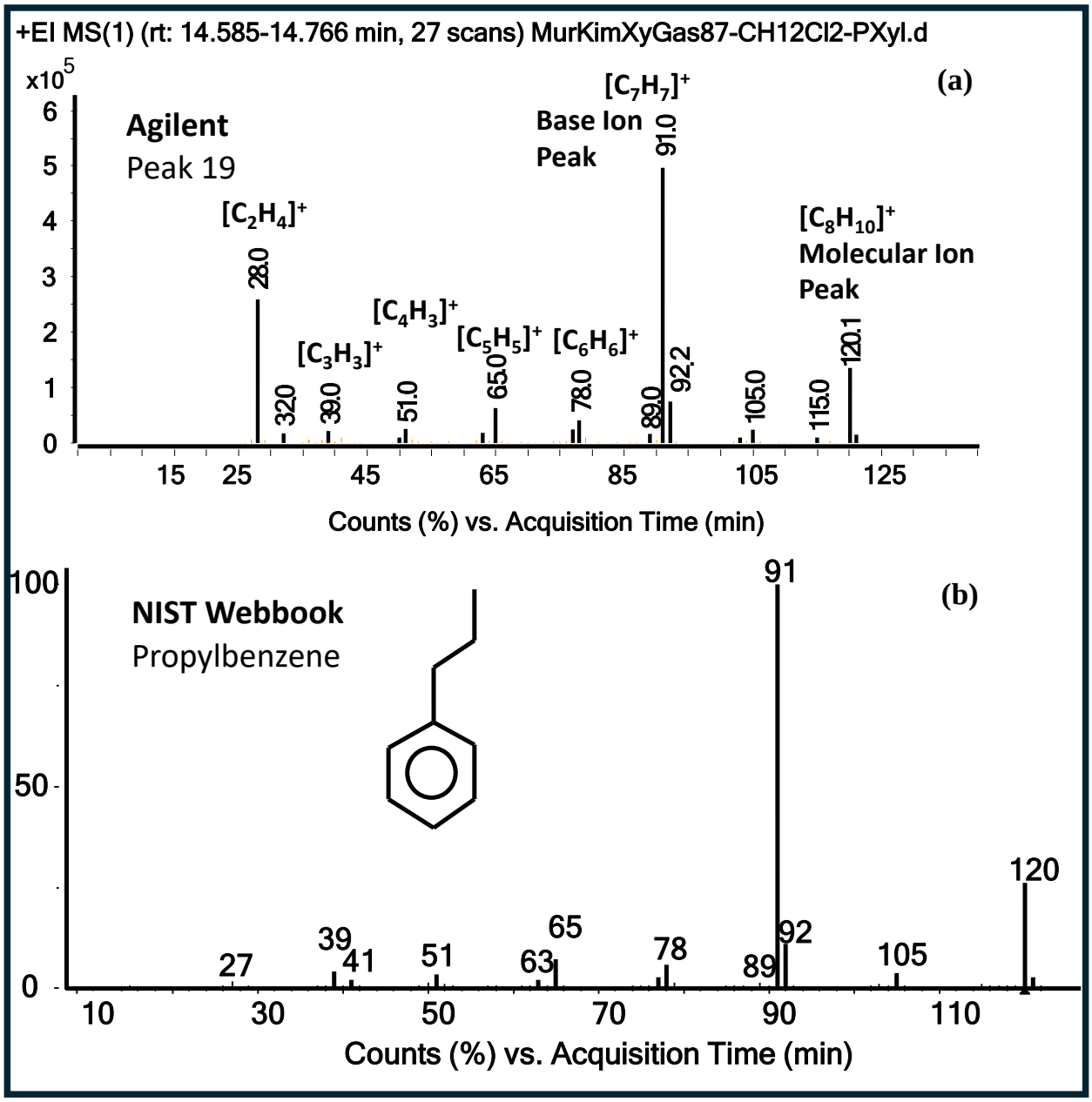
+EI MS(1) (rt: 14.585-14.766 min, 27 scans) MurKimXyGas87-CH12Cl2-PXyl.d
x10^5
(a)
Agilent
Peak 19
[C7H7]+
Base Ion
Peak
91.0
[C2H4]+
28.0
[C8H10]+
Molecular Ion
Peak
[C4H3]+
[C5H5]+
[C6H6]+
[C3H3]+
32.0
39.0
51.0
65.0
78.0
89.0
92.2
105.0
115.0
120.1
Counts (%) vs. Acquisition Time (min)
(b)
NIST Webbook
Propylbenzene
91
120
65
92
39
41
51
63
78
89
105
27
Counts (%) vs. Acquisition Time (min)

Figure 14

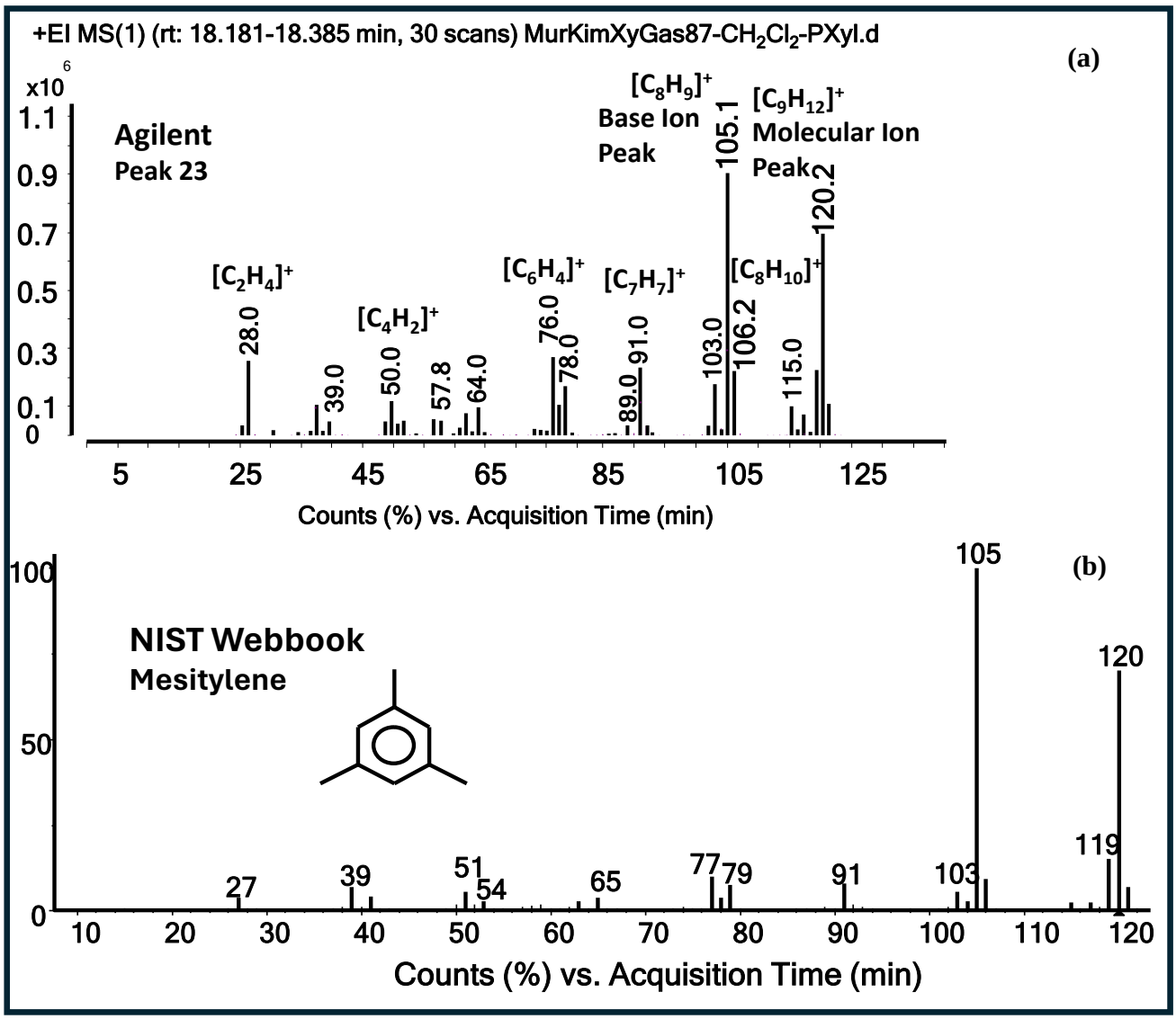
+EI MS(1) (rt: 18.181-18.385 min, 30 scans) MurKimXyGas87-CH2Cl2-PXyl.d
(a)
x10 6
Agilent
Peak 23
[C8H9]+
Base Ion
Peak
[C9H12]+
Molecular Ion
Peak
[C2H4]+
[C4H2]+
[C6H4]+
[C7H7]+
[C8H10]+
28.0
39.0
50.0
57.8
64.0
76.0
78.0
89.0
91.0
103.0
105.1
106.2
115.0
120.2
Counts (%) vs. Acquisition Time (min)
(b)
NIST Webbook
Mesitylene
105
120
119
27
39
51
54
65
77
79
91
103
Counts (%) vs. Acquisition Time (min)

Figure 15

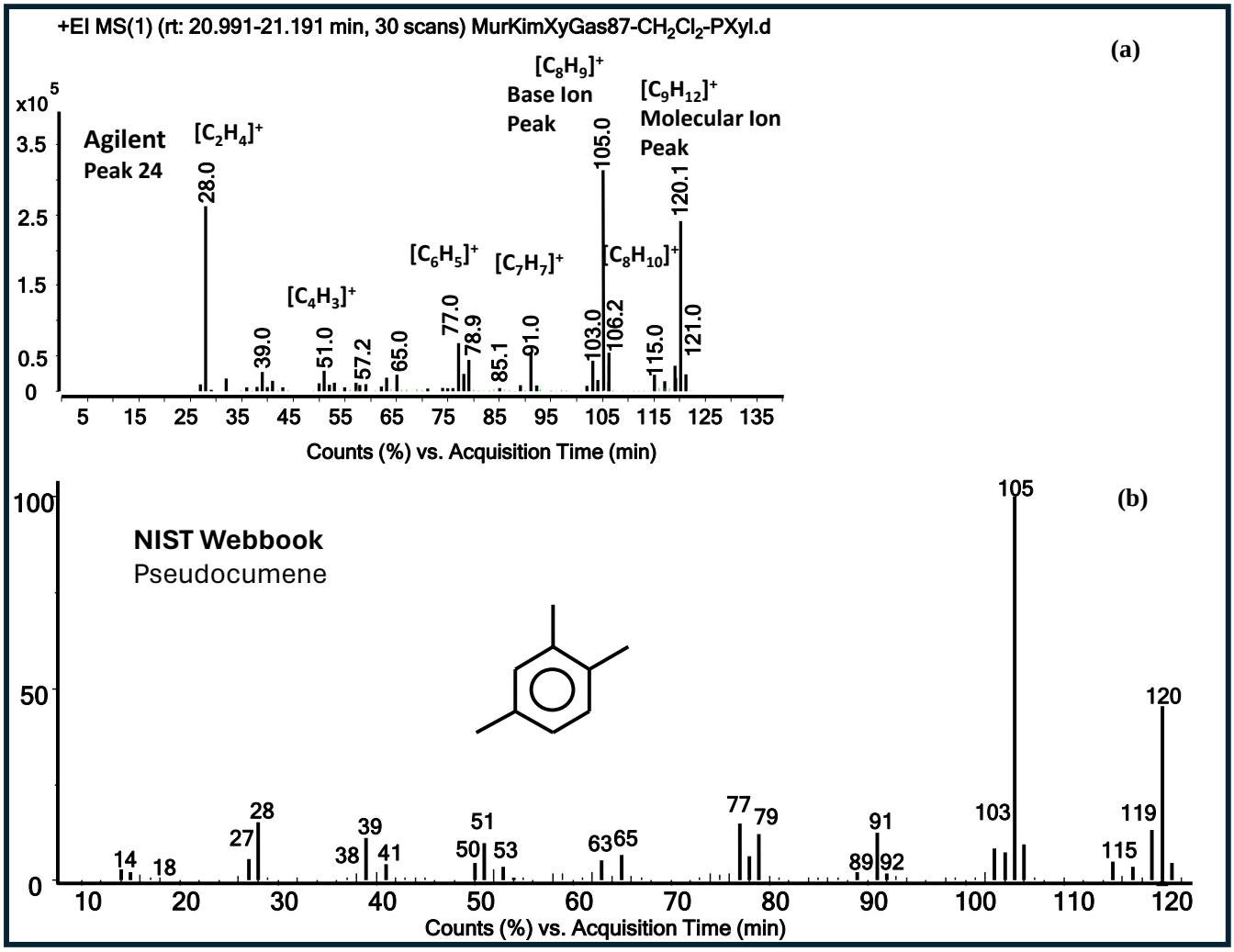
+EI MS(1) (rt: 20.991-21.191 min, 30 scans) MurKimXyGas87-CH2Cl2-PXyl.d
(a)
Agilent
Peak 24
[C2H4]+
[C8H9]+
Base Ion
Peak
[C9H12]+
Molecular Ion
Peak
[C6H5]+
[C7H7]+
[C4H3]+
[C8H10]+
Counts (%) vs. Acquisition Time (min)
(b)
NIST Webbook
Pseudocumene
Counts (%) vs. Acquisition Time (min)

Table 1. A comparison of the chromatographic data of alkanes (C6-C12) run under isothermal conditions (a) versus temperature programmed conditions (b).

a	**hexane**	**heptane**	**octane**	**nonane**	**decane**	**undecane**	**dodecane**
Trial 1 t_R	1.250	1.524	1.835	2.456	3.699	6.161	11.020
Trial 2 t_R	1.249	1.525	1.836	2.458	3.701	6.151	11.022
Trial 3 t_R	1.252	1.522	1.836	2.458	3.701	6.163	11.034
Avg t_R	1.250	1.524	1.836	2.457	3.700	6.158	11.025
corr avg t_R	1.250	1.524	1.836	2.457	3.700	6.158	11.025
std dev	0.002	0.002	0.001	0.001	0.001	0.006	0.008
RSD	0.12	0.10	0.03	0.05	0.03	0.10	0.07
Efficiency	385	929	1348	2415	2434	3793	5403
α		1.2	1.2	1.3	1.5	1.7	1.8
R_S		1.20	1.26	3.11	4.97	7.03	9.72
b	**hexane**	**Heptane**	**octane**	**nonane**	**decane**	**undecane**	**Dodecane**
Trial 1 t_R	1.579	2.058	2.628	3.276	3.937	4.585	5.206
Trial 2 t_R	1.579	2.058	2.628	3.276	3.937	4.585	5.206
Trial 3 t_R	1.579	2.058	2.628	3.276	3.937	4.585	5.206
Avg t_R	1.579	2.058	2.628	3.276	3.937	4.585	5.206
corr avg t_R	1.579	2.058	2.628	3.276	3.937	4.585	5.206
std dev	-	-	-	-	-	-	-
RSD	-	-	-	-	-	-	-
N	443	1694	2763	7632	6200	8409	10841
α		1.3	1.3	1.2	1.2	1.2	1.1
R_S		1.92	2.85	3.70	3.78	3.24	3.11

* All efficiency standard deviations are below 10. Those of the programmed trials were below 1. All values below the level of precision, or close enough to zero as to be indistinguishable on this hardware, show as a dash.

Table 2 Average values for retention time, peak area, peak height, peak width, separation and resolution for gasoline trials[1]. Full data available in Supplemental Information.

Peak ID /Avgs	t_R (min)	Peak Area (mV.s)	Peak Height (mV)	Peak Width (mV)	α	R_S
1	1.506	5790234	9694417	0.084		
2	1.771	87622555	26306787	0.181	0.85	0.16
3	2.177	7380444	6101565	0.064	0.81	0.21
4	2.524	14504867	7841656	0.099	0.86	0.15
5	2.609	8544673	5144084	0.049	0.97	0.03
6	2.788	11660437	6281358	0.070	0.94	0.07
7	2.970	9509191	4624623	0.089	0.94	0.06
8	3.365	4993393	3009754	0.066	0.88	0.12
9	3.555	5502482	2527225	0.079	0.95	0.05
10	3.938	4013393	2324814	0.052	0.90	0.10
11	4.057	5448098	2408293	0.063	0.97	0.03
12	4.393	32088090	9424073	0.060	0.92	0.08
13	4.593	6749625	2881726	0.060	0.96	0.04
14	5.483	8108401	2712106	0.103	0.84	0.18
15	8.224	15597012	3901805	0.187	0.67	0.40
16	8.698	75136637	21754772	0.138	0.95	0.06
17	10.061	22963289	5283980	0.110	0.86	0.15
18	10.747	11049544	1834373	0.222	0.94	0.07
19[1]	14.686	36383156	9624375	0.157	0.73	0.31
20	15.444	1229515	3037428	0.014	0.95	0.05
21	15.730	13280200	3214277	0.168	0.98	0.02
22	16.227	9480545	2675723	0.216	0.97	0.03
23	18.315	22061631	5537286	0.162	0.89	0.12
24	21.088	19446681	2423984	0.376	0.87	0.14
25	22.320	10762828	1280421	0.321	0.94	0.06
26	24.592	13587351	1556208	0.307	0.91	0.10
27	25.066	6687778	770308	0.284	0.98	0.02
28	25.493	13697041	1445177	0.516	0.98	0.02
29	27.795	12429773	1210941	0.348	0.92	0.09
30	28.865	15453016	1483690	0.413	0.96	0.04
31	34.273	11868671	1149383	0.502	0.84	0.17
32	35.778	7812895	1187577	0.154	0.96	0.04
33	36.355	10865966	1688899	0.109	0.98	0.02
34	37.521	12039046	2188318	0.105	0.97	0.03
Dodecane	38.347	55016324	284616	0.259	0.98	0.02
35	39.895	11717588	2131132	0.209	0.96	0.04

[1] Some trial sets returned no peak information at the approximate retention time of the peak ID listed, so was used from different trial sets average values, so long as they matched the retention times and position.

5.0 REFERENCES

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6.0 SUPPLEMENTAL INFORMATION

6.1 Formulas

Sample calculations

Resolution Equation 1

$$R_S = \frac{2*(t_{R2}-t_{R1})}{(W_{p2}+W_{p1})}$$

$$1.5 = \frac{2*(2.067-1.676)}{(0.33+0.19)}$$

Separation Equation 2

$$\alpha = \frac{t_{R2}}{t_{R1}}$$

$$1.233 = \frac{2.067}{1.676}$$

6.2 Raw Data and Supplemental files

Excel

Alkane trial analysis.xlsx	*Computed R_S and α data*
GasComponents_withProperties.xlsx	*BP and MW data for common gas constituents*
AlkanesAndGasolineData.xlsx	*Alkane & Gasoline peak data*
GC DataDetails_Gas_wDoDecane.xlsx	

PowerPoint

Blank-Gas87-mXyl-pXyl-mpXyl.pptx
Gas87 spike_w_mXyl-pXyl-mpXyl.pptx
MurrayGas87-MeCl2-1.pptx
XylenesExamined.pptx
alkane90-1d.pptx
alkane90-2d.pptx
alkane90-3d.pptx
AlkaneTempProg35-250-1.pptx
AlkaneTempProg35-250-2.pptx

AlkaneTempProg35-250-3.pptx

Blank-MeCl2.pptx

Figures.pptx *Chromatograph Figures in PowerPoint*

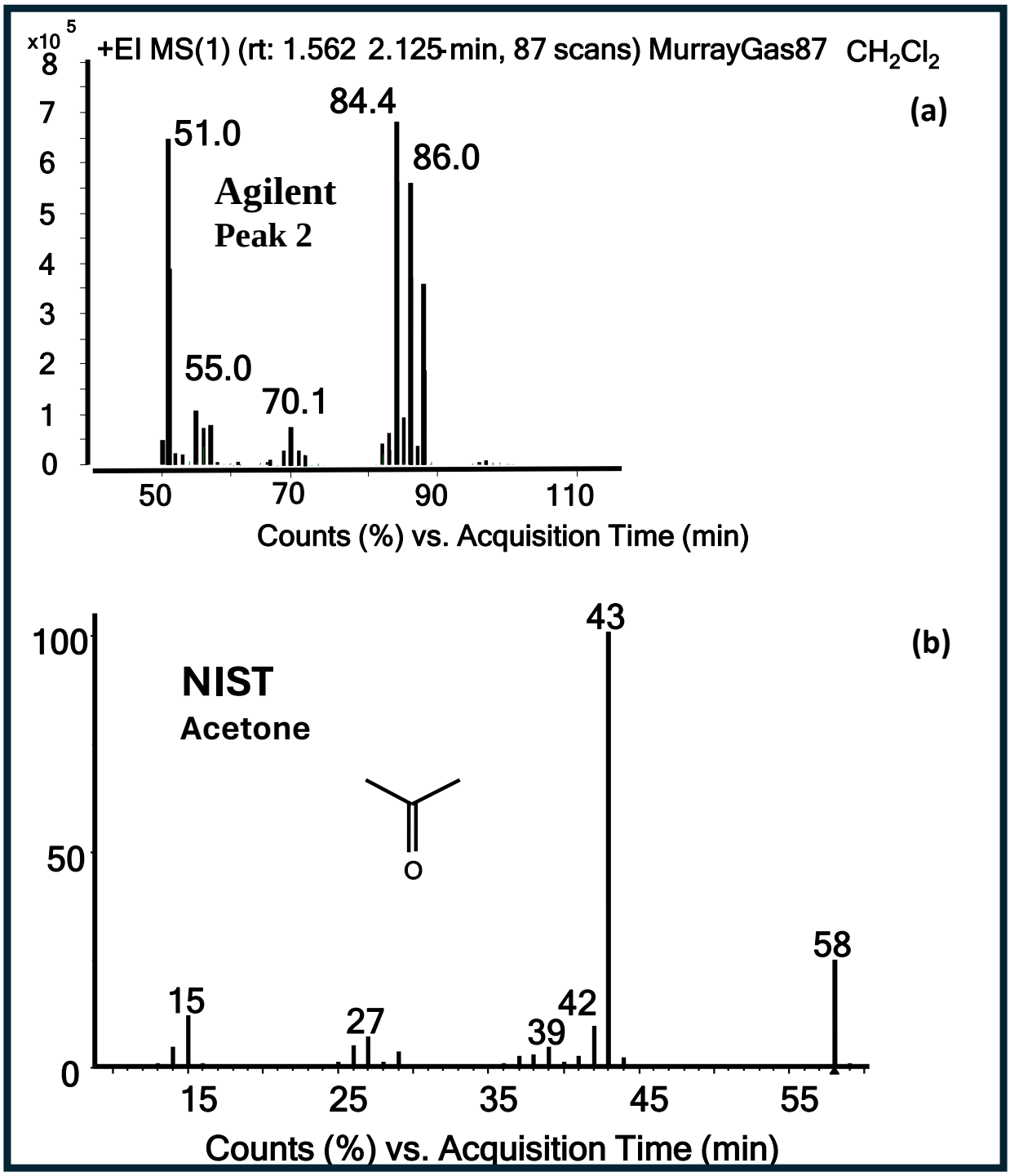
File Locations on GC/MS Computer

Computer: DESKTOP-JC8IBCJ, with GC/MS SN: CN2117D002

Folder: D:\MassHunter\GCMS\1\data\Murray87Gas

6.3 Tables, Graphs, and Plots

Figure S1



Peak 2 (a) from an acetone solvent gasoline trial (b) NIST library MS for acetone

Table S1 These are a series of tables with the retention time, peak area, peak height, and width for the chosen peaks 1 – 35. Note that some positions will be empty as the software didn't return information for that peak on that trial. (a) Data from gasoline spiked with dodecane, in acetone solvent. (b) Data from gasoline in dichloromethane solve, possibly spiked with xylene.

(a)

Peak	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Retention Time								
Trial 1 t_R (min)	1.510	1.854	2.164		2.626	2.792	2.975	3.380
Trial 2 t_R (min)	1.506	1.794	2.173	2.531	2.631	2.804	2.984	3.390
Trial 3 t_R (min)	1.520	1.812	2.165	2.527	2.631	2.801	2.976	3.381
Avg (min)	1.512	1.820	2.167	2.529	2.629	2.799	2.978	3.384
Std Dev (min)	0.007	0.031	0.005	0.003	0.003	0.006	0.005	0.006
RSD	0.48	1.69	0.23	0.11	0.11	0.22	0.17	0.16
Area								
Trial 1 (mV.s)	8293846	186419671	24720635		9201702	13074582	9286199	5525550
Trial 2 (mV.s)	7406512	153945054	13486349	12388556	7631810	12057222	8057097	5388776
Trial 3 (mV.s)	6145711	161530996	16989318	13101425	8082504	12674267	8897736	5882364
Avg (mV.s)	7282023	167298574	18398767	12744991	8305339	12602024	8747011	5598897
Std Dev (mV.s)	1079465	16988199	5748235	504075	808320	512513	628261	254837
RSD (%)	14.82	10.15	31.24	3.96	9.73	4.07	7.18	4.55
Height, peak								
Trial 1 (mV)	1540270	8214383	2963255		1575863	1939529	1064987	878898
Trial 2 (mV)	1466757	7906924	1879346	2035678	1382377	1891343	1022326	896909
Trial 3 (mV)	1330703	7860690	2068959	2018084	1429382	1871704	1045858	901069
Avg (mV)	1445910	7993999	2303853	2026881	1462541	1900859	1044390	892292
Std Dev (mV)	106328	192253	578875	12441	100915	34900	21369	11785
RSD (%)	7.35	2.40	25.13	0.61	6.90	1.84	2.05	1.32
Width, peak								
Trial 1 (min)	0.126	0.562	0.222		0.126			0.187
Trial 2 (min)	0.118	0.562	0.214	0.148	0.126	0.187	0.257	0.192
Trial 3 (min)	0.113	0.567	0.222	0.153	0.122	0.192	0.262	0.196
Avg (min)	0.119	0.564	0.219	0.151	0.125	0.190	0.260	0.192
Std Dev (min)	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RSD (%)	5.51	0.51	2.11	2.35	1.85	1.87	1.36	2.35
Separation & Resolution α		1.20	1.19	1.17	1.04	1.06	1.06	1.14
R_S		0.90	0.89	1.96	0.73	1.08	0.80	1.80

(a continued)

Peak	9	10	11	12	13	14	15	16
Retention Time								
Trial 1 t_R (min)			4.061	4.413		5.478		8.643
Trial 2 t_R (min)	3.577	3.952	4.074	4.430	4.610	5.500	8.234	8.674
Trial 3 t_R (min)	3.573	3.944	4.07	4.423	4.606	5.496	8.234	8.674
Avg (min)	3.575	3.948	4.068	4.422	4.608	5.491	8.234	8.664
Std Dev (min)	0.003	0.006	0.007	0.009	0.003	0.012	0.000	0.018
RSD	0.08	0.14	0.16	0.19	0.06	0.21	0.00	0.21
Area								
Trial 1 (mV.s)		5525550	3703139	29602625		2837838		27448077
Trial 2 (mV.s)	4343427	2978135	3898579	32635902	3947996	3246319	9891910	32146875
Trial 3 (mV.s)	4797638	3336564	4201017	31430799	4239222	3535404	9687028	30660129
Avg (mV.s)	4570533	3946749	3934245	31223109	4093609	3206520	9789469	30085027
Std Dev (mV.s)	321175	1378976	250848	1527267	205928	350482	144874	2401610
RSD (%)	7.03	34.94	6.38	4.89	5.03	10.93	1.48	7.98
Height, peak								
Trial 1 (mV)			556157	4619342		473988		4119098
Trial 2 (mV)	611030	506550	589269	5128315	644540	536094	1706720	4813480
Trial 3 (mV)	617365	528841	596631	4808662	666233	537377	1552150	4411099
Avg (mV)	614197	517695	580686	4852106	655386	515820	1629435	4447892
Std Dev (mV)	4479	15762	21559	257252	15339	36233	109298	348650
RSD (%)	0.73	3.04	3.71	5.30	2.34	7.02	6.71	7.84
Width, peak								
Trial 1 (min)	0.270	0.183	0.157	0.244		0.170		0.283
Trial 2 (min)	0.201	0.170	0.157	0.240	0.140	0.170	0.257	0.275
Trial 3 (min)	0.201	0.170	0.161	0.249	0.140	0.179	0.288	0.288
Avg (min)	0.224	0.174	0.158	0.244	0.140	0.173	0.273	0.282
Std Dev (min)	0.04	0.01	0.00	0.00	0.00	0.01	0.02	0.01
RSD (%)	17.78	4.31	1.46	1.85	0.00	3.00	8.04	2.33
Separation & Resolution α	1.06	1.10	1.03	1.09	1.04	1.19	1.50	1.05
R_S	0.92	1.87	0.72	1.76	0.97	5.64	12.31	1.55

(a continued)

Peak	17	18[1]	19	20	21	22	23	24
Retention Time								
Trial 1 t_R (min)	10.038				16.007	16.996		21.103
Trial 2 t_R (min)	10.073		14.734	15.462	16.055	17.045	18.327	21.152
Trial 3 t_R (min)	10.074		14.734	15.467	16.055	17.045	18.331	21.152
Avg (min)	10.062		14.734	15.465	16.039	17.029	18.329	21.136
Std Dev (min)	0.021		-	0.004	0.028	0.028	0.003	0.028
RSD	0.20		-	0.02	0.17	0.17	0.02	0.13
Area								
Trial 1 (mV.s)	11324307				3849307	2745719		2959793
Trial 2 (mV.s)	13757742		2900923	15089363	4971495	3647083	15813915	3879854
Trial 3 (mV.s)	13288420		2683434	14116710	4637410	3403669	14728904	3548357
Avg (mV.s)	12790157		2792179	14603037	4486071	3265490	15271410	3462668
Std Dev (mV.s)	1290969		153788	687769	576198	466299	767218	465978
RSD (%)	10.09		5.51	4.71	12.84	14.28	5.02	13.46
Height, peak								
Trial 1 (mV)	1897234				576630	418168		406971
Trial 2 (mV)	2318436		467000	1614444	751507	557660	2275162	538550
Trial 3 (mV)	2095176				663019	490111	2033320	477651
Avg (mV)	2103615		467000	1614444	663719	488646	2154241	474391
Std Dev (mV)	210728				87440	69758	171008	65850
RSD (%)	10.02				13.17	14.28	7.94	13.88
Width, peak								
Trial 1 (min)	0.283				0.323	0.341	0.484	0.353
Trial 2 (min)	0.259		0.276	0.423	0.306	0.379	0.456	0.344
Trial 3 (min)	0.412				0.327	0.392	0.519	0.357
Avg (min)	0.318		0.276	0.423	0.319	0.371	0.486	0.351
Std Dev (min)	0.08				0.01	0.03	0.03	0.01
RSD (%)	25.88				3.50	7.15	6.49	1.90
Separation & Resolution α	1.16		1.46	1.05	1.04	1.06	1.08	1.15
R_S	4.66		15.73	2.09	1.55	2.87	3.03	6.70

Some chromatograms reported no information for peaks identified on other chromatograms. In these cases, the resolution and separation were calculated with data from the adjacent peaks

(a continued)

Peak	24	25	26	27[1]	28	29	30	31	32[1]
Retention Time									
Trial 1 t_R (min)	21.103								
Trial 2 t_R (min)	21.152	22.381	24.657		25.560		28.938	34.340	
Trial 3 t_R (min)	21.152	22.386	24.662		25.564	27.866	28.939	34.349	
Avg (min)	21.136	22.384	24.660		25.562	27.866	28.939	34.345	
Std Dev (min)	0.028	0.004	0.004		0.003		0.001	0.006	
RSD	0.13	0.02	0.01		0.01		0.00	0.02	
Area									
Trial 1 (mV.s)	2959793								
Trial 2 (mV.s)	3879854	2060081	2515057		2455368	2001753	2741221	1996341	
Trial 3 (mV.s)	3548357	1875549	2352671		2292475	1887695	2532477	1901300	
Avg (mV.s)	3462668	1967815	2433864		2373922	1944724	2636849	1948821	
Std Dev (mV.s)	465978	130484	114824		115183	80651	147604	67204	
RSD (%)	13.46	6.63	4.72		4.85	4.15	5.60	3.45	
Height, peak									
Trial 1 (mV)	406971								
Trial 2 (mV)	538550	266616	323662		205558	215935	282654	215935	
Trial 3 (mV)	477651	236300	290012		252597	193556	252858	190694	
Avg (mV)	474391	251458	306837		229078	204745	267756	203314	
Std Dev (mV)	65850	21437	23794		33261	15824	21069	17848	
RSD (%)	13.88	8.53	7.75		14.52	7.73	7.87	8.78	
Width, peak									
Trial 1 (min)	0.353								
Trial 2 (min)	0.344	0.327	0.301		0.615	0.506		0.506	
Trial 3 (min)	0.357	0.327	0.301		0.510	0.323	0.602	0.628	
Avg (min)	0.351	0.327	0.301		0.563	0.415	0.602	0.567	
Std Dev (min)	0.01	0.00	0.00		0.07	0.13		0.09	
RSD (%)	1.90	0.00	0.00		13.20	31.22		15.21	
Separation & Resolution α	1.15	1.06	1.10		1.04	1.09	1.04	1.19	
R_S	6.70	3.68	7.25		2.09	4.98	2.11	9.25	

[1] Some chromatograms reported no information for peaks identified on other chromatograms. In these cases, the resolution and separation were calculated with data from the adjacent peaks.

(a continued)

Peak	33	34	Dodecane
Retention Time			
Trial 1 t_R (min)			
Trial 2 t_R (min)	36.377	37.532	38.347
Trial 3 t_R (min)		37.532	38.356
Avg (min)	36.377	37.532	38.352
Std Dev (min)	-	0.000	0.006
RSD	-	0.00	0.02
Area			
Trial 1 (mV.s)			50237220
Trial 2 (mV.s)	1844910	2491512	58522773
Trial 3 (mV.s)		2314543	56288978
Avg (mV.s)	1844910	2403027	55016324
Std Dev (mV.s)	-	125136	4286879
RSD (%)	-	5.21	7.79
Height, peak			
Trial 1 (mV)			
Trial 2 (mV)	372479	594967	12596764
Trial 3 (mV)		480765	12194256
Avg (mV)	372479	537866	12395510
Std Dev (mV)	-	80754	284616
RSD (%)	-	15.01	2.30
Width, peak			
Trial 1 (min)		0.301	0.301
Trial 2 (min)	0.497	0.497	0.174
Trial 3 (min)			0.301
Avg (min)	0.497	0.399	0.259
Std Dev (min)	-	0.14	0.07
RSD (%)	-	34.74	28.35
Separation & Resolution α	1.06	1.03	1.02
R_S	3.82	2.58	2.49

(b)

Retention Time	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Trial 1 t_R (min)	1.507	1.771	2.167	2.524	2.613	2.789	2.97
Trial 2 t_R (min)	1.506	1.771	2.161	2.524	2.607	2.788	2.97
Trial 3 t_R (min)	1.506	1.771	2.231	2.524	2.607	2.788	2.97
Avg (min)	1.506	1.771	2.186	2.524	2.609	2.788	2.970
Std Dev (min)	0.001	0.000	0.039	0.000	0.003	0.001	0.000
RSD	0.04	0.00	1.77	0.00	0.13	0.02	0.00
Area							
Trial 1 (mV.s)	46874147	235982275	15768611	36072867	21007375	29210093	24333846
Trial 2 (mV.s)	5617045	13614393	4447041.3	3817574	2348033.5	2986953.2	2194154.4
Trial 3 (mV.s)	5698736	13270998	2682114	3624160	2278610	2784263	1999571
Avg (mV.s)	19396643	87622555	7632589	14504867	8544673	11660437	9509191
Std Dev (mV.s)	23796252	128483401	7101048	18678686	10793072	15198786	12838897
RSD (%)	122.7	146.6	93.0	128.8	126.3	130.3	135.0
Height, peak							
Trial 1 (mV)	6054921	14102577	2558851	5368814	3933148	4563677	3675639
Trial 2 (mV)	13685350	32830771	10897184	9316561	5841665	7393090	5327986
Trial 3 (mV)	13857631	31987012	6655815	8839594	5657439	6887308	4870243
Avg (mV)	11199301	26306787	6703950	7841656	5144084	6281358	4624623
Std Dev (mV)	4455996	10577572	4169375	2154782	1052739	1508899	853118
RSD (%)	39.8	40.2	62.2	27.5	20.5	24.0	18.4
Width, peak							
Trial 1 (min)	0.224	0.516	0.165	0.269	0.12	0.181	0.239
Trial 2 (min)	0.014	0.014	0.014	0.014	0.014	0.014	0.014
Trial 3 (min)	0.014	0.014	0.014	0.014	0.014	0.014	0.014
Avg (min)	0.084	0.181	0.064	0.099	0.049	0.070	0.089
Std Dev (min)	0.121	0.290	0.087	0.147	0.061	0.096	0.130
RSD (%)	144.3	159.8	135.5	148.7	124.1	138.4	146.0
Separation & Resolution α		1.18	1.23	1.15	1.03	1.07	1.07
R_S		1.99	3.38	4.13	1.15	3.01	2.29

(b)

Retention Time	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Trial 1 t_R (min)	3.365	3.555	3.923	4.043	4.397	4.578	5.465
Trial 2 t_R (min)	3.374	3.555	3.945	4.057	4.391	4.600	5.492
Trial 3 t_R (min)	3.374	3.555	3.945	4.071	4.391	4.6	5.492
Avg (min)	3.365	3.555	3.938	4.057	4.393	4.593	5.483
Std Dev (min)	3.374	0.000	0.013	0.014	0.003	0.013	0.016
RSD	100.27	0.00	0.32	0.35	0.08	0.28	0.28
Area							
Trial 1 (mV.s)	12371892	14462594	10154566	14450101	82107067	18163946	20169547
Trial 2 (mV.s)	1365368.9	1063022	981681.66	968368.35	7346789.6	1173976	1011230.4
Trial 3 (mV.s)	1242918	981830	903932	912511	6810415	1073699	909339
Avg (mV.s)	4993393	5502482	4013393	5443660	32088090	6803874	7363372
Std Dev (mV.s)	6390261	7759791	5318554	7799857	43318534	9838239	11090590
RSD (%)	128.0	141.0	132.5	143.3	135.0	144.6	150.6
Height, peak							
Trial 1 (mV)	2291656	2218270	1966069	2225394	11679277	2918535	3105238
Trial 2 (mV)	3528449	2789350	2609802	2577896	8729207	2992803	2646443
Trial 3 (mV)	3209157	2574056	2398570	2421589	7863734	2733839	2384637
Avg (mV)	3009754	2527225	2324814	2408293	9424073	2881726	2712106
Std Dev (mV)	642056	288406	328143	176627	2000430	133348	364761
RSD (%)	21.3	11.4	14.1	7.3	21.2	4.6	13.4
Width, peak							
Trial 1 (min)	0.169	0.209	0.128	0.162	0.251	0.153	0.28
Trial 2 (min)	0.014	0.014	0.014	0.014	0.042	0.014	0.014
Trial 3 (min)	0.014	0.014	0.014	0.014	0.042	0.014	0.014
Avg (min)	0.066	0.079	0.052	0.063	0.112	0.060	0.103
Std Dev (min)	0.089	0.113	0.066	0.085	0.121	0.080	0.154
RSD (%)	136.3	142.5	126.6	134.9	108.1	133.0	149.6
Separation & Resolution α	1.13	1.06	1.11	1.03	1.08	1.05	1.19
R_S	5.11	2.63	5.84	2.07	3.84	2.32	10.92

(b)

Retention Time	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Trial 1 t_R (min)	8.196	8.698	10.027	10.747				16.982
Trial 2 t_R (min)	8.238	8.698	10.078					
Trial 3 t_R (min)	8.238	8.698	10.078			15.444		15.472
Avg (min)	8.224	8.698	10.061	10.747		15.444		16.227
Std Dev (min)	0.024	0.000	0.029					1.068
RSD	0.29	0.00	0.29					6.58
Area								
Trial 1 (mV.s)	33293461	204777937	46466443	11049544				17736722
Trial 2 (mV.s)	4365454	17170412	12714147					
Trial 3 (mV.s)	9132120	3461561	9709276			1173341		1224369
Avg (mV.s)	15597012	75136637	22963289	11049544		1173341		9480545
Std Dev (mV.s)	15509788	112481702	20409704					11675997
RSD (%)	99.4	149.7	88.9					123.2
Height, peak								
Trial 1 (mV)	5065330	22043818	7153048	1834373				2336769
Trial 2 (mV)	3443694	36230495	4721314					
Trial 3 (mV)	3196392	6990002	3977577			2900655		3014677
Avg (mV)	3901805	21754772	5283980	1834373		2900655		2675723
Std Dev (mV)	1015200	14622389	1660828					479354
RSD (%)	26.0	67.2	31.4					17.9
Width, peak								
Trial 1 (min)	0.226	0.385	0.233	0.222				0.418
Trial 2 (min)	0.042	0.014	0.098					
Trial 3 (min)	0.321	0.014	0.084			0.014		0.014
Avg (min)	0.196	0.138	0.138	0.222		0.014		0.216
Std Dev (min)	0.142	0.214	0.082					0.286
RSD (%)	72.2	155.6	59.5					132.3
Separation & Resolution α	1.50	1.06	1.16	1.07		1.44		1.05
R_S	18.33	2.84	9.88	3.81		39.81		6.81

(b)

Retention Time	**23**	**24**	**25**	**26**	**27**	**28**	**29**
Trial 1 t_R (min)	18.287	21.088	22.32	24.592	25.066	25.493	27.795
Trial 2 t_R (min)	18.301						
Trial 3 t_R (min)	18.329						
Avg (min)	18.306	21.088	22.320	24.592	25.066	25.493	27.795
Std Dev (min)	0.021						
RSD	0.12						
Area							
Trial 1 (mV.s)	62533389	19446681	10762828	13587351	6687778	13697041	12429773
Trial 2 (mV.s)	1597650						
Trial 3 (mV.s)	1728791						
Avg (mV.s)	21953277	19446681	10762828	13587351	6687778	13697041	12429773
Std Dev (mV.s)	35143469						
RSD (%)	160						
Height, peak							
Trial 1 (mV)	7736972	2423984	1280421	1556208	770308	1445177	1210941
Trial 2 (mV)	3931568						
Trial 3 (mV)	4208395						
Avg (mV)	5292312	2423984	1280421	1556208	770308	1445177	1210941
Std Dev (mV)	2121658						
RSD (%)	40						
Width, peak							
Trial 1 (min)	0.458	0.376	0.321	0.307	0.284	0.516	0.348
Trial 2 (min)	0.014						
Trial 3 (min)	0.014						
Avg (min)	0.162	0.376	0.321	0.307	0.284	0.516	0.348
Std Dev (min)	0.256						
RSD (%)	158						
Separation & Resolution α	1.13	1.15	1.06	1.10	1.02	1.02	1.09
R_S	11.00	10.34	3.54	7.24	1.60	1.07	5.33

(b)

Retention Time	**30**	**31**	**32**	**33**	**34**	**35**
Trial 1 t_R (min)	28.865	34.273	35.778	36.355	37.521	39.895
Trial 2 t_R (min)						
Trial 3 t_R (min)						
Avg (min)	28.865	34.273	35.778	36.355	37.521	39.895
Std Dev (min)						
RSD						
Area						
Trial 1 (mV.s)	15453016	11868671	7812895	10865966	12039046	11717588
Trial 2 (mV.s)						
Trial 3 (mV.s)						
Avg (mV.s)	15453016	11868671	7812895	10865966	12039046	11717588
Std Dev (mV.s)						
RSD (%)						
Height, peak						
Trial 1 (mV)	1483690	1149383	1187577	1688899	2188318	2131132
Trial 2 (mV)						
Trial 3 (mV)						
Avg (mV)	1483690	1149383	1187577	1688899	2188318	2131132
Std Dev (mV)						
RSD (%)						
Width, peak						
Trial 1 (min)	0.413	0.502	0.293	0.204	0.195	0.209
Trial 2 (min)						
Trial 3 (min)						
Avg (min)	0.413	0.502	0.293	0.204	0.195	0.209
Std Dev (min)						
RSD (%)						
Separation & Resolution α	1.04	1.19	1.04	1.02	1.03	1.06
R_S	2.81	11.82	4.59	4.40	10.92	15.15

Table S2 T.his table gives the name, molecular weight, alternative name, and potential function in gasoline. It shows the peak ID of the tentative ID of the peak found in the chromatograms.

Peak ID	MW	BP	Name	Alt Name	Function
1	72.1	36.1	n-pentane		
2	84.9	39.6	dichloromethane		Solvent
	86	49.8	2,2-dimethylbutane		
	88	55.0	methyl, t-butyl ether		Anti-knock additive
	58	56.1	acetone		Solvent
	86	58.1	2,3-dimethylbutane	neohexane	
	86	61.0	2-methylpentane		
	86	63.5	3-methylpentane		
	86	68.7	n-hexane		
	46.0	78	ethanol		Anti-knock additive
	100	79.2	2,2-dimethylpentane		
	78	80.1	benzene		Anti-knock additive
3	84	80.9	cyclohexane		
	100	80.2	2,2,3-trimethylbutane	Triptane	
	100	80.4	2,4-dimethylpentane		
	80	82.6	2-propanol		Anti-icing agent
	100	86.1	3,3-dimethylpentane		
	100	89.7	2,3-dimethylpentane		
5	100	90.2	2-methylhexane		
	100	91.9	3-methylhexane		
	100	93.5	3-ethylpentane		
	100	98.4	n-heptane		
	100	100.0	3,3-dimethylpentane		
	114	106.0	2,2,3,3-tetramethylbutane		
	114	108.5	2,5-dimethylhexane		
14	114	109.0	2,4-dimethylhexane		
12	92	110.6	toluene		Anti-knock additive
	114	112.0	3,3-dimethylhexane		
	114	113.0	2,2,4-trimethylpentane		
	114	114.0	2,2,3-trimethylpentane		
	114	117.0	2-methylheptane		
	114	118.0	4-methylheptane		
	114	119.0	3-methylheptane		
14	114	125.5	n-octane		
15	106	136.2	ethylbenzene		Anti-knock additive
16	106	138.3	p-xylene		Anti-knock additive
16	106	139.1	m-xylene		Anti-knock additive
17	106	144.4	o-xylene		Anti-knock additive
18	128	150.7	n-nonane		
	120	152.0	isopropylbenzene	cumene	
19	120	159.0	n-propylbenzene		

23	120	167.0	1,3,5-trimethylbenzene	mesitylene	
24	120	170.0	1,2,4-trimethylbenzene	pseudocumene	Fuel stabilizer
	142	174.2	n-decane		
	120	176.0	1,2,3-trimethylbenzene	hemimellitene	
	118	176.5	indane		
	156	195.0	n-undecane		