UC Berkeley College of Chemistry

Chemistry 105

Instrumental Methods in Analytical Chemistry

Whiskey Analysis with Gas Chromatography

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1 Purpose

In this lab, we utilized a GC/FID to identify the presence and quantity of specific additives in two different brands of whiskey. Aside from alcohol proof, the presence of trace compounds (technically impurities) in the otherwise pure ethanol-water matrix is the only thing that differentiates alcoholic beverages from each other. Identifying these trace elements in a quantitative manner allows us to isolate the qualities that make each drink unique. In this lab, we tested Jim Beam and Jameson brand whiskey for the presence of 2-methyl-1-butanol, ethyl acetate, and 1-propanol.

2 Theory

Gas chromatography (also known as gas-liquid partition chromatography or vapor-phase chromatography) is a form of chromatography that utilizes differences in retention time of gases to separate a sample. To this end, a "mobile-phase" is chosen that will not interact with the sample, usually a relatively inert gas such as helium, argon, or nitrogen. This mobile-phase gas is then laced with sample and flowed through a tube lined with a "stationary-phase" substance, often consisting of a waxy nonpolar liquid or polymer (though differing stationary phases can be used depending on the situation); depending on the amount of intermolecular attraction between the stationary phase and each component of the sample, differing constituents will elute through the column at different times[1]. The more a specific component of the sample is attracted to the stationary phase, the longer it will take to elute through the entire column (thus, for a nonpolar stationary phase, more polar compounds will exit the column first. The detector used in this experiment is a Flame-Ionization Detector, which uses a flame placed at the end of the column to pyrolyse compounds exiting the GC; organic compounds pyrolysed in such a manner form charged products that are detectable by electron flow[2]. The combination of these two methods, also known as GC/FID, allows for the detection of many compounds with good separation and at outstanding sensitivities (as low as a few picograms per second retention[2]). However, this method is not able to detect all compounds universally;

many compounds that do not pyrolyse or do not form charged pyrolysis products are undetectable by this method, limiting its use largely to hydrocarbons and other organic molecules[1]. However, this precision comes at a price: because the FID's signal is proportional to the number of carbon atoms pyrolysed (at least roughly speaking, with regards to hydrocarbons), it measures mass, not concentration; a single large hydrocarbon with many carbon atoms will send the same signal as many small hydrocarbons with the same total number of carbons. We can calculate the relative response factors by comparing the signal strengths (in peak area) of different concentrations of the same analyte, but to turn these into absolute data points instead of ratios we need to use an internal standard as a reference point. By measuring the signal strength of a specific compound in our unknown, and comparing it to the peak area of an internal standard of known concentration, we can determine the amount of unknown substance in our compound absolutely.

3   Experimental

In this lab, we prepared two whiskey samples with an internal 1-butanol standard, to act as the primary subjects of our analysis. For calibration purposes, we used serial dilutions to create 6 standard solutions of each of the unknowns we were looking for (2-methyl-1-butanol, ethyl acetate, and 1-propanol), along with our internal standard (1-butanol), ranging from 25 ppm to 1000 ppm (in increasing order: 25 ppm, 50 ppm, 100 ppm, 250 ppm, 500 ppm, and 1000 ppm). It is relevant to note that because all of the standards were of known concentration, an internal standard was unnecessary because no reference point was necessary. By plotting peak area against standard concentration, we were able to draw a calibration curve, to which we could fit a linear function that would allow us to find reference values of unknown concentrations in our samples (by applying the inverse of our regressed function to the peak area of our sample). To aid in calculation, we experimentally determined the density of the 40% ethanol solution we used to create the standards, simply by finding the mass of a fixed volume of ethanol (by taring out the container) and dividing it by the volume to get density.

4 Results and Discussion

This section contains only tabulated results from the Appendix. Derivations can be found in Appendix A on page 8. Raw data can be found in Appendix B on page 12.

4.1 [Relative] Response Factor Analysis

4.1.1 Results

Compound	Formula	f_i	F_i	Carbon/Oxygen ratio
EtAc	$C_4H_8O_2$	0.0587	1.00	2
PrOH	C_3H_8O	0.0641	1.09	3
BuOH	$C_4H_{10}O$	0.0766	1.30	4
MeBuOH	$C_5H_{12}O$	0.0971	1.65	5

(f_i is absolute response factor, and F_i is relative response factor)

4.1.2 Discussion

The response factors[1] (summarized in the above table) tell us much about the sensitivity of the FID to the various analytes. The fact that simply sorting by increasing carbon to oxygen ratio places the compounds in order of increasing response factor is no coincidence; rather, it tells us that the FID more efficiently detects longer-chain hydrocarbons with less substitution than smaller, more substituted alkyls. In fact, if we multiply the standard response factor f_i by a factor of 51.5 (an arbitrary number that conveniently scales up), we find that nearly all the hydrocarbons have integral response factors that approximate the number of carbons in their skeleton, with the highly substituted ethyl acetate having the lowest f_i due to the greatest number of heteroatoms in its structure. Whereas retention time tells us how much each structure prefers to bond to to the stationary phase in the column (longer retention time = larger affinity to stationary phase), response factor merely indicates to us the affinity of the sample to the FID, vis-à-vis the the the structure of the compound (FIDs are more responsive to long-chain hydrocarbons with fewer substituents).

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[1]Calculations in section A.3 on page 9.

4.2 Calculated Sample Analyte Concentrations

4.2.1 Results

Sample→	Jameson		Jim Beam	
Analyte↓	Concentration	Mixing Ratio	Concentration	Mixing Ratio
EtAc	52.48 ppm	5.25×10^{-5}	181.04 ppm	1.81×10^{-4}
PrOH	80.99 ppm	8.11×10^{-5}	78.28 ppm	7.82×10^{-5}
MeBuOH	176.69 ppm	1.77×10^{-4}	1421.89 ppm	1.424×10^{-3}

4.2.2 Discussion

Armed with this data[2], we can identify the chemical "fingerprint" of the whiskeys we sampled, in terms of the relative concentrations of each of the three analytes we looked at. Perhaps the most significant difference we can identify between the two beverages is a nearly tenfold increase in concentration of 2-methyl-1-butanol from Jameson to Jim Beam, along with a corresponding increase in mixing ratio. We are also able to see that Jim Beam contains approximately thrice as much ethyl acetate per unit volume as Jameson. Finally, we can note that the two brands of whiskeys have nearly identical 1-propanol mixing ratios. There are several explanations for the significant differences in these trace compounds: they may be unintentional adulterants, and Jameson brand whiskey has a more thorough filtration process; alternatively, these compounds may be intentionally left in the drink to add aroma or flavor, and Jim Beam brand whiskey is subject to processes that bring out these qualities (or perhaps they are directly added to the drink). Whichever of these reasons is the cause for the differing chemical footprints of Jim Beam and Jameson, it is likely that the treatment of 1-propanol between the brands is similar if not identical, because the final mixing ratios of this analyte are very similar.

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[2]Calculations in section A.4 on page 9.

4.3 Predicted Sample Analyte Concentrations

Sample→	Jameson		Jim Beam	
Analyte↓	Concentration	Mixing Ratio	Concentration	Mixing Ratio
EtAc	52.31 ppm	5.23×10^{-5}	193.96 ppm	1.94×10^{-4}
PrOH	66.24 ppm	6.62×10^{-5}	64.32 ppm	6.43×10^{-5}
MeBuOH	214.20 ppm	2.14×10^{-4}	1713.59 ppm	1.72×10^{-3}

By plotting our calibration curves[3] and fitting curves to them (again, see Appendix A on page 8 for graphs), we find ourselves with a linear correlation of astoundingly good fit (our lowest R^2 values is 0.997). The correlation function gives us a good way of relating peak area with concentration; by taking the peak areas of our samples and plugging them into the inverse of our regression, we can determine the corresponding concentration value on our trendline. These predicted values, based on interpolation (or extrapolation) of the 6 standard solutions we created, can be used to determine the accuracy of our *calculated* analyte concentrations; if our data is good, our calculated values should fall close to the trendline of our standards.

4.4 Accuracy and Error

Sample→	Jameson			Jim Beam		
Analyte↓	Calculated	Predicted	% Error	Calculated	Predicted	% Error
EtAc	52.48	52.31	0.333%	181.04	193.96	-6.66%
PrOH	80.99	66.24	22.2%	78.28	64.32	21.7%
MeBuOH	176.69	214.195	-17.5%	1421.89	1713.59	-17.1%

Unfortunately, our deviation from the standard trendline is rather significant for all both 1-propanol and 2-methyl-1-butanol, though our ethyl acetate data aligns very well with the fit. The fact that our deviation from the expected values is similar for both whiskeys, even at different concentrations, hints at some sort of systematic error. A possible explanation for this could be inaccurate concentrations of our calibration standards;

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[3]Calculations in section A.5 on page 10.

because our samples were serially diluted from each other, if our original concentration was off, all of our following data points would be off by the same relative amount. This could cause our trendline to have an incorrect slope, while still fitting a linear curve very tightly. Properly executed, GC/FID should be an ideal tool for this sort of quantitative analysis, because the ethanol matrix of whiskey along with all the trace components are of a class that is easily detected by FID to high accuracy, due to the dominating presence of hydrocarbons in the sample. GC/FID works better than GC/MS for these sorts of samples because we are dealing with simple, ignitable compounds that pyrolyse easily, forming spectra that are far more identifiable than the electron-ionized alkyl ions created using GC/MS. While GC/MS is capable of analyzing a far greater variety of samples, it is at the cost of less precision on samples that FID can analyze. When the samples in question are mostly flammable, small-chain alkyl derivatives, GC/FID is the clear choice.

5   Conclusion

Though we have reason to doubt the accuracy of our standards, we nevertheless received answers that, while far from the theoretical limit on accuracy of a GC/FID, displayed relatively very reasonable fits and trends. We were able to accurately calculate the relative concentrations of various trace components of Jameson and Jim Beam brand whiskeys, and identified several characteristic features of each (notably, Jim Beam contains far greater concentrations of ethyl acetate and 2-methyl-1-butanol, but the two whiskeys contain almost identical quantities of 1-propanol). Unfortunately, though our relative values appeared accurate, there may be some systematic inaccuracy in our calibration curve, as both of our samples deviate from the expected linear fit by near-identical amounts. Despite this, we can still maintain relative confidence in our results, even if we don't have perfect predicted values to back them up, simply because our *relative* data points fix extremely well. Though our data may not be good enough for an institute of standards (again, mostly due to the lack of accurate standards), we were still able to receive informative data regarding the importance of trace elements in alcohol differentiation, all

while honing our GC/FID and quantitative analysis skills for the future.

References

[1] *Gas Chromatography* [Online]; The Linde Group. http://hiq.linde-gas.com/en/analytical_methods/gas_chromatography/index.html (accessed Feb 6, 2014).

[2] *Theory, Analysis and Methods of Gas Liquid Chromatography* [Online]; Analytical Chemistry Research Foundation. http://www.gas-chromatography.net/gas-chromatography.php (accessed Feb 6, 2014).

A   Calculations

A.1   Integrated Peak Areas by Analyte

Sample	2-Methyl-1-Butanol	Ethyl Acetate	1-Propanol	1-Butanol
25 ppm	2.02031	1.50115	1.89623	2.05119
50 ppm	3.34871	2.7806	3.37107	3.65682
100 ppm	8.42192	5.60155	6.33308	5.74012
250 ppm	19.41587	13.61902	16.1463	17.35365
500 ppm	41.13889	27.535	32.53373	35.27502
1000 ppm	80.19011	53.27674	71.27694	179.67223
100 ppm EtAc		16.52408		555.50897
100 ppm PrOH			12.68271	726.14496
Jameson	17.15689	3.08045	5.19168	719.90717
Jim Beam	138.06551	10.62693	5.0176	235.30447

A.2 Ethanol Density Calculation

Trial 1	$0.939\frac{\text{g}}{\text{mL}}$
Trial 2	$0.9417\frac{\text{g}}{\text{mL}}$
Trial 3	$0.940\frac{\text{g}}{\text{mL}}$
$\overline{\mu} = \frac{x_1+...+x_n}{n}$	$0.940\frac{\text{g}}{\text{mL}}$

A.3 Response Factor Calibration

A.3.1 2-Methyl-1-Butanol

$$100\text{ ppm}(\tfrac{\text{v}}{\text{v}}) = \frac{100\mu\text{L MeBuOH}}{1\text{L solvent}} \times \frac{0.8152\text{mg MeBuOH}}{\mu\text{L MeBuOH}} \times \frac{1\text{L solvent}}{0.940\text{kg solvent}} = 86.72\frac{\text{mg solute}}{\text{kg solvent}} = 86.72\text{ ppm}(\tfrac{\text{m}}{\text{m}})$$

$$f_{MeBuOH} = \frac{A_i}{A_{std}}f_{std} = \frac{8.42192}{86.72\text{ ppm}(\frac{\text{m}}{\text{m}})} \times 1\text{ ppm} = 0.0971$$

A.3.2 Ethyl Acetate

$$100\text{ ppm}(\tfrac{\text{v}}{\text{v}}) = \frac{100\mu\text{L EtAc}}{1\text{L solvent}} \times \frac{0.897\text{mg EtAc}}{\mu\text{L EtAc}} \times \frac{1\text{L solvent}}{0.940\text{kg solvent}} = 95.43\frac{\text{mg solute}}{\text{kg solvent}} = 95.43\text{ ppm}(\tfrac{\text{m}}{\text{m}})$$

$$f_{EtAc} = \frac{A_i}{A_{std}}f_{std} = \frac{5.60155}{95.43\text{ ppm}(\frac{\text{m}}{\text{m}})} \times 1\text{ ppm} = 0.0587$$

A.3.3 1-Propanol

$$100\text{ ppm}(\tfrac{\text{v}}{\text{v}}) = \frac{100\mu\text{L PrOH}}{1\text{L solvent}} \times \frac{0.803\text{mg PrOH}}{\mu\text{L PrOH}} \times \frac{1\text{L solvent}}{0.940\text{kg solvent}} = 85.43\frac{\text{mg solute}}{\text{kg solvent}} = 85.43\text{ ppm}(\tfrac{\text{m}}{\text{m}})$$

$$f_{PrOH} = \frac{A_i}{A_{std}}f_{std} = \frac{6.33308}{85.43\text{ ppm}(\frac{\text{m}}{\text{m}})} \times 1\text{ ppm} = 0.0641$$

A.3.4 1-Butanol

$$100\text{ ppm}(\tfrac{\text{v}}{\text{v}}) = \frac{100\mu\text{L BuOH}}{1\text{L solvent}} \times \frac{0.81\text{mg BuOH}}{\mu\text{L BuOH}} \times \frac{1\text{L solvent}}{0.940\text{kg solvent}} = 86.17\frac{\text{mg solute}}{\text{kg solvent}} = 86.17\text{ ppm}(\tfrac{\text{m}}{\text{m}})$$

$$f_{BuOH} = \frac{A_i}{A_{std}}f_{std} = \frac{5.74}{86.01217\text{ ppm}(\frac{\text{m}}{\text{m}})} \times 1\text{ ppm} = 0.0766$$

A.4 Calculated Analyte Concentrations and Mixing Ratios

A.4.1 Jameson

2-Methyl-1-Butanol $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$$\frac{17.15689}{0.0971} \times 1\text{ ppm} = 176.69\text{ ppm}; \frac{176.69\text{ ppm}}{1\times10^6\text{ ppm}-176.69\text{ ppm}} = 1.77\times10^{-4}$$

Ethyl Acetate $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$\frac{3.08045}{0.0587} \times 1$ ppm $= 52.48$ ppm; $\frac{52.48 \text{ ppm}}{1\times10^6 \text{ ppm}-52.48 \text{ ppm}} = 5.25 \times 10^{-5}$

1-Propanol $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$\frac{5.19168}{0.0641} \times 1$ ppm $= 80.99$ ppm; $\frac{80.99 \text{ ppm}}{1\times10^6 \text{ ppm}-80.99 \text{ ppm}} = 8.11 \times 10^{-5}$

A.4.2   Jim Beam

2-Methyl-1-Butanol $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$\frac{138.06551}{0.0971} \times 1$ ppm $= 1421.89$ ppm; $\frac{1421.89 \text{ ppm}}{1\times10^6 \text{ ppm}-1421.89 \text{ ppm}} = 1.424 \times 10^{-3}$

Ethyl Acetate $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$\frac{10.62693}{0.0587} \times 1$ ppm $= 181.04$ ppm; $\frac{181.04 \text{ ppm}}{1\times10^6 \text{ ppm}-181.04 \text{ ppm}} = 1.81 \times 10^{-4}$

1-Propanol $\quad r_i = \frac{n_i}{n_{tot}-ni}$

$\frac{5.0176}{0.0641} \times 1$ ppm $= 78.28$ ppm; $\frac{78.28 \text{ ppm}}{1\times10^6 \text{ ppm}-78.28 \text{ ppm}} = 7.82 \times 10^{-5}$

A.5   Predicted Analyte Concentrations and Mixing Ratios

A.5.1   2-Methyl-1-Butanol

Calibration Curve of 2-Methyl-1-Butanol

$f(x) = 0.0806380491x - 0.1154057467$
$R^2 = 0.999578592$
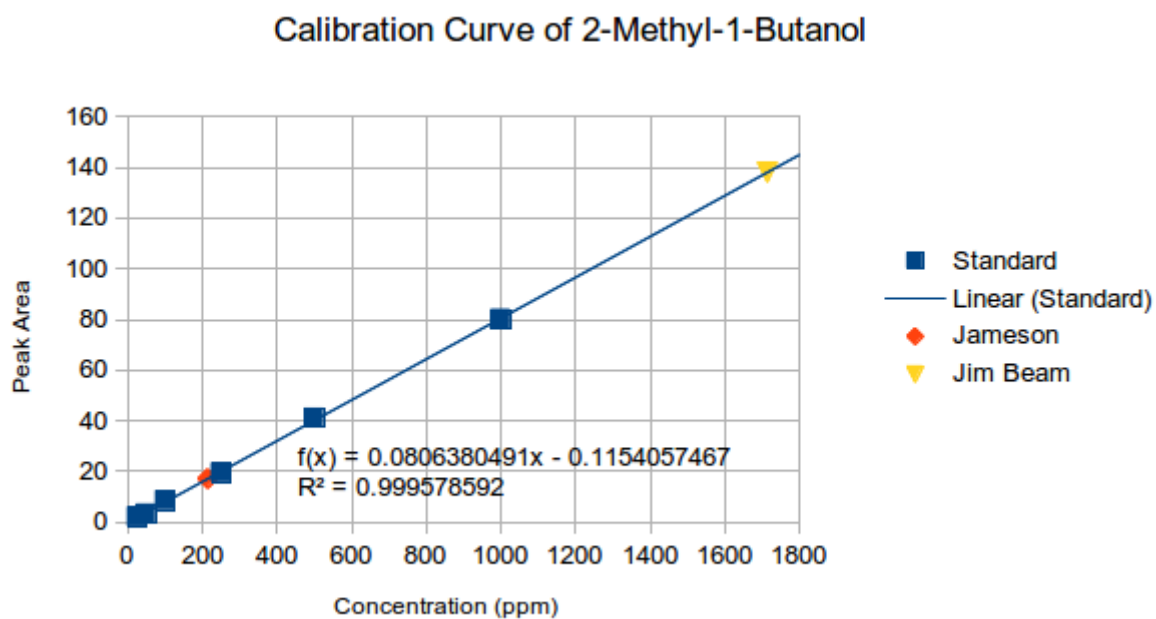
Jameson $f(x) = 0.08064x - 0.1154; 17.15689 = 0.08064x - 0.1154; x = 214.20$ ppm;

$\frac{214.20 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 214.20 \text{ ppm}} = 2.14 \times 10^{-4}$

Jim Beam $f(x) = 0.08064x - 0.1154; 138.06551 = 0.08064x - 0.1154; x = 1713.59$ ppm;

$\frac{1713.59 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 1713.59 \text{ ppm}} = 1.72 \times 10^{-3}$

A.5.2 Ethyl Acetate

Calibration Curve of Ethyl Acetate

$f(x) = 0.0532728408x + 0.2939735633$
$R^2 = 0.99975272$
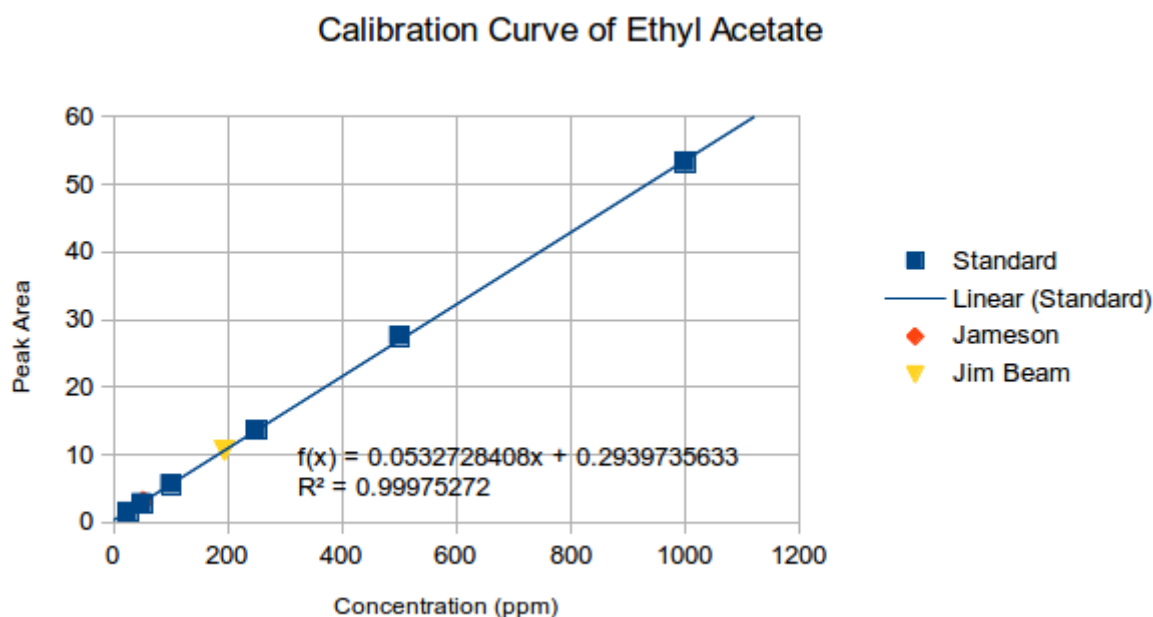
Jameson $f(x) = 0.0532728x + 0.2939735; 3.08045 = 0.0532728x + 0.2939735; x = 52.31$ ppm; $\frac{52.31 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 52.31 \text{ ppm}} = 5.23 \times 10^{-5}$

Jim Beam $f(x) = 0.0532728x + 0.2939735; 10.62693 = 0.0532728x + 0.2939735; x = 193.96$ ppm; $\frac{193.96 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 193.96 \text{ ppm}} = 1.94 \times 10^{-4}$

A.5.3 1-Propanol

Jameson $f(x) = 0.0709324x - 0.8312747; 5.1916 = 0.0709324x - 0.8312747; x = 66.24$ ppm;

$\frac{66.24 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 66.24 \text{ ppm}} = 6.62 \times 10^{-5}$

Calibration Curve of 1-Propanol
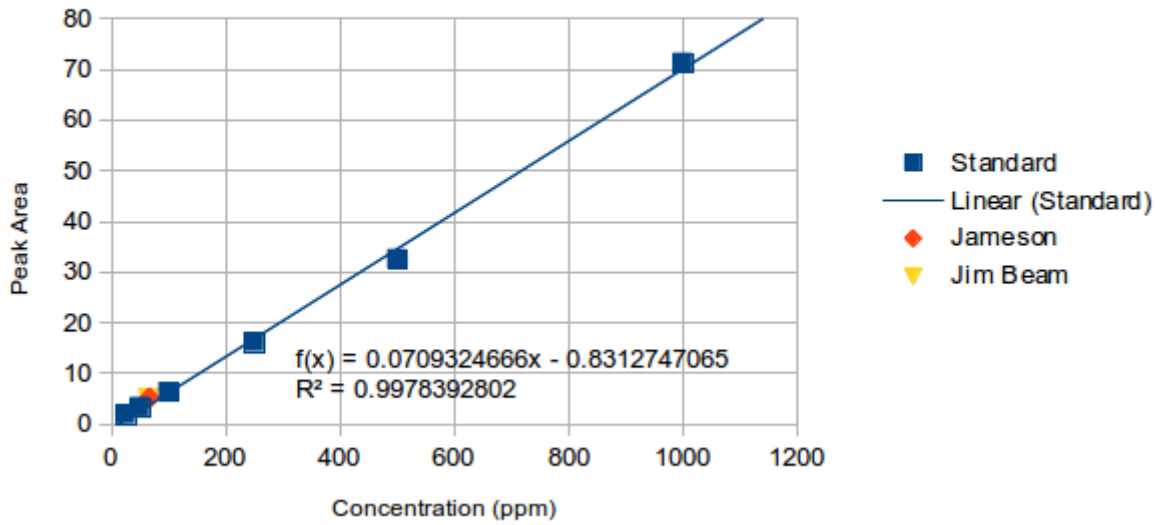
Jim Beam $f(x) = 0.0709324x - 0.8312747; 5.0176 = 0.0709324x - 0.8312747; x = 64.32$ ppm; $\frac{64.32 \text{ ppm}}{1 \times 10^6 \text{ ppm} - 64.32 \text{ ppm}} = 6.43 \times 10^{-5}$

A.6 Accuracy and Error

Jameson $\frac{176.69 - 214.195}{214.195} \times 100\% = -17.5\%$ error

Jim Beam $\frac{1421.89 - 1713.594479}{1713.594479} \times 100\% = -17.1\%$ error

Jameson $\frac{52.48 - 52.30576021}{52.30576021} \times 100\% = 0.333\%$ error

Jim Beam $\frac{181.04 - 193.9629327}{193.9629327} \times 100\% = -6.66\%$ error

Jameson $\frac{80.99 - 66.23547047}{66.23547047} \times 100\% = 22.2\%$ error

Jim Beam $\frac{78.28 - 64.32108272}{64.32108272} \times 100\% = 21.7\%$ error

B   Raw Data

```
Data File C:\HPCHEM\1\DATA\29JAN13\016B0901.D
    ==================================================================
    Injection Date  : 1/29/2014 7:09:15 PM          Seq. Line :   9
    Sample Name     : JJJP10std                     Location : Vial 16
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                       Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ==================================================================


    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By           :      Signal
    Multiplier          :      1.0000
    Dilution            :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width      Area       Height      Area
     #   [min]        [min]     [pA*s]       [pA]         %
    ----|-------|----|-------|----------|----------|--------|
      1   3.547 PB    0.0469 2.27449e4  5750.56494 99.99123
      2   4.147 PP    0.0342    1.99431 6.97517e-1  0.00877

    Totals :                   2.27469e4  5751.26246

     Results obtained with enhanced integrator!
    ==================================================================
                         Summed Peaks Report
    ==================================================================

    Signal 1: FID2 B,
    ==================================================================
                      Final Summed Peaks Report
    ==================================================================

    Signal 1: FID2 B.
                          *** End of Report ***




DEA GC 1/29/2014 7:30:04 PM Chem 105
```

Figure 1: GC/FID Report for 10 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\017B1001.D
    ======================================================================
    Injection Date  : 1/29/2014 7:32:40 PM           Seq. Line :  10
    Sample Name     : JJJP25std                      Location : Vial 17
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                       Inj Volume : 1 µl
    Acq. Method     : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Analysis Method : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 2/5/2014 2:05:40 PM by Chem 105
                      (modified after loading)
    Chem 105 Whiskey Method
    ======================================================================


    ======================================================================
                            Area Percent Report
    ======================================================================


    Sorted By           :      Signal
    Multiplier          :      1.0000
    Dilution            :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height     Area
     #   [min]        [min]   [pA*s]       [pA]        %
    ----|-------|----|-------|----------|----------|--------|
     1   3.545 PB    0.0513 2.28894e4  5727.20850 99.94582
     2   4.147 PP    0.0324    4.93948    1.79896  0.02157
     3   5.268 PP    0.0696    1.89623 3.25120e-1  0.00828
     4   7.004 PP    0.0647    1.50115 3.37332e-1  0.00655
     5   9.490 MM    0.1643    2.05119 2.08070e-1  0.00896
     6  14.905 MM    0.1994    2.02031 1.68850e-1  0.00882

    Totals :                2.29018e4  5730.04683

     Results obtained with enhanced integrator!
    ======================================================================
                            Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
    ======================================================================
                         Final Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
                          *** End of Report ***



DEA GC 2/5/2014 2:06:07 PM Chem 105
```

Figure 2: GC/FID Report for 25 ppm standard

14

```
Data File C:\HPCHEM\1\DATA\29JAN13\018B1101.D
    ======================================================================
    Injection Date  : 1/29/2014 7:56:02 PM          Seq. Line :  11
    Sample Name     : JJJP50std                     Location : Vial 18
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                       Inj Volume : 1 µl
    Acq. Method     : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Analysis Method : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 2/5/2014 2:00:12 PM by Chem 105
                      (modified after loading)
    Chem 105 Whiskey Method
    ======================================================================


    ======================================================================
                          Area Percent Report
    ======================================================================


    Sorted By           :       Signal
    Multiplier          :       1.0000
    Dilution            :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height     Area
     #   [min]        [min]   [pA*s]       [pA]         %
    ----|-------|----|-------|----------|----------|--------|
     1   3.545 PB     0.0509 2.27937e4  5726.41064 99.89956
     2   4.148 PP     0.0347    9.75901    3.61582  0.04277
     3   5.265 PP     0.0648    3.37107 6.14842e-1  0.01477
     4   7.006 PP     0.0673    2.78060 6.42413e-1  0.01219
     5   9.470 MM     0.1535    3.65682 3.97128e-1  0.01603
     6  14.912 MM     0.2143    3.34871 2.60439e-1  0.01468

    Totals :                  2.28167e4  5731.94128

     Results obtained with enhanced integrator!
    ======================================================================
                          Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
    ======================================================================
                       Final Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
                         *** End of Report ***



DEA GC 2/5/2014 2:03:31 PM Chem 105
```

Figure 3: GC/FID Report for 50 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\019B1201.D
    =========================================================================
    Injection Date  : 1/29/2014 8:19:24 PM          Seq. Line :  12
    Sample Name     : JJJP100std                    Location : Vial 19
    Acq. Operator   : Chem 105                          Inj :   1
    Acq. Instrument : DEA GC                      Inj Volume : 1 µl
    Acq. Method     : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Analysis Method : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 2/5/2014 1:39:14 PM by Chem 105
                      (modified after loading)
    Chem 105 Whiskey Method
    =========================================================================


    =========================================================================
                          Area Percent Report
    =========================================================================


    Sorted By          :       Signal
    Multiplier         :       1.0000
    Dilution           :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area        Height      Area
     #   [min]        [min]    [pA*s]        [pA]          %
    ----|-------|----|-------|----------|----------|--------|
      1   3.547 PB   0.0499 2.27373e4 5750.89014 99.79786
      2   4.147 PP   0.0343   19.95820    7.34313  0.08760
      3   5.263 PB   0.0668    6.33308    1.13308  0.02780
      4   7.005 PP   0.0665    5.60155    1.31570  0.02459
      5   9.463 PB   0.1143    5.74012 6.49526e-1  0.02519
      6  14.921 MM   0.2546    8.42192 5.51225e-1  0.03697

    Totals :                  2.27833e4 5761.88281

     Results obtained with enhanced integrator!
    =========================================================================
                          Summed Peaks Report
    =========================================================================

    Signal 1: FID2 B,
    =========================================================================
                        Final Summed Peaks Report
    =========================================================================

    Signal 1: FID2 B,
                          *** End of Report ***




DEA GC 2/5/2014 1:41:39 PM Chem 105
```

Figure 4: GC/FID Report for 100 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\020B1301.D
    ====================================================================
    Injection Date  : 1/29/2014 8:42:53 PM          Seq. Line :  13
    Sample Name     : JJJP250std                   Location : Vial 20
    Acq. Operator   : Chem 105                           Inj :   1
    Acq. Instrument : DEA GC                      Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ====================================================================


    ====================================================================
                          Area Percent Report
    ====================================================================

    Sorted By           :       Signal
    Multiplier          :       1.0000
    Dilution            :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height      Area
      #   [min]        [min]    [pA*s]       [pA]          %
    ----|-------|----|-------|----------|----------|--------|
      1    3.546 PB   0.0493 2.23033e4  5703.04541 99.47802
      2    4.145 PB   0.0355   50.49440   18.95547  0.22522
      3    5.260 PP   0.0692   16.14630    2.85494  0.07202
      4    7.001 PP   0.0651   13.61902    3.29027  0.06074
      5    9.461 PB   0.1512   17.35365    1.69817  0.07740
      6   14.909 BB   0.2248   19.41587    1.28148  0.08660

    Totals :                 2.24203e4   5731.12574

     Results obtained with enhanced integrator!
    ====================================================================
                          Summed Peaks Report
    ====================================================================

    Signal 1: FID2 B,
    ====================================================================
                       Final Summed Peaks Report
    ====================================================================

    Signal 1: FID2 B.
                        *** End of Report ***




DEA GC 1/29/2014 9:03:42 PM Chem 105
```

Figure 5: GC/FID Report for 250 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\021B1401.D
     ==========================================================================
     Injection Date  : 1/29/2014 9:06:14 PM            Seq. Line :  14
     Sample Name     : JJJP500std                      Location : Vial 21
     Acq. Operator   : Chem 105                             Inj :   1
     Acq. Instrument : DEA GC                       Inj Volume : 1 µl
     Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
     Method          : C:\HPCHEM\1\METHODS\C105 S13.M
     Last changed    : 1/29/2014 2:05:32 PM by Chem 105
     Chem 105 Whiskey Method
     ==========================================================================


     ==========================================================================
                            Area Percent Report
     ==========================================================================

     Sorted By            :       Signal
     Multiplier           :       1.0000
     Dilution             :       1.0000
     Use Multiplier & Dilution Factor with ISTDs


     Signal 1: FID2 B,

     Peak RetTime Type  Width      Area        Height      Area
      #   [min]        [min]    [pA*s]        [pA]         %
     ----|-------|----|-------|----------|-----------|--------|
       1   3.546 PB   0.0493 2.24686e4  5720.34229 98.94853
       2   4.143 PP   0.0392  102.27948   37.94732  0.45042
       3   5.258 PP   0.0706   32.53373    5.73139  0.14327
       4   7.000 BP   0.0665   27.53500    6.67231  0.12126
       5   9.454 PB   0.1485   35.27502    3.48438  0.15535
       6  14.904 BB   0.2334   41.13889    2.63432  0.18117

     Totals :                  2.27074e4  5776.81201

      Results obtained with enhanced integrator!
     ==========================================================================
                            Summed Peaks Report
     ==========================================================================

     Signal 1: FID2 B,
     ==========================================================================
                          Final Summed Peaks Report
     ==========================================================================

     Signal 1: FID2 B.
                            *** End of Report ***




DEA GC 1/29/2014 9:27:03 PM Chem 105
```

Figure 6: GC/FID Report for 500 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\022B1501.D
    ========================================================================
    Injection Date  : 1/29/2014 9:29:33 PM              Seq. Line :  15
    Sample Name     : JJJP1000std                       Location : Vial 22
    Acq. Operator   : Chem 105                               Inj :   1
    Acq. Instrument : DEA GC                         Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ========================================================================


    ========================================================================
                            Area Percent Report
    ========================================================================


    Sorted By              :      Signal
    Multiplier             :      1.0000
    Dilution               :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height     Area
     #   [min]        [min]    [pA*s]       [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   3.544 PB   0.0488 2.18603e4  5635.85840 98.27188
       2   5.256 PP   0.0669   71.27694   12.53314  0.32042
       3   7.000 BP   0.0646   53.27674   12.88620  0.23950
       4   9.435 PB   0.1328  179.67223   18.72349  0.80771
       5  14.898 PB   0.2312   80.19011    5.15182  0.36049

    Totals :                  2.22447e4  5685.15306

     Results obtained with enhanced integrator!
    ========================================================================
                            Summed Peaks Report
    ========================================================================

    Signal 1: FID2 B,
    ========================================================================
                          Final Summed Peaks Report
    ========================================================================

    Signal 1: FID2 B,
                        *** End of Report ***




DEA GC 1/29/2014 9:50:22 PM Chem 105
```

Figure 7: GC/FID Report for 1000 ppm standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\023B1601.D
    ====================================================================
    Injection Date  : 1/29/2014 9:53:01 PM           Seq. Line :  16
    Sample Name     : JJJPEtOAc                       Location : Vial 23
    Acq. Operator   : Chem 105                             Inj :   1
    Acq. Instrument : DEA GC                      Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ====================================================================


    ====================================================================
                          Area Percent Report
    ====================================================================


    Sorted By          :      Signal
    Multiplier         :      1.0000
    Dilution           :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area        Height      Area
     #   [min]         [min]    [pA*s]        [pA]         %
    ----|-------|----|-------|----------|----------|--------|
      1   3.543 PB    0.0486 2.13884e4  5583.80078 97.39517
      2   7.000 PP    0.0497   16.52408    4.04379  0.07524
      3   9.421 PB    0.1093  555.50897   67.70264  2.52959

    Totals :                   2.19605e4  5655.54720

     Results obtained with enhanced integrator!
    ====================================================================
                        Summed Peaks Report
    ====================================================================

    Signal 1: FID2 B,
    ====================================================================
                     Final Summed Peaks Report
    ====================================================================

    Signal 1: FID2 B,
                        *** End of Report ***




DEA GC 1/29/2014 10:13:50 PM Chem 105
```

Figure 8: GC/FID Report for Ethyl Acetate standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\024B1701.D
    ===================================================================
    Injection Date  : 1/29/2014 10:16:18 PM         Seq. Line :  17
    Sample Name     : JJJPMeBuOH                    Location : Vial 24
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                       Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ===================================================================


    ===================================================================
                          Area Percent Report
    ===================================================================

    Sorted By            :       Signal
    Multiplier           :       1.0000
    Dilution             :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height     Area
      #   [min]        [min]    [pA*s]       [pA]        %
    ----|-------|----|-------|-----------|-----------|--------|
      1   3.544 PB   0.0494 2.16634e4  5601.41309 98.03670
      2   9.422 PB   0.1017  433.83368   50.98830  1.96330

    Totals :                  2.20972e4  5652.40138

     Results obtained with enhanced integrator!
    ===================================================================
                          Summed Peaks Report
    ===================================================================

    Signal 1: FID2 B,
    ===================================================================
                       Final Summed Peaks Report
    ===================================================================

    Signal 1: FID2 B.
                          *** End of Report ***




DEA GC 1/29/2014 10:37:07 PM Chem 105
```

Figure 9: GC/FID Report for 2-Methyl-1-Butanol standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\025B1801.D
    ======================================================================
    Injection Date  : 1/29/2014 10:39:38 PM           Seq. Line :  18
    Sample Name     : JJJPPrOH                       Location : Vial 25
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                      Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ======================================================================


    ======================================================================
                          Area Percent Report
    ======================================================================


    Sorted By          :      Signal
    Multiplier         :      1.0000
    Dilution           :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area       Height      Area
      #   [min]        [min]    [pA*s]       [pA]         %
    ----|-------|----|-------|----------|----------|--------|
      1   3.545 PB    0.0495 2.20565e4  5666.13184 96.75887
      2   5.262 PB    0.0677   12.68271    2.23731  0.05564
      3   9.422 PB    0.1052  726.14496   91.72792  3.18549

    Totals :                   2.27954e4  5760.09706

     Results obtained with enhanced integrator!
    ======================================================================
                         Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
    ======================================================================
                      Final Summed Peaks Report
    ======================================================================

    Signal 1: FID2 B,
                         *** End of Report ***




DEA GC 1/29/2014 11:00:27 PM Chem 105
```

Figure 10: GC/FID Report for 1-Propanol standard

```
Data File C:\HPCHEM\1\DATA\29JAN13\026B1901.D
    ===================================================================
    Injection Date  : 1/29/2014 11:03:06 PM         Seq. Line :  19
    Sample Name     : JJJPJameson                   Location : Vial 26
    Acq. Operator   : Chem 105                            Inj :   1
    Acq. Instrument : DEA GC                       Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ===================================================================


    ===================================================================
                         Area Percent Report
    ===================================================================


    Sorted By        :       Signal
    Multiplier       :       1.0000
    Dilution         :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area        Height      Area
     #   [min]        [min]     [pA*s]        [pA]         %
    ----|-------|----|-------|-----------|-----------|--------|
      1   2.930 PV   0.0305 9.10329e-1 3.51067e-1  0.00624
      2   2.989 VP   0.0375 8.39123e-1 2.67985e-1  0.00575
      3   3.522 PB   0.0546 1.38413e4  4224.49414 94.82206
      4   5.257 PP   0.0735    5.19168 9.72497e-1  0.03557
      5   7.003 PP   0.0666    3.08045 7.33770e-1  0.02110
      6   7.442 PP   0.1231    8.74831    1.08273  0.05993
      7   9.421 PB   0.1228  719.90717   86.38404  4.93182
      8  14.662 PB   0.1748   17.15689    1.45033  0.11754

    Totals :                 1.45972e4   4315.73656

     Results obtained with enhanced integrator!
    ===================================================================
                         Summed Peaks Report
    ===================================================================

    Signal 1: FID2 B,
    ===================================================================
                      Final Summed Peaks Report
    ===================================================================

    Signal 1: FID2 B,
                        *** End of Report ***



DEA GC 1/29/2014 11:23:55 PM Chem 105
```

Figure 11: GC/FID Report for Jameson sample

```
Data File C:\HPCHEM\1\DATA\29JAN13\027B2001.D
    ================================================================
    Injection Date  : 1/29/2014 11:26:27 PM          Seq. Line :  20
    Sample Name     : JJJPJimBeam                    Location : Vial 27
    Acq. Operator   : Chem 105                             Inj :   1
    Acq. Instrument : DEA GC                        Inj Volume : 1 µl
    Sequence File   : C:\HPCHEM\1\SEQUENCE\DEF GC.S
    Method          : C:\HPCHEM\1\METHODS\C105 S13.M
    Last changed    : 1/29/2014 2:05:32 PM by Chem 105
    Chem 105 Whiskey Method
    ================================================================


    ================================================================
                          Area Percent Report
    ================================================================


    Sorted By           :      Signal
    Multiplier          :      1.0000
    Dilution            :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID2 B,

    Peak RetTime Type  Width     Area        Height      Area
     #   [min]        [min]    [pA*s]        [pA]          %
    ----|-------|----|-------|----------|----------|--------|
      1   2.933 BV   0.0328   1.76248  6.35073e-1  0.00809
      2   2.991 VP   0.0568   3.01364  6.28103e-1  0.01384
      3   3.544 PB   0.0672 2.13491e4  5559.71045 98.02202
      4   5.265 PP   0.0680   5.01760  8.82174e-1  0.02304
      5   7.003 BP   0.0647  10.62693    2.58567  0.04879
      6   7.247 VV   0.0800   4.82224 9.01938e-1  0.02214
      7   7.444 VB   0.1281  32.19041    3.84552  0.14780
      8   9.435 PB   0.1393 235.30447   24.84536  1.08037
      9  14.646 PB   0.2718 138.06551    7.09476  0.63391

    Totals :                 2.17799e4  5601.12904

     Results obtained with enhanced integrator!
    ================================================================
                          Summed Peaks Report
    ================================================================

    Signal 1: FID2 B,
    ================================================================
                        Final Summed Peaks Report
    ================================================================

    Signal 1: FID2 B,



DEA GC 1/29/2014 11:47:16 PM Chem 105
```

Figure 12: GC/FID Report for Jim Beam sample