Verification of Analytical Reports Produced by SMCReporter for Method 8261 Determinations

Michael H. Hiatt
U.S. Environmental Protection Agency
National Exposure Research Laboratory
Environmental Sciences Division
P.O. Box 93478, Las Vegas, Nevada 89193-3478

Table of Contents

Introduction

Method 8261 is a GC/MS/vacuum distillation procedure used to determine the amount of volatile analytes in samples. Besides the incorporation of a vacuum to volatilize analytes and separate them from sample matrices, this method is unique in that it uses internal standards to measure analyte performance as a function of its chemical properties. In addition to internal standards, the method incorporates surrogate compounds that are monitored for additional method performance data. The quantitation report generated for method 8261 analysis is unlike any other quantitation reporting, and, therefore, EPA has developed a software program (SMCReporter) to perform method 8261 data processing and generating reports.

This document is meant to assist technical review of SMCReporter analytical reports and to identify the sources of information that are used in generating reports. See the presentation, “Creating the Calibration Curve and Generating Method 8261 Quantitation Reports through SMCReporter V4.0” for a description of how to use SMCReporter to generate quantitation reports (http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm#calibration).

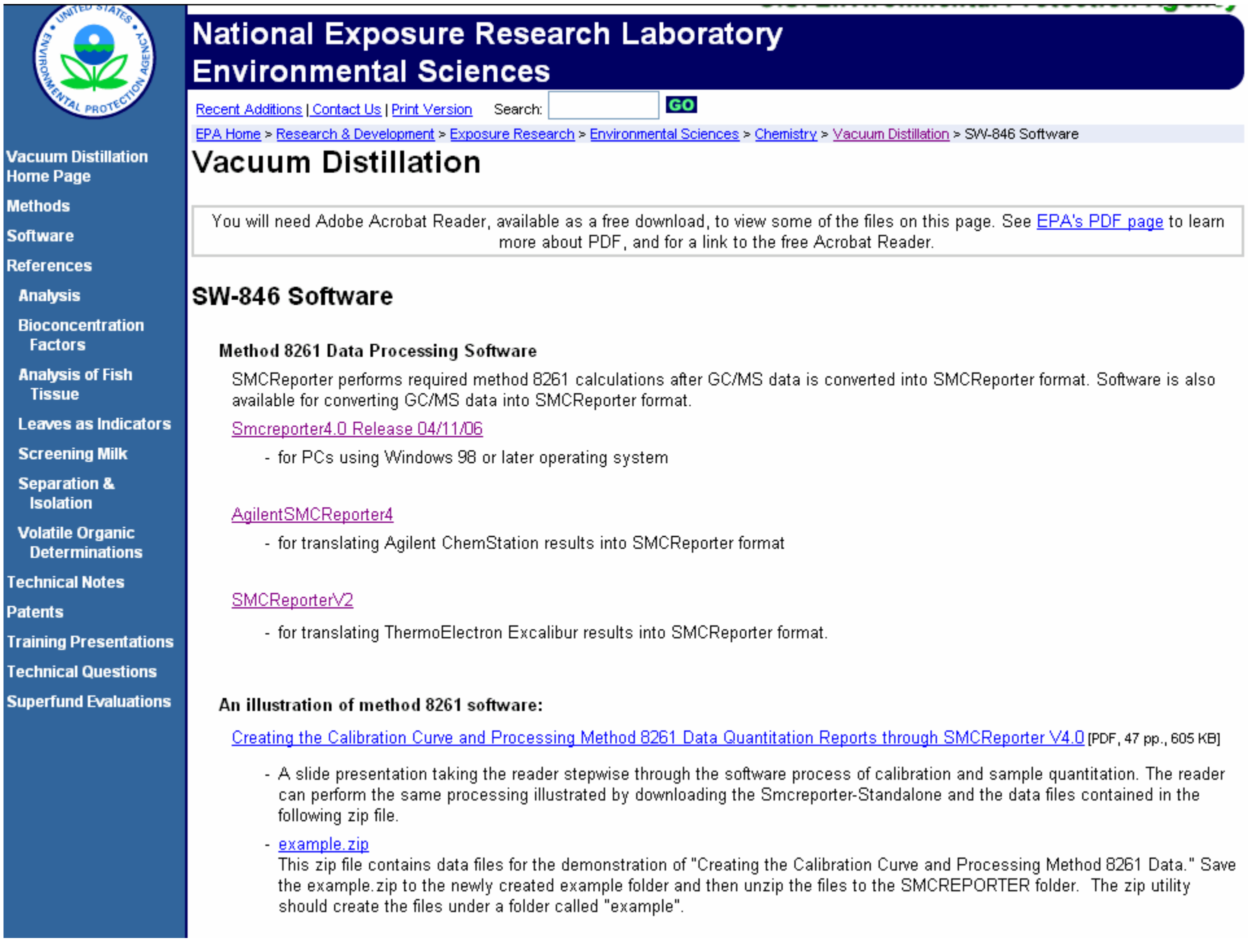
In this document, the sample quantitation output from SMCReporter is called an *analytical report* and includes the *quantitation report* containing the analyte results, the *internal standard report* containing the matrix correction data, and the *surrogate report* containing the results of special monitoring compounds that are added to each sample prior to analysis. This document shows how to verify that the information provided by SMCReporter in the analytical report is accurate. Each result can be reproduced outside the SMCReporter Program to demonstrate calculations are valid and all information. This report provides a demonstration of how to reproduce the matrix corrections for a given sample from integrated responses from the GC/MS, reproduce the surrogate data and finally reproduce the quantitation report.

The first section examines the Internal Standard Report. The second section addresses the surrogate results, and the last section addresses the generation of the analytical results.

Source of SMCReporter and Raw Data Used in Following Examples

Method 8261 calculations are performed by the program “SMCReporter”. This program is available from the EPA’s Vacuum Distillation website (http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm) and can be downloaded without cost (http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm). See the Training Presentation, “Creating the Calibration Curve and Generating Method 8261 Quantitation Reports through SMCReporter V4.0” for instruction on generating quantitation reports.

The raw data used in the examples are from the example.zip file, which is also available from the software webpage (Figure 1).



Vacuum Distillation

You will need Adobe Acrobat Reader, available as a free download, to view some of the files on this page. See EPA's PDF page to learn more about PDF, and for a link to the free Acrobat Reader.

SW-846 Software

Method 8261 Data Processing Software

SMCReporter performs required method 8261 calculations after GC/MS data is converted into SMCReporter format. Software is also available for converting GC/MS data into SMCReporter format.

Smcreporter4.0 Release 04/11/06

- for PCs using Windows 98 or later operating system

AgilentSMCReporter4

- for translating Agilent ChemStation results into SMCReporter format

SMCReporterV2

- for translating ThermoElectron Excalibur results into SMCReporter format.

An illustration of method 8261 software:

Creating the Calibration Curve and Processing Method 8261 Data Quantitation Reports through SMCReporter V4.0 [PDF, 47 pp., 605 KB]

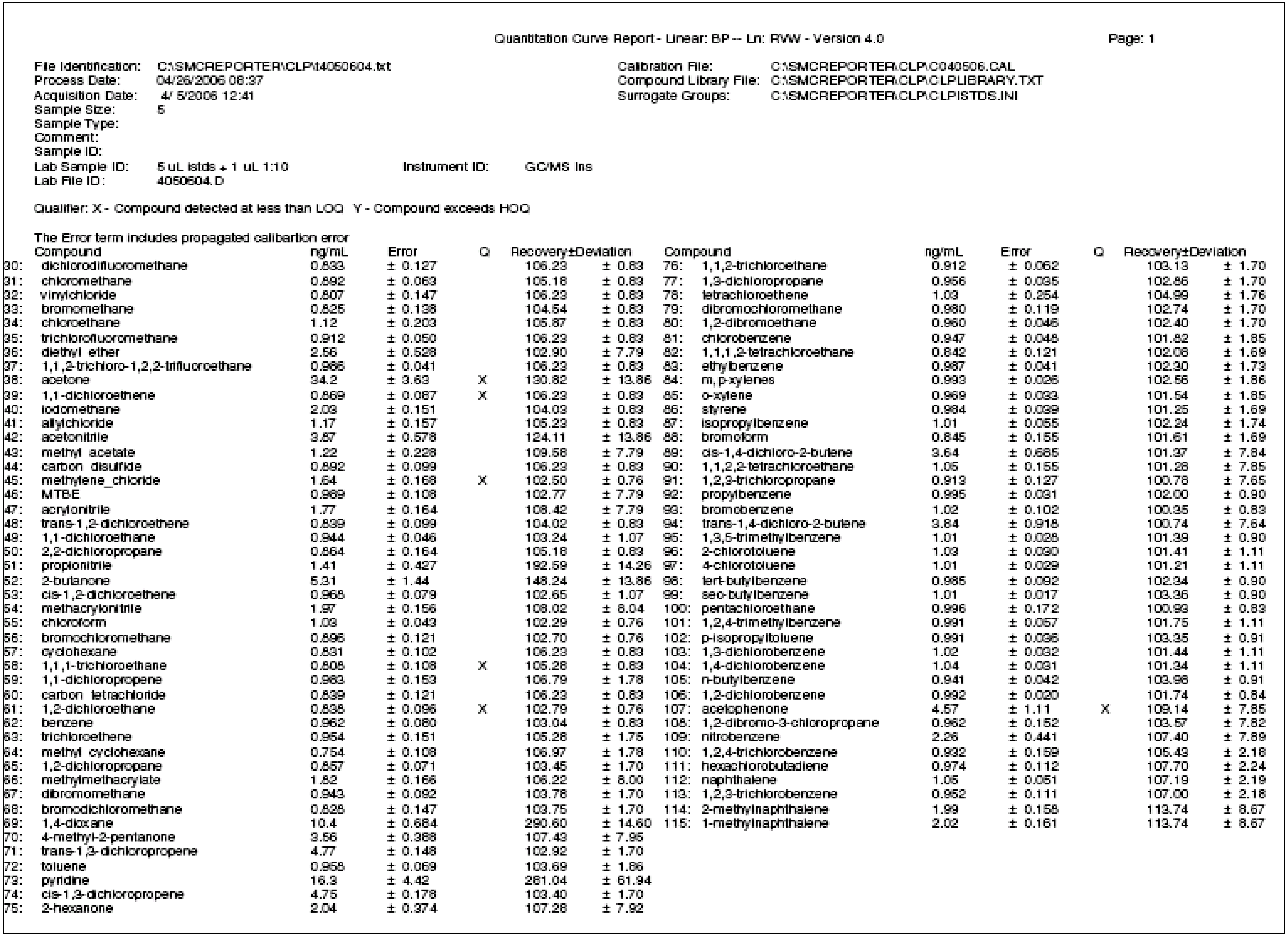
- A slide presentation taking the reader stepwise through the software process of calibration and sample quantitation. The reader can perform the same processing illustrated by downloading the Smcreporter-Standalone and the data files contained in the following zip file.
- example.zip
  This zip file contains data files for the demonstration of "Creating the Calibration Curve and Processing Method 8261 Data." Save the example.zip to the newly created example folder and then unzip the files to the SMCREPORTER folder. The zip utility should create the files under a folder called "example".

Figure 1: Software webpage: http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm

The SMCReporter Program generates analytical results in three parts, quantitation, internal standard and surrogate reports. This document traces the steps a verification of data might require. The verification steps presented here includes the scheme method 8261employs to measure effects relating to boiling points and relative volatilities, how this information translates to the recovery of analytes, and how the software generates concentrations with associated method performance information as associated error.

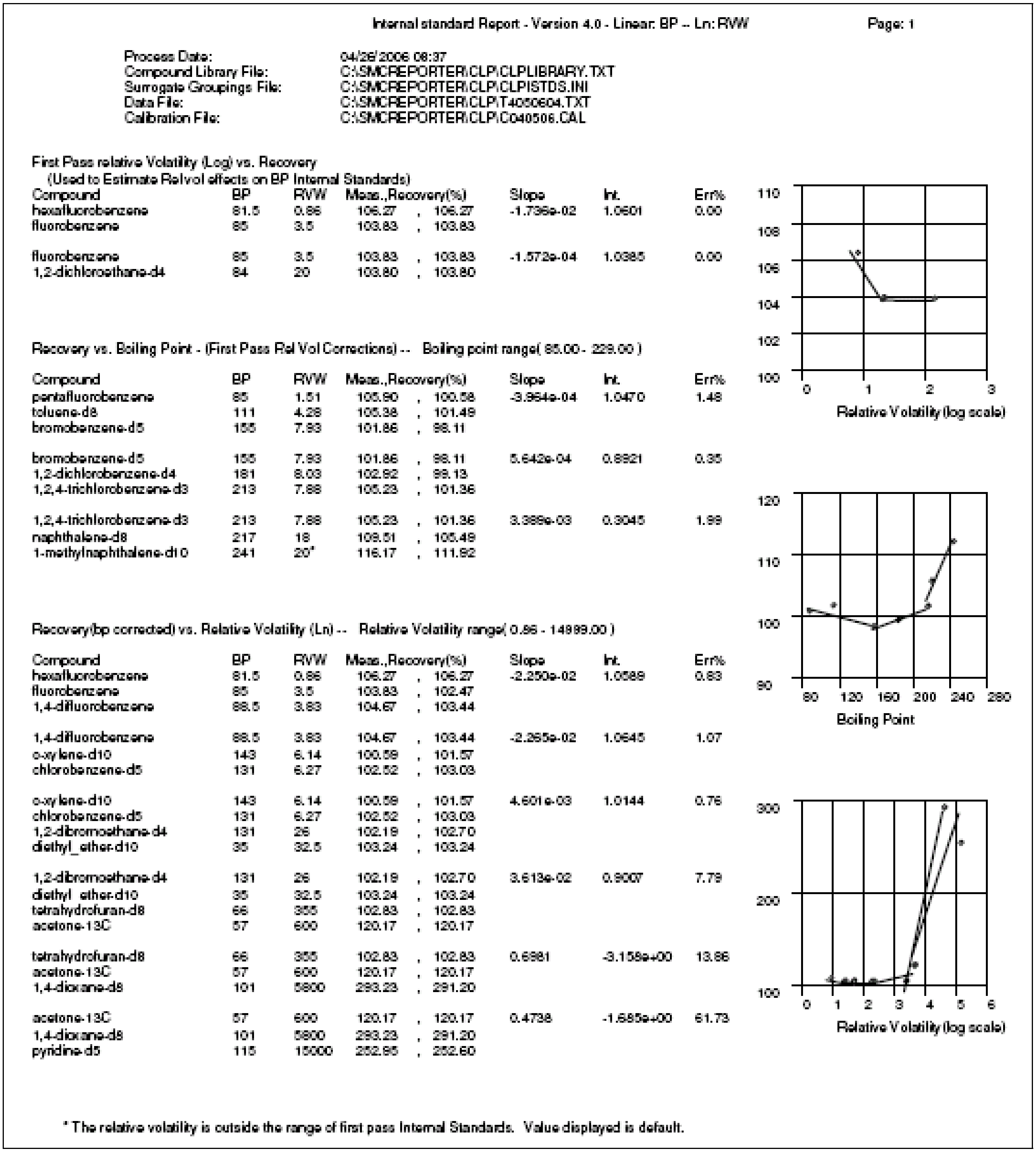
Generating Example Print Outs

If you have performed the Calibration exercise identified in the presentation, “SMCReporter - Standalone Demo: Creating the Calibration Curve and Processing Method 8261 Data” you can reproduce the example that is discussed in this presentation using the additional data provided with this document. The example is generated by performing a 5-point calibration curve using the library, CLPlibrary, the internal standard file, CLPistds.ini and calibration runs (t4050601 (blank), t4050609 (dilution at 0.006), t4050604 (dilution at 0.02), t4050605 (dilution at 0.1), t4050606 (dilution at 0.6) and t4050607 (dilution at 2.0). After creating calibration, save as C040506.cal. Then quantitate t4050604.txt as a 5-mL water sample, and print the quantitation and QC reports. The generated report is the example being addressed in this presentation and presented in the following slides. SMCReporter generates a quantitation report that includes sample description, analytes, and their concentration and predicted recoveries. The analytical example report is presented in Figures 2-4.



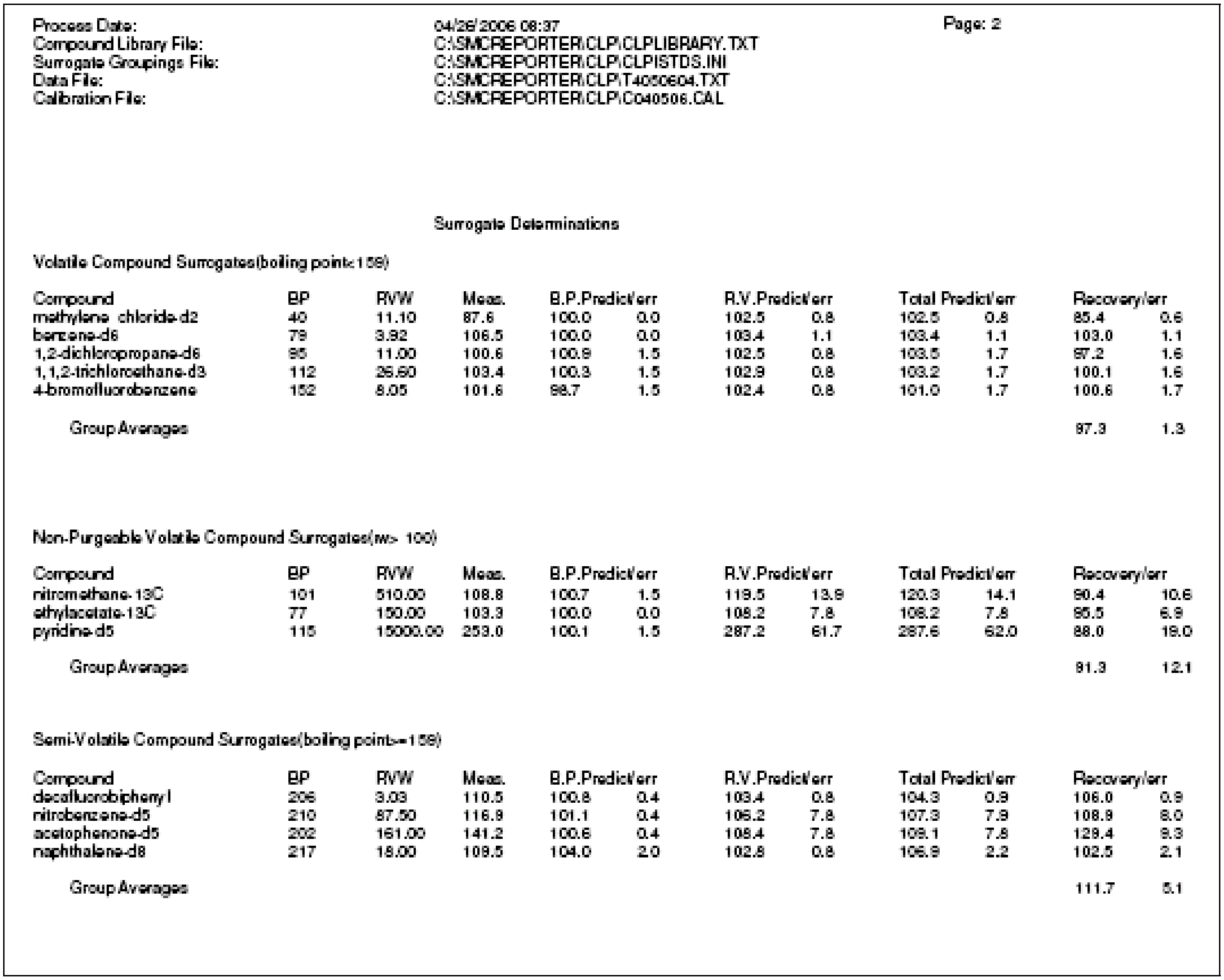
```
                                        Quantitation Curve Report - Linear: BP -- Ln: RVW - Version 4.0                              Page: 1

File Identification:  C:\SMCREPORTER\CLP\t4050604.txt                              Calibration File:         C:\SMCREPORTER\CLP\C040506.CAL
Process Date:         04/26/2006 08:37                                             Compound Library File:    C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Acquisition Date:      4/ 5/2006 12:41                                             Surrogate Groups:         C:\SMCREPORTER\CLP\CLPISTDS.INI
Sample Size:          5
Sample Type:
Comment:
Sample ID:
Lab Sample ID:        5 uL istds + 1 uL 1:10              Instrument ID:      GC/MS Ins
Lab File ID:          4050604.D

Qualifier: X - Compound detected at less than LOQ  Y - Compound exceeds HOQ

The Error term includes propagated calibartion error
    Compound                                   ng/mL     Error      Q   Recovery±Deviation    Compound                           ng/mL     Error      Q   Recovery±Deviation
30:  dichlorodifluoromethane                   0.833   ± 0.127          106.23   ± 0.83      76:  1,1,2-trichloroethane          0.912   ± 0.062         103.13   ± 1.70
31:  chloromethane                             0.892   ± 0.063          105.18   ± 0.83      77:  1,3-dichloropropane            0.956   ± 0.035         102.86   ± 1.70
32:  vinylchloride                             0.807   ± 0.147          106.23   ± 0.83      78:  tetrachloroethene              1.03    ± 0.254         104.99   ± 1.76
33:  bromomethane                              0.825   ± 0.138          104.54   ± 0.83      79:  dibromochloromethane           0.980   ± 0.119         102.74   ± 1.70
34:  chloroethane                              1.12    ± 0.203          105.87   ± 0.83      80:  1,2-dibromoethane              0.960   ± 0.046         102.40   ± 1.70
35:  trichlorofluoromethane                    0.912   ± 0.050          106.23   ± 0.83      81:  chlorobenzene                  0.947   ± 0.048         101.82   ± 1.85
36:  diethyl  ether                            2.56    ± 0.528          102.90   ± 7.79      82:  1,1,1,2-tetrachloroethane      0.842   ± 0.121         102.08   ± 1.69
37:  1,1,2-trichloro-1,2,2-trifluoroethane     0.986   ± 0.041          106.23   ± 0.83      83:  ethylbenzene                   0.987   ± 0.041         102.30   ± 1.73
38:  acetone                                   34.2    ± 3.63       X   130.82   ± 13.86     84:  m, p-xylenes                   0.993   ± 0.026         102.56   ± 1.86
39:  1,1-dichloroethene                        0.869   ± 0.087      X   106.23   ± 0.83      85:  o-xylene                       0.969   ± 0.033         101.54   ± 1.85
40:  iodomethane                               2.03    ± 0.151          104.03   ± 0.83      86:  styrene                        0.984   ± 0.039         101.25   ± 1.69
41:  allylchloride                             1.17    ± 0.157          105.23   ± 0.83      87:  isopropylbenzene               1.01    ± 0.055         102.24   ± 1.74
42:  acetonitrile                              3.87    ± 0.578          124.11   ± 13.86     88:  bromoform                      0.845   ± 0.155         101.61   ± 1.69
43:  methyl  acetate                           1.22    ± 0.228          109.58   ± 7.79      89:  cis-1,4-dichloro-2-butene      3.64    ± 0.685         101.37   ± 7.84
44:  carbon  disulfide                         0.892   ± 0.099          106.23   ± 0.83      90:  1,1,2,2-tetrachloroethane      1.05    ± 0.155         101.28   ± 7.85
45:  methylene_chloride                        1.64    ± 0.168      X   102.50   ± 0.76      91:  1,2,3-trichloropropane         0.913   ± 0.127         100.78   ± 7.65
46:  MTBE                                      0.989   ± 0.108          102.77   ± 7.79      92:  propylbenzene                  0.995   ± 0.031         102.00   ± 0.90
47:  acrylonitrile                             1.77    ± 0.164          108.42   ± 7.79      93:  bromobenzene                   1.02    ± 0.102         100.35   ± 0.83
48:  trans-1,2-dichloroethene                  0.839   ± 0.099          104.02   ± 0.83      94:  trans-1,4-dichloro-2-butene    3.84    ± 0.918         100.74   ± 7.64
49:  1,1-dichloroethane                        0.944   ± 0.046          103.24   ± 1.07      95:  1,3,5-trimethylbenzene         1.01    ± 0.028         101.39   ± 0.90
50:  2,2-dichloropropane                       0.864   ± 0.164          105.18   ± 0.83      96:  2-chlorotoluene                1.03    ± 0.030         101.41   ± 1.11
51:  propionitrile                             1.41    ± 0.427          192.59   ± 14.26     97:  4-chlorotoluene                1.01    ± 0.029         101.21   ± 1.11
52:  2-butanone                                5.31    ± 1.44           148.24   ± 13.86     98:  tert-butylbenzene              0.985   ± 0.092         102.34   ± 0.90
53:  cis-1,2-dichloroethene                    0.968   ± 0.079          102.65   ± 1.07      99:  sec-butylbenzene               1.01    ± 0.017         103.36   ± 0.90
54:  methacrylonitrile                         1.97    ± 0.156          108.02   ± 8.04      100: pentachloroethane              0.996   ± 0.172         100.93   ± 0.83
55:  chloroform                                1.03    ± 0.043          102.29   ± 0.76      101: 1,2,4-trimethylbenzene         0.991   ± 0.057         101.75   ± 1.11
56:  bromochloromethane                        0.896   ± 0.121          102.70   ± 0.76      102: p-isopropyltoluene             0.991   ± 0.096         103.35   ± 0.91
57:  cyclohexane                               0.831   ± 0.102          106.23   ± 0.83      103: 1,3-dichlorobenzene            1.02    ± 0.032         101.44   ± 1.11
58:  1,1,1-trichloroethane                     0.808   ± 0.108      X   105.28   ± 0.83      104: 1,4-dichlorobenzene            1.04    ± 0.031         101.34   ± 1.11
59:  1,1-dichloropropene                       0.983   ± 0.153          106.79   ± 1.78      105: n-butylbenzene                 0.941   ± 0.042         103.96   ± 0.91
60:  carbon  tetrachloride                     0.839   ± 0.121          106.23   ± 0.83      106: 1,2-dichlorobenzene            0.992   ± 0.020         101.74   ± 0.84
61:  1,2-dichloroethane                        0.838   ± 0.096      X   102.79   ± 0.76      107: acetophenone                   4.57    ± 1.11      X   109.14   ± 7.85
62:  benzene                                   0.962   ± 0.080          103.04   ± 0.83      108: 1,2-dibromo-3-chloropropane    0.962   ± 0.152         103.57   ± 7.82
63:  trichloroethene                           0.954   ± 0.151          105.28   ± 1.75      109: nitrobenzene                   2.26    ± 0.441         107.40   ± 7.89
64:  methyl  cyclohexane                       0.754   ± 0.108          106.97   ± 1.78      110: 1,2,4-trichlorobenzene         0.932   ± 0.159         105.43   ± 2.18
65:  1,2-dichloropropane                       0.857   ± 0.071          103.45   ± 1.70      111: hexachlorobutadiene            0.974   ± 0.112         107.70   ± 2.24
66:  methylmethacrylate                        1.82    ± 0.166          106.22   ± 8.00      112: naphthalene                    1.05    ± 0.051         107.19   ± 2.19
67:  dibromomethane                            0.943   ± 0.092          103.78   ± 1.70      113: 1,2,3-trichlorobenzene         0.952   ± 0.111         107.00   ± 2.18
68:  bromodichloromethane                      0.828   ± 0.147          103.75   ± 1.70      114: 2-methylnaphthalene            1.99    ± 0.158         113.74   ± 8.67
69:  1,4-dioxane                               10.4    ± 0.684          290.60   ± 14.60     115: 1-methylnaphthalene            2.02    ± 0.161         113.74   ± 8.67
70:  4-methyl-2-pentanone                      3.56    ± 0.388          107.43   ± 7.95
71:  trans-1,3-dichloropropene                 4.77    ± 0.148          102.92   ± 1.70
72:  toluene                                   0.958   ± 0.069          103.69   ± 1.86
73:  pyridine                                  16.3    ± 4.42           281.04   ± 61.94
74:  cis-1,3-dichloropropene                   4.75    ± 0.178          103.40   ± 1.70
75:  2-hexanone                                2.04    ± 0.374          107.28   ± 7.92
```

Figure 2: Quantitation report



```
                                         Internal standard Report - Version 4.0 - Linear: BP -- Ln: RVW                Page: 1

              Process Date:                   04/26/2006 08:37
              Compound Library File:          C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
              Surrogate Groupings File:       C:\SMCREPORTER\CLP\CLPISTDS.INI
              Data File:                      C:\SMCREPORTER\CLP\T4050604.TXT
              Calibration File:               C:\SMCREPORTER\CLP\C040506.CAL

First Pass relative Volatility (Log) vs. Recovery
   (Used to Estimate Relvol effects on BP Internal Standards)
Compound                         BP       RVW    Meas.,Recovery(%)       Slope         Int.          Err%
hexafluorobenzene                81.5     0.86      106.27   ,  106.27   -1.736e-02    1.0601        0.00
fluorobenzene                    85       3.5       103.83   ,  103.83

fluorobenzene                    85       3.5       103.83   ,  103.83   -1.572e-04    1.0385        0.00
1,2-dichloroethane-d4            84       20        103.80   ,  103.80



Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) --   Boiling point range( 85.00 - 229.00 )

Compound                         BP       RVW    Meas.,Recovery(%)       Slope         Int.          Err%
pentafluorobenzene               85       1.51      105.90   ,  100.58   -3.964e-04    1.0470        1.48
toluene-d8                       111      4.28      105.38   ,  101.49
bromobenzene-d5                  155      7.93      101.86   ,  98.11

bromobenzene-d5                  155      7.93      101.86   ,  98.11    5.642e-04     0.8921        0.35
1,2-dichlorobenzene-d4           181      8.03      102.92   ,  99.13
1,2,4-trichlorobenzene-d3        213      7.88      105.23   ,  101.36

1,2,4-trichlorobenzene-d3        213      7.88      105.23   ,  101.36   3.389e-03     0.3045        1.99
naphthalene-d8                   217      18        109.51   ,  105.49
1-methylnaphthalene-d10          241      20*       116.17   ,  111.92



Recovery(bp corrected) vs. Relative Volatility (Ln) --   Relative Volatility range( 0.86 - 14999.00 )

Compound                         BP       RVW    Meas.,Recovery(%)       Slope         Int.          Err%
hexafluorobenzene                81.5     0.86      106.27   ,  106.27   -2.250e-02    1.0589        0.83
fluorobenzene                    85       3.5       103.83   ,  102.47
1,4-difluorobenzene              88.5     3.83      104.67   ,  103.44

1,4-difluorobenzene              88.5     3.83      104.67   ,  103.44   -2.265e-02    1.0645        1.07
o-xylene-d10                     143      6.14      100.59   ,  101.57
chlorobenzene-d5                 131      6.27      102.52   ,  103.09

o-xylene-d10                     143      6.14      100.59   ,  101.57   4.601e-03     1.0144        0.76
chlorobenzene-d5                 131      6.27      102.52   ,  103.09
1,2-dibromoethane-d4             131      26        102.19   ,  102.70
diethyl_ether-d10                35       32.5      103.24   ,  103.24

1,2-dibromoethane-d4             131      26        102.19   ,  102.70   3.613e-02     0.9007        7.79
diethyl_ether-d10                35       32.5      103.24   ,  103.24
tetrahydrofuran-d8               66       355       102.83   ,  102.83
acetone-13C                      57       600       120.17   ,  120.17

tetrahydrofuran-d8               66       355       102.83   ,  102.83   0.6981        -3.159e+00    13.86
acetone-13C                      57       600       120.17   ,  120.17
1,4-dioxane-d8                   101      5800      293.23   ,  291.20

acetone-13C                      57       600       120.17   ,  120.17   0.4738        -1.685e+00    61.73
1,4-dioxane-d8                   101      5800      293.23   ,  291.20
pyridine-d5                      115      15000     252.95   ,  252.60


       * The relative volatility is outside the range of first pass Internal Standards.  Value displayed is default.
```

Figure 3: Internal standard report



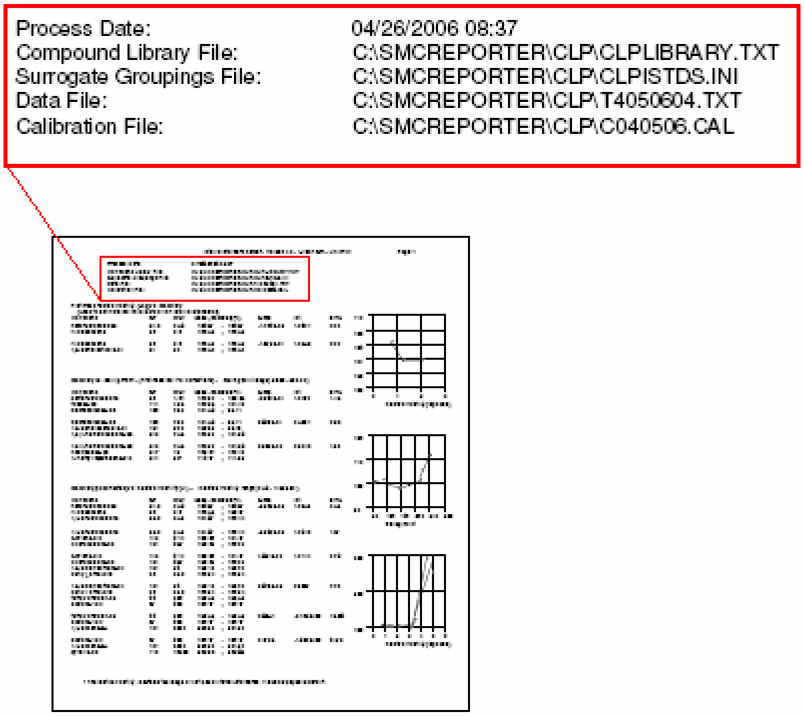
```
Process Date:                    04/26/2006 08:37                    Page: 2
Compound Library File:           C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Surrogate Groupings File:        C:\SMCREPORTER\CLP\CLPISTDS.INI
Data File:                       C:\SMCREPORTER\CLP\T4050604.TXT
Calibration File:                C:\SMCREPORTER\CLP\C040506.CAL



                                 Surrogate Determinations

Volatile Compound Surrogates(boiling point<159)

Compound                 BP     RVW       Meas.   B.P.Predict/err    R.V.Predict/err    Total Predict/err   Recovery/err
methylene chloride-d2    40     11.10     87.6    100.0    0.0       102.5    0.8       102.5    0.8        85.4     0.6
benzene-d6               79     3.92      106.5   100.0    0.0       103.4    1.1       103.4    1.1        103.0    1.1
1,2-dichloropropane-d6   95     11.00     100.6   100.9    1.5       102.5    0.8       103.5    1.7        97.2     1.6
1,1,2-trichloroethane-d3 112    26.60     103.4   100.3    1.5       102.9    0.8       103.2    1.7        100.1    1.6
4-bromofluorobenzene     152    8.05      101.6   98.7     1.5       102.4    0.8       101.0    1.7        100.6    1.7

     Group Averages                                                                                       97.3     1.3



Non-Purgeable Volatile Compound Surrogates(rw> 100)

Compound                 BP     RVW       Meas.   B.P.Predict/err    R.V.Predict/err    Total Predict/err   Recovery/err
nitromethane-13C         101    510.00    108.8   100.7    1.5       119.5    13.9      120.3    14.1       90.4     10.6
ethylacetate-13C         77     150.00    103.3   100.0    0.0       108.2    7.8       108.2    7.8        95.5     6.9
pyridine-d5              115    15000.00  253.0   100.1    1.5       287.2    61.7      287.6    62.0       88.0     19.0

     Group Averages                                                                                       91.3     12.1


Semi-Volatile Compound Surrogates(boiling point>=159)

Compound                 BP     RVW       Meas.   B.P.Predict/err    R.V.Predict/err    Total Predict/err   Recovery/err
decafluorobiphenyl       206    3.03      110.5   100.8    0.4       103.4    0.8       104.3    0.9        106.0    0.9
nitrobenzene-d5          210    87.50     116.9   101.1    0.4       106.2    7.8       107.3    7.9        108.9    8.0
acetophenone-d5          202    161.00    141.2   100.6    0.4       108.4    7.8       109.1    7.8        129.4    9.3
naphthalene-d8           217    18.00     109.5   104.0    2.0       102.8    0.8       106.9    2.2        102.5    2.1

     Group Averages                                                                                       111.7    5.1
```

Figure 4: Surrogate report

Internal Standard Report

The internal standard report (Figure 3) is the heart of the analytical report and must be understood in order to verify any analytical results. This page describes the matrix and method effects on a sample as measured by the suite of internal standards. All of the algorithms used in generating the quantitation report are presented in the internal standard report.

The header of the internal standard report summarizes sources of the data that went into generating the internal standard report (Figure 5). The pathway to these files is also shown for convenience. The header identifies the SMCReporter processing date. The compound library file identifies the list of analytes and internal standards, their chemical properties and calibration. The internal standard/surrogate file (surrogate groupings file) identifies the assigned use of each internal standard. The data file contains GC/MS raw data in a format for SMCReporter to read. The calibration file contains the data that was used to generate a calibration curve and results.

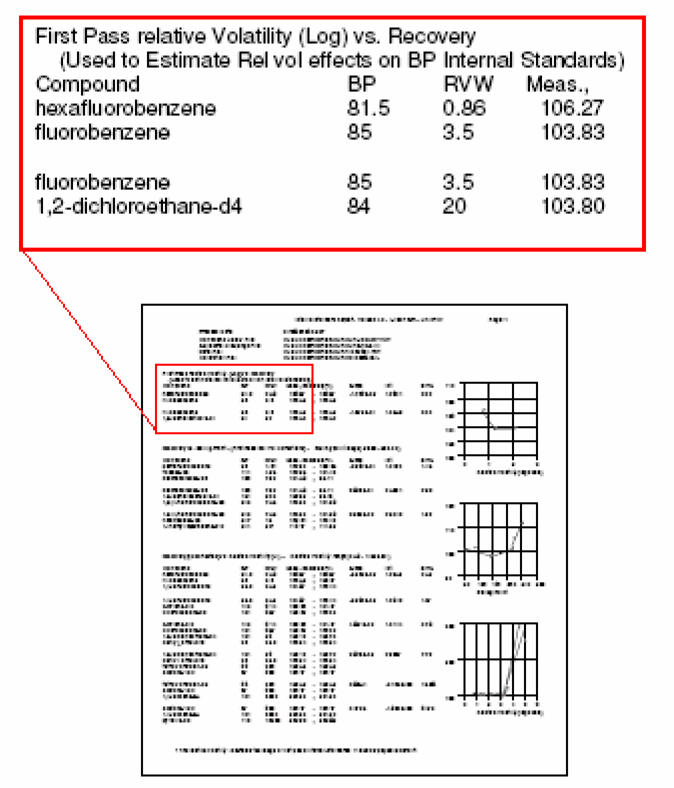


Process Date:	04/26/2006 08:37
Compound Library File:	C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Surrogate Groupings File:	C:\SMCREPORTER\CLP\CLPISTDS.INI
Data File:	C:\SMCREPORTER\CLP\T4050604.TXT
Calibration File:	C:\SMCREPORTER\CLP\C040506.CAL

Figure 5: Header of the internal standard report

Experimental Recoveries

An initial review of the data begins with the verification of the raw data results. One can test the correctness of the header information by regenerating the experimentally measured recovery of an internal standard. The header (Fig 5) identifies that the compound library, CLPlibrary.txt, and the internal standard file, CLPistds.ini, and calibration file, C040506.cal, were used for generating the analytical report.



First Pass relative Volatility (Log) vs. Recovery
(Used to Estimate Rel vol effects on BP Internal Standards)

Compound	BP	RVW	Meas.,
hexafluorobenzene	81.5	0.86	106.27
fluorobenzene	85	3.5	103.83
fluorobenzene	85	3.5	103.83
1,2-dichloroethane-d4	84	20	103.80

Figure 6: Experimental recoveries under "Meas."

The Experimental $_{\text{recovery}}$ of each of the internal standards is determined as its response in an analysis compared to its calibrated response.

Experimental $_{\text{recovery}}$ = **Raw integration area from data file ÷ (average calibration response × spike amount)** (Eq1)

The spike amount is the amount (mass) of internal standard added to each analysis (this value is stored in the compound library).

The experimental recovery is reported as % in the column “Meas.” Note: SMCReporter uses fractional recoveries in all calculations but presents the value as a % in the Internal Standard Report.

Example 1: We want to reproduce the experimental recovery of hexafluorobenzene from the example. The average calibration response (16059.125) for the hexafluorobenzene is obtained from the calibration file, C040506.cal. The amount of hexafluorobenzene added to all analyses is obtained from the compound library, CLPlibrary.txt (250 ng). The total response expected for hexafluorobenzene is the calibration response (area/ng) times the spike amount (250 ng) and yields a response of 4014781. The response of hexafluorobenzene in the data file, T4050604.txt, is 4266423. Therefore, Experimental $_{\text{recovery}}$ of hexafluorobenzene = 4266423/4014781 =1.06268 = 106.27%.

Internal Standards for Different Functions

As noted in the presentation “Method 8261 Chemistry” posted on EPA’s Vacuum Distillation webpage, there are two important chemical properties of compounds that determine how well a compound will be extracted from a sample and transferred to the GC/MS for analysis. One type of internal standard is a relative volatility internal standard. These internal standards are used to measure relative volatility effects and create functions to describe recovery vs. relative volatility. Another type of internal standard is the boiling point internal standard. These internal standards are used to measure boiling point effects and create functions to describe recovery vs. boiling point.

These boiling point and relative volatility effects are calculated as recoveries. The experimental recovery of a compound is a product of these combined effects and can be expressed as

$$\text{Experimental Measurement}_{\text{recovery}} = \text{BP}_{\text{recovery}} \times \text{RV}_{\text{recovery}}{}^{1} \qquad \text{(Eq2)}$$

Where $\text{BP}_{\text{recovery}}$ = the recovery reflecting boiling-point effects
$\text{RV}_{\text{recovery}}$ = the recovery reflecting relative-volatility effects
$\text{Experimental Measurement}_{\text{recovery}}$ = the GC/MS response divided by the calibrated GC/MS response

The internal standards are then used to equate experimental recoveries to both boiling point and relative-volatility effects. In Method 8261, we determine the boiling-point recovery as a function of compound boiling point and relative-volatility recovery as function of compound’s relative volatility.

One problem with these variables is that each compound experiences both boiling-point and relative-volatility effects. Method 8261 incorporates the first-pass internal standards to separate the effects of these variables.

First-Pass Relative Volatility Effects

The first-pass internal standards are like the relative volatility internal standards but with a limited use. First-pass internal standards are used solely to clarify experimental recoveries of the boiling-point internal standards so that relative-volatility effects on the experimental recovery of boiling-point internal standards are mitigated. This procedure is only used to clarify boiling point effects.

First-Pass Internal Standards Are Selected by their Ability to Measure solely Relative-Volatility Effects

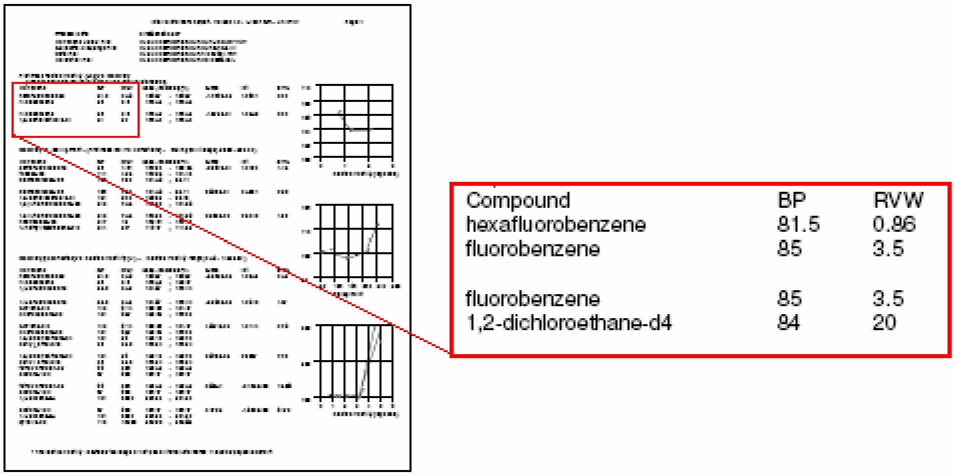
The previously-introduced equation that breaks experimental recoveries into boiling point and relative volatility effects is

$$\text{Experimental Measurement}_{\text{recovery}} = \text{BP}_{\text{recovery}} \times \text{RV}_{\text{recovery}} \quad \text{(Eq2)}$$

By minimizing boiling point effects and assume that $\text{BP}_{\text{recovery}}$ is 100%, the equation becomes

$$\text{Experimental Measurement}_{\text{recovery}} = \text{RV}_{\text{recovery}} \qquad \text{(Eq3)}$$

Equation 3 is a special condition that is narrowly defined. In practice, there are few compounds that we can use as internal standards (compounds that are labeled or rare in environment) that would yield 100% recovery. Having a limited number of compounds, the range of relative volatility effects, Equation 3 is not applicable to all Method 8261 compounds. Therefore, Method 8261 uses first-pass internal standards to describe a narrow range of relative volatility values and that range that is only applied to the boiling-point internal standards.



Compound	BP	RVW
hexafluorobenzene	81.5	0.86
fluorobenzene	85	3.5
fluorobenzene	85	3.5
1,2-dichloroethane-d4	84	20

Figure 6: First-pass internal standards

The three first pass internal standards (Figure 7) are hexafluorobenzene, fluorobenzene, and 1,2-dichloroethane-d_4 and have boiling points that span a 3.5 ºC range (81.5, 85, and 84 ºC respectively). However the compounds span a relative volatility range of 0.86 to 20. The boiling point of the first pass internal standards should be 85 ºC or less where boiling point effects are expected to be minimal (Figure 8).

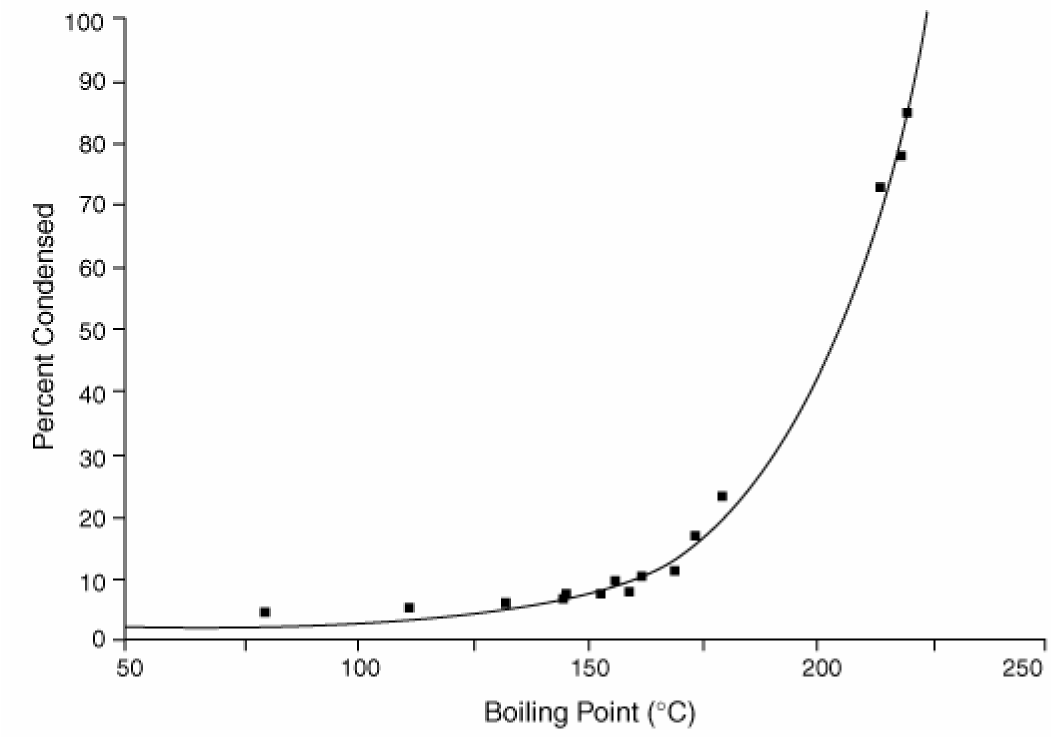
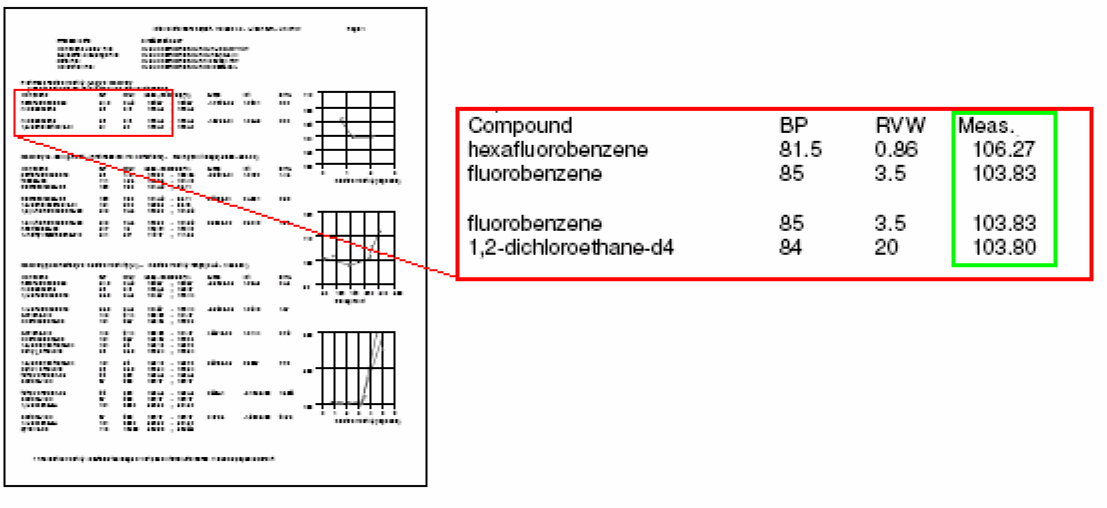


Figure 7: Losses by boiling point

Determining First-Pass Effects, Step 1: Calculate First-Pass Internal Standard Recoveries

The first-pass effects are measured by relating the recoveries of the first-pass internal standards to their relative volatility values. Any experimental deviation of recovery from 100 % for these compounds is considered a first-pass effect. Therefore the experimental recoveries of the first-pass internal standards are used to describe first-pass effects.



Compound	BP	RVW	Meas.
hexafluorobenzene	81.5	0.86	106.27
fluorobenzene	85	3.5	103.83
fluorobenzene	85	3.5	103.83
1,2-dichloroethane-d4	84	20	103.80

Figure 8: Experimental recoveries of first-pass internal standards

Determining First-Pass Effects, Step 2: Determine Relationship of Recovery to Relative Volatility

The internal standards in the first-pass section are put into two groups, hexafluorobenzene and fluorobenzene and fluorobenzene and 1, 2-dichloroethane-d4. Separating the internal standards into groups allows description of effects over a narrow range, which can make the description more precise and easier to determine. The experimental recoveries of the three first pass internal standard are used to generate a line for each group (y = m × x + B where recovery is "y" and ln [relative volatility] = "x"). The relative volatility relationship to recovery is logarithmic as illustrated in the presentation "Method 8261 Chemistry". Therefore, the natural log of relative volatility is used for determining the lines. SMCReporter, as an option, does not use the logarithm of the relative volatilities. How SMCReporter uses values is identified in the topmost row of the internal-standard report Figure 9.

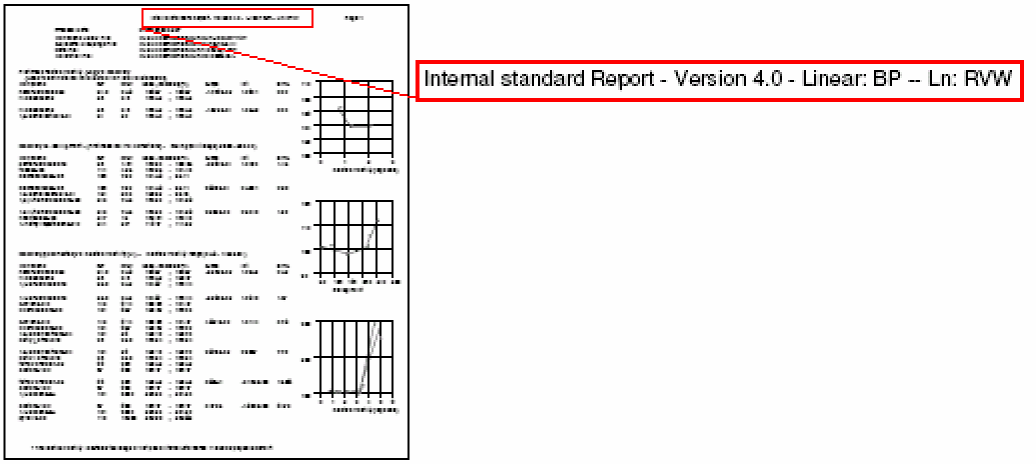


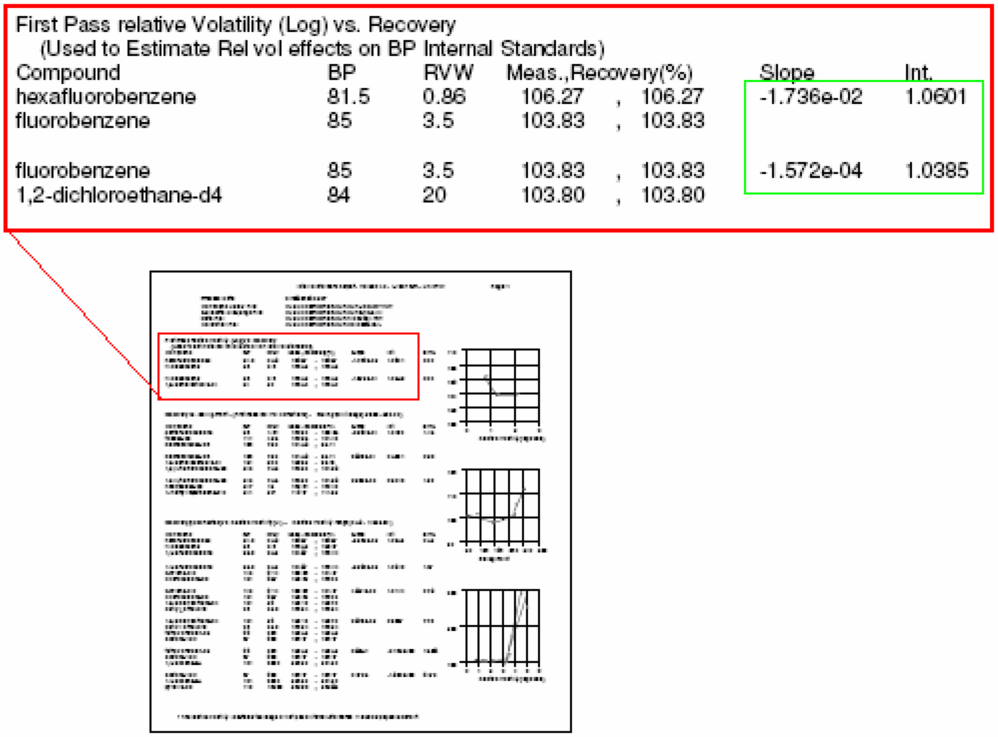
Figure 9: Top line of internal standard report identifies if values or logarithm of values are used in calculations

The first first-pass line has two points. The first line is determined using points for hexachlorobenzene (ln (0.86), 1.0626788) and fluorobenzene (ln (3.5), 1.0383073). Using these points to determine the line between them (Y = m × X + B), we get the slope and intercept presented in Figure 10. This equation can now be used to predict recovery of compounds with a relative volatility value of V (if it is between 0.86 and 3.5) by the equation,

$$\text{Recovery} = -1.736\text{e-}2\ (\ln(V)) + 1.0601$$

Note: When checking values to the last decimal place do not round numbers as SMCReporter only rounds numbers for displaying values. If you use the displayed first-pass recoveries (rounded to 1.0627 and 1.0383) then the slope will be -0.01738.

The second first-pass line is generated in the same manner but addresses relative volatility values lying between 3.5 and 20. After the first-pass internal standard equations have been solved, they are used to determine the relative-volatility effects on the boiling-point internal standards.



First Pass relative Volatility (Log) vs. Recovery
(Used to Estimate Rel vol effects on BP Internal Standards)

Compound	BP	RVW	Meas.,Recovery(%)	Slope	Int.
hexafluorobenzene	81.5	0.86	106.27 , 106.27	-1.736e-02	1.0601
fluorobenzene	85	3.5	103.83 , 103.83		
fluorobenzene	85	3.5	103.83 , 103.83	-1.572e-04	1.0385
1,2-dichloroethane-d4	84	20	103.80 , 103.80		

Figure 10: First-pass linear equations

Determining First-Pass Effects, Step 3: Present First-Pass Internal Standards Graphics

A graphical presentation of the first-pass internal standard data and the resulting lines are provided for easier review of data. The graph presents each internal standard data point as well as the determined lines.

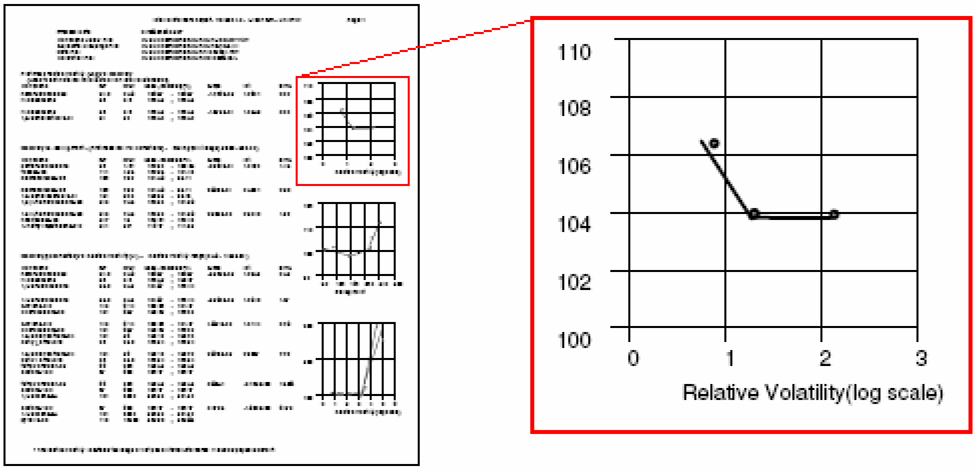


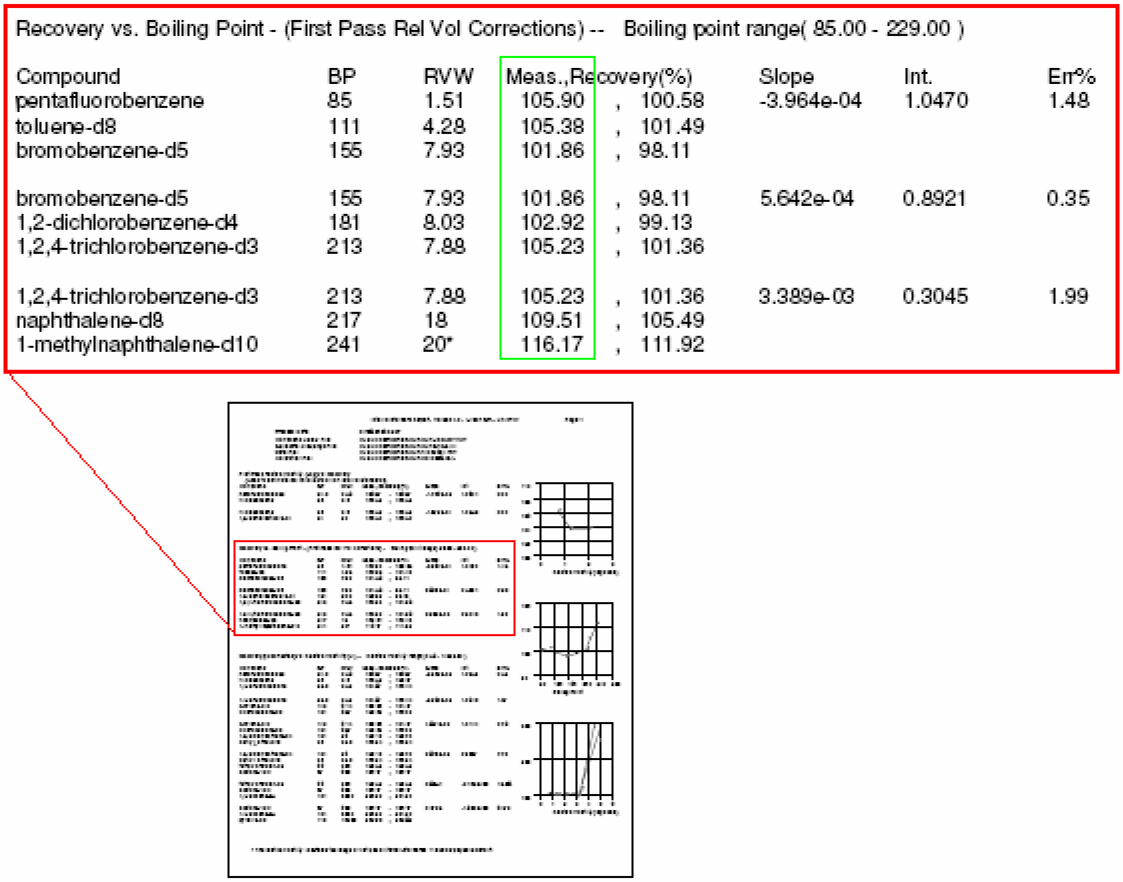
Figure 11: First-pass internal standard graphics

Boiling Point Effects

After the first-pass internal standards have described the first-pass relativity effects as line functions, they are used to determine the first-pass relativity effects on the boiling-point internal standards. Canceling the first-pass relativity effects in the measured recovery of the boiling-point internal standards provides recoveries that reflect just boiling point effects. To make the boiling point relationships easier to define, the range of values are divided into smaller segments (or groupings). Each grouping contains three or more boiling-point internal standards. The boiling point vs. recovery relationship for each grouping is calculated as a line.

Determining Boiling-Point Effects, Step 1: Determine the Experimental Recovery of the Boiling-Point Internal Standards

The experimental recoveries of the boiling-point internal standards are determined from the raw data as described in the section "Experimental Recoveries". This data is displayed in the "Meas." column as Figure 12.

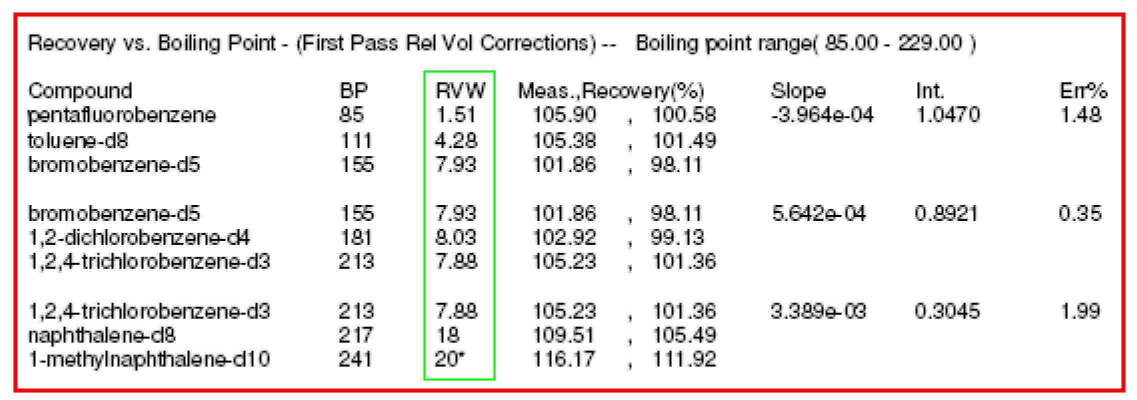


```
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) --   Boiling point range( 85.00 - 229.00 )

Compound                     BP      RVW     Meas.,Recovery(%)      Slope         Int.        Err%
pentafluorobenzene           85      1.51     105.90  ,  100.58     -3.964e-04    1.0470      1.48
toluene-d8                   111     4.28     105.38  ,  101.49
bromobenzene-d5              155     7.93     101.86  ,  98.11

bromobenzene-d5              155     7.93     101.86  ,  98.11      5.642e-04     0.8921      0.35
1,2-dichlorobenzene-d4       181     8.03     102.92  ,  99.13
1,2,4-trichlorobenzene-d3    213     7.88     105.23  ,  101.36

1,2,4-trichlorobenzene-d3    213     7.88     105.23  ,  101.36     3.389e-03     0.3045      1.99
naphthalene-d8               217     18       109.51  ,  105.49
1-methylnaphthalene-d10      241     20*      116.17  ,  111.92
```

Figure 12: Experimental recovery of boiling-point internal standards

Determining Boiling-Point Effects, Step 2: Measure the First-Pass Relative Volatility Effects on the Boiling-Point Internal Standards

The relative volatility related recoveries of the boiling-point internal standards are calculated using the equations determined by the first-pass internal standards. This is done by taking the natural log of each boiling-point internal standard's relative-volatility value and interpolating their predicted recovery as a function of first-pass equations. The relative volatility values of the internal standards are highlighted in Figure 13.



```
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) --   Boiling point range( 85.00 - 229.00 )

Compound                      BP      RVW    Meas.,Recovery(%)      Slope         Int.        Err%
pentafluorobenzene            85      1.51     105.90   ,  100.58   -3.964e-04    1.0470      1.48
toluene-d8                    111     4.28     105.38   ,  101.49
bromobenzene-d5               155     7.93     101.86   ,  98.11

bromobenzene-d5               155     7.93     101.86   ,  98.11    5.642e-04     0.8921      0.35
1,2-dichlorobenzene-d4        181     8.03     102.92   ,  99.13
1,2,4-trichlorobenzene-d3     213     7.88     105.23   ,  101.36

1,2,4-trichlorobenzene-d3     213     7.88     105.23   ,  101.36   3.389e-03     0.3045      1.99
naphthalene-d8                217     18       109.51   ,  105.49
1-methylnaphthalene-d10       241     20*      116.17   ,  111.92
```

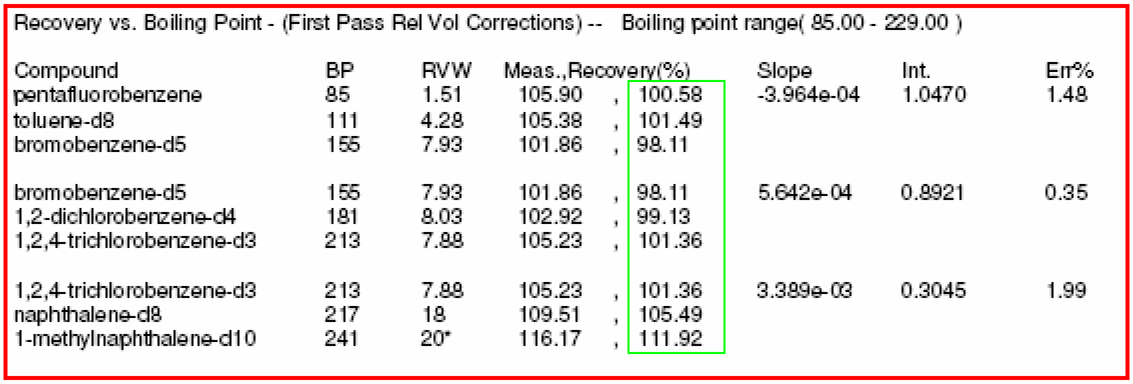
Figure 13: Determine relative volatility effects on boiling-point internal standards using first-pass equations

Example 2: What are the first-pass effects on pentafluorobenzene? Pentafluorobenzene has a relative volatility of 1.5, which means the first first-pass equation (values below 3.5) should be used. We know the equation is a line ($y = m \times X+B$) and we have the solutions for M and B (slope and intercept). Substitution gives

$$\text{FP recovery} = -1.736 \times 10^{-02} \times \ln(1.5) + 1.0601 = 1.0529$$

Determining Boiling-Point Effects, Step 3: Determining the Recovery of Boiling-Point Internal Standards that Reflect Boiling-Point Effects

The measured recovery values of the boiling-point internal standards are high-lighted in Figure 14 (as fraction not %). The first group of boiling-point internal standards has measured recoveries of 1.0529, 1.0383, and 1.0382 and these must first be revised to mitigate effects from their relative volatility values (1.51, 4.28, and 7.93, respectively).



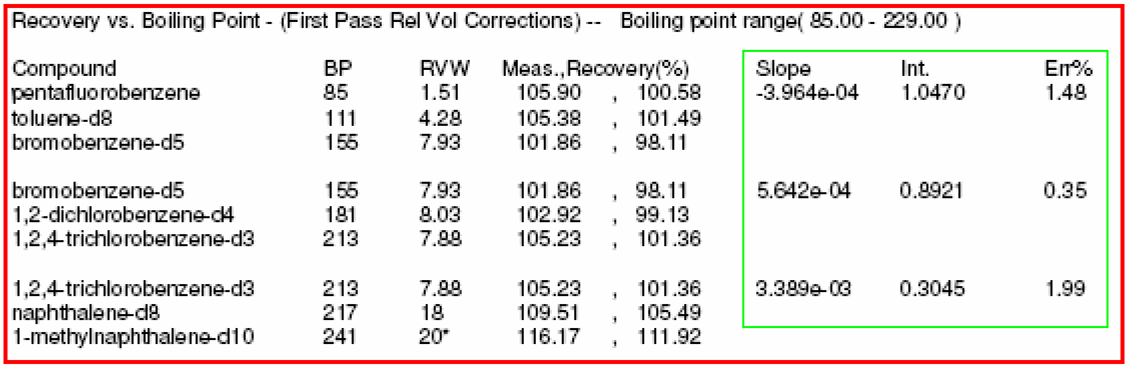
```
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) --   Boiling point range( 85.00 - 229.00 )

Compound                          BP      RVW      Meas.,Recovery(%)        Slope          Int.        Err%
pentafluorobenzene                85      1.51      105.90   ,  100.58      -3.964e-04     1.0470      1.48
toluene-d8                        111     4.28      105.38   ,  101.49
bromobenzene-d5                   155     7.93      101.86   ,  98.11

bromobenzene-d5                   155     7.93      101.86   ,  98.11       5.642e-04      0.8921      0.35
1,2-dichlorobenzene-d4            181     8.03      102.92   ,  99.13
1,2,4-trichlorobenzene-d3         213     7.88      105.23   ,  101.36

1,2,4-trichlorobenzene-d3         213     7.88      105.23   ,  101.36      3.389e-03      0.3045      1.99
naphthalene-d8                    217     18        109.51   ,  105.49
1-methylnaphthalene-d10           241     20*       116.17   ,  111.92
```

Figure 14: Recovery of boiling-point internal standards after first-pass corrections

Looking at the Example 2 results, if there were no boiling-point effects on pentafluorobenzene, its measured recovery should have been 1.0529 and not the 1.0590 we found from the raw data. The measured value is fractionally 1.0058 greater than expected from just the first-pass relative volatility effects (1.0590/1.0529). The comparison of measured recovery to the first-pass predicted recovery is calculated as the boiling point effect on pentafluorobenzene. This recovery is reported in the Report Recovery (%) column as 100.58 in figure 14.

Determining Boiling-Point Effects, Step 4: Determine Boiling-Point Effects as Functions of Recovery Relative to Boiling Point

Compensating the experimental recovery of the boiling-point internal standards for relative volatility effects predicted by the first-pass internal standards, yields recoveries that are attributed to boiling point effects. Fig 12-15 shows that the boiling point effects are described as three ranges in our analytical report example. Using the three compounds in each group, a line describing the relationship of boiling point to recovery is determined and these are highlighted in Figure 15. The line determinations require regression analyses and it is suggested to use spreadsheet functions to verify the slope, intercept, and standard error (1 sigma).



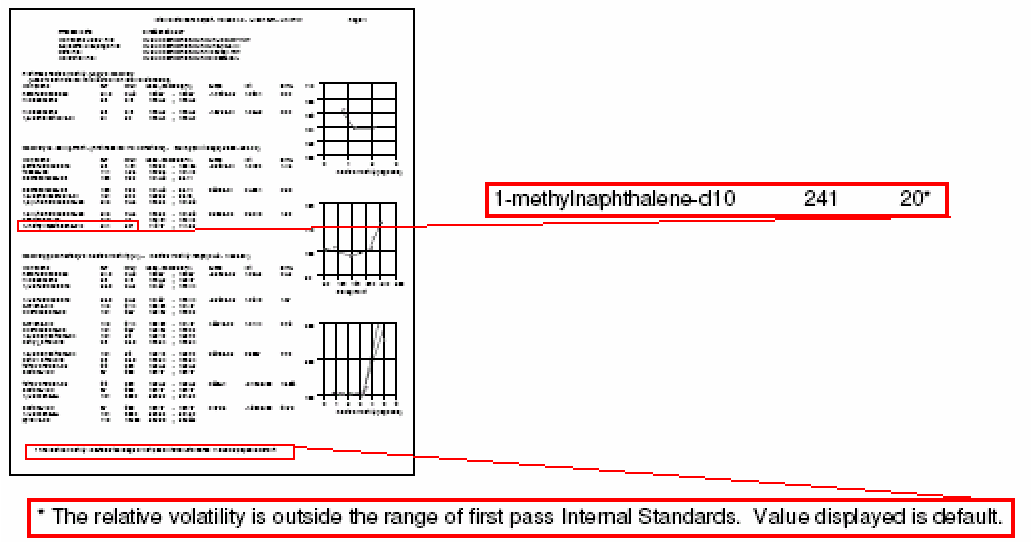
```
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) --   Boiling point range( 85.00 - 229.00 )

Compound                          BP      RVW      Meas.,Recovery(%)        Slope          Int.        Err%
pentafluorobenzene                85      1.51      105.90   ,  100.58      -3.964e-04     1.0470      1.48
toluene-d8                        111     4.28      105.38   ,  101.49
bromobenzene-d5                   155     7.93      101.86   ,  98.11

bromobenzene-d5                   155     7.93      101.86   ,  98.11       5.642e-04      0.8921      0.35
1,2-dichlorobenzene-d4            181     8.03      102.92   ,  99.13
1,2,4-trichlorobenzene-d3         213     7.88      105.23   ,  101.36

1,2,4-trichlorobenzene-d3         213     7.88      105.23   ,  101.36      3.389e-03      0.3045      1.99
naphthalene-d8                    217     18        109.51   ,  105.49
1-methylnaphthalene-d10           241     20*       116.17   ,  111.92
```

Figure 15: Boiling-point effects expressed as functions

Example 3: Using a Lotus spreadsheet, the line for the first boiling point group is solved by the regression function. First create Range A (contains boiling points 85, 111, 155) and Range B (recoveries 1.0058, 1.0149, 0.9811). The Lotus functions are used to duplicate SMCReporter calculations as

intercept = @regression(Range A, Range B, 1, 1) = 1.0470
slope = @regression(Range A, Range B, 101, 1) = -3.964×10^{-04}
err = @regression(Range A, Range B, 2) = .0148

Notice that the highest boiling compound, 1-methylnaphthalene has a relative volatility value of 20 with an asterisk (Figure 16). The actual relative-volatility value for 1-methylnaphthalene is 67 but only a value of 20 is used because the largest relative-volatility value of the first-pass internal standards is 20. This substituted value can be a source for some error but a better internal standard has not been found for the upper boiling point. SMCReporter, as a default, does not extrapolate values.



1-methylnaphthalene-d10 241 20*

* The relative volatility is outside the range of first pass Internal Standards. Value displayed is default.

Figure 16: SMCReporter default values

Determining Boiling-Point Effects, Step 5: Present the Boiling-Point Effects as a Graph

The boiling-point effects are displayed graphically as individual points (boiling-point internal standard recovery and boiling point values) as well as the lines that were determined for the three groups. The graph provides a quick view of how the boiling point internal standards behaved (compared to the calibration curve) during the vacuum distillation. A review of the trends in the graph as well as the error values in the determination of boiling point to recovery lines (Figure 17) provides insight as to how uniform the analysis was.

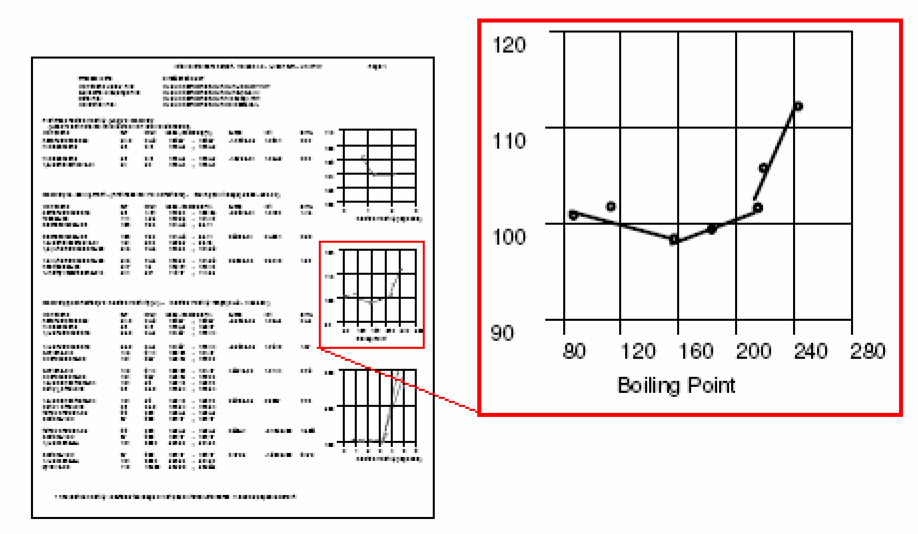


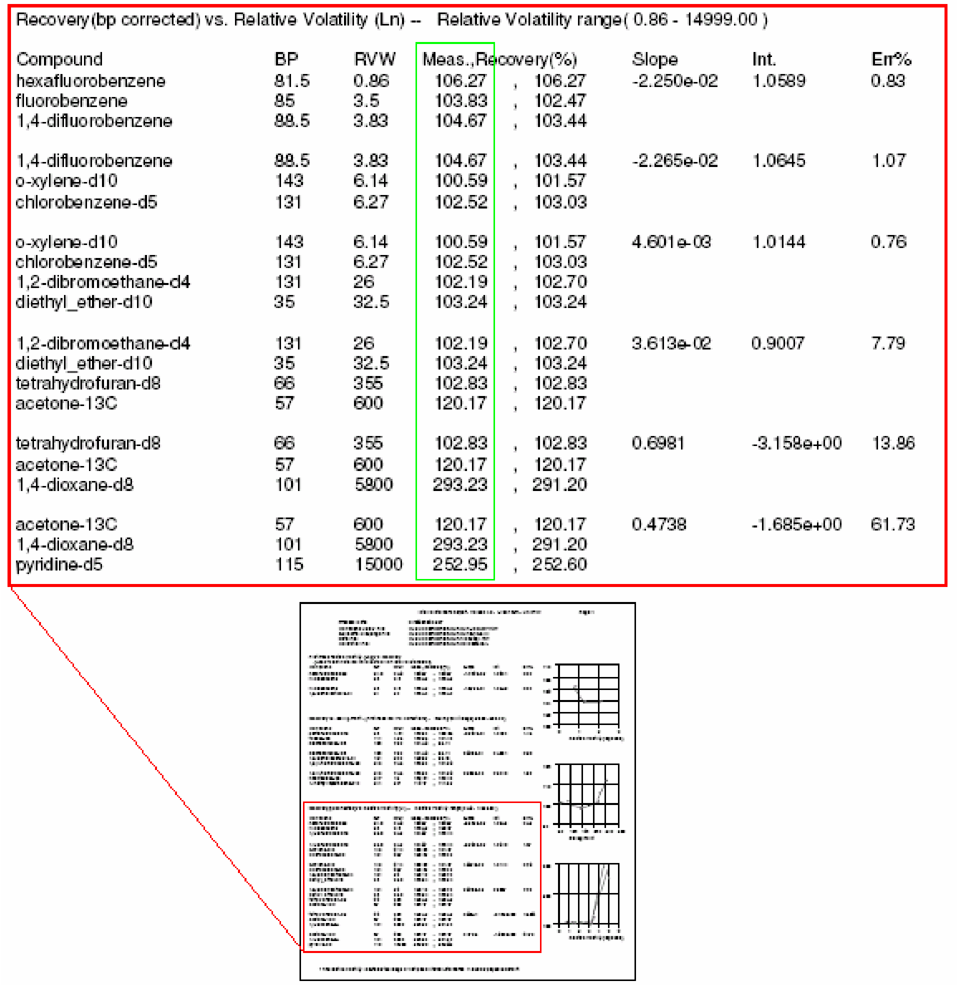
Figure 17: Graphic display of boiling-point effects

Relative Volatility Effects

After the boiling-point internal standards have described boiling point effects as line functions, the line functions are used to determine the boiling-point effects on the relative-volatility internal standards. In the same manner that experimental recoveries of the boiling point internal standards were made to reflect only boiling point effects, the recoveries of the relative-volatility internal standards are compensated to reflect only losses from relative volatility effects. This is done by compensating the relative-volatility internal standards experimental recoveries for boiling-point effects. After the experimental recoveries are adjusted, the effects from relative volatility can be described. To make the relative-volatility relationships easier to define, the range of values are divided into smaller segments (or groupings). Each grouping contains three or more internal standards. The natural log of relative volatility vs. recovery relationship is calculated as a line for the five relative-volatility internal standard groupings.

Determining Relative-Volatility Effects, Step 1: Determine the Experimental Recovery of the Relative-Volatility Internal Standards

As in the first-pass and boiling-point sections, the “Meas.” column highlighted in Figure 18 reflects the experimental recovery of the relative-volatility internal standards.



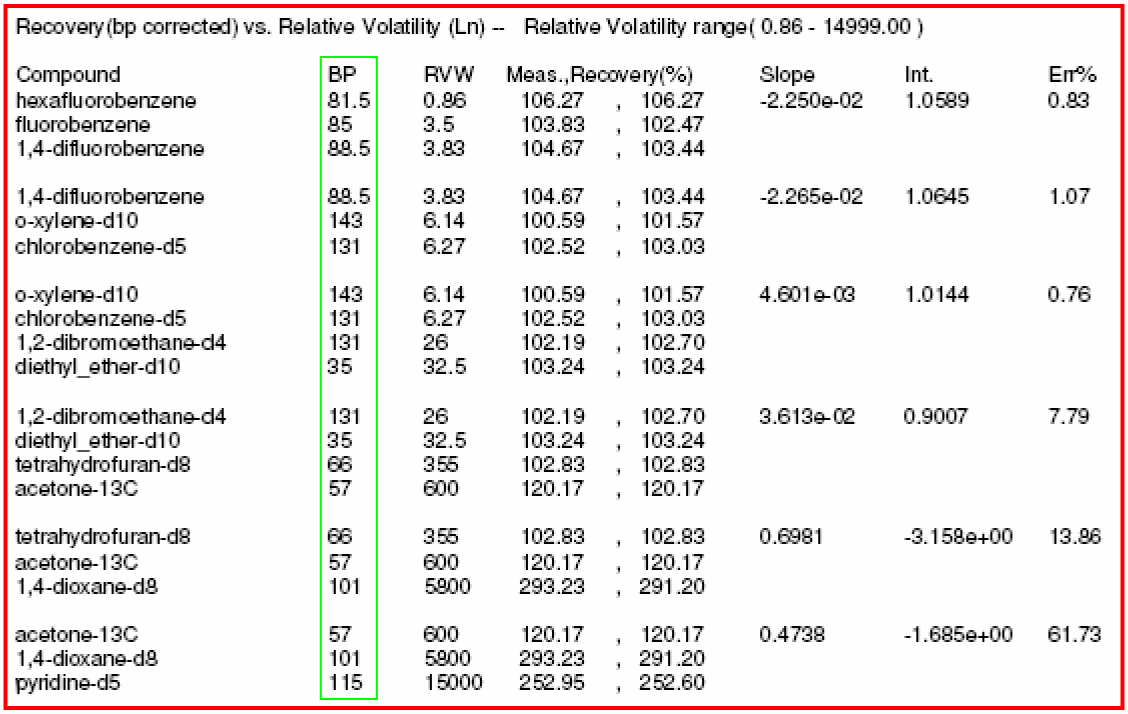
Recovery(bp corrected) vs. Relative Volatility (Ln) -- Relative Volatility range(0.86 - 14999.00)

Compound	BP	RVW	Meas.,Recovery(%)	Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	106.27 , 106.27	-2.250e-02	1.0589	0.83
fluorobenzene	85	3.5	103.83 , 102.47			
1,4-difluorobenzene	88.5	3.83	104.67 , 103.44			
1,4-difluorobenzene	88.5	3.83	104.67 , 103.44	-2.265e-02	1.0645	1.07
o-xylene-d10	143	6.14	100.59 , 101.57			
chlorobenzene-d5	131	6.27	102.52 , 103.03			
o-xylene-d10	143	6.14	100.59 , 101.57	4.601e-03	1.0144	0.76
chlorobenzene-d5	131	6.27	102.52 , 103.03			
1,2-dibromoethane-d4	131	26	102.19 , 102.70			
diethyl_ether-d10	35	32.5	103.24 , 103.24			
1,2-dibromoethane-d4	131	26	102.19 , 102.70	3.613e-02	0.9007	7.79
diethyl_ether-d10	35	32.5	103.24 , 103.24			
tetrahydrofuran-d8	66	355	102.83 , 102.83			
acetone-13C	57	600	120.17 , 120.17			
tetrahydrofuran-d8	66	355	102.83 , 102.83	0.6981	-3.158e+00	13.86
acetone-13C	57	600	120.17 , 120.17			
1,4-dioxane-d8	101	5800	293.23 , 291.20			
acetone-13C	57	600	120.17 , 120.17	0.4738	-1.685e+00	61.73
1,4-dioxane-d8	101	5800	293.23 , 291.20			
pyridine-d5	115	15000	252.95 , 252.60			

Figure 18: Experimental recoveries of relative volatility standards

Determining Relative-Volatility Effects, Step 2: Calculate the boiling-point Effects on the Relative-Volatility Internals Standards

The experimental recoveries of the relative-volatility internal standards reflect both relative volatility and boiling-point effects. As the boiling-point internal standard recoveries were modified to remove relative volatility effects measured by the first-pass internal standards, the boiling point effects are removed from the relative volatility internal standards. Boiling-point recoveries are calculated by the boiling-point equations (see Boiling-Point Effects). Taking the boiling point of each relative-volatility internal standard (Figure 19), their boiling-point-recoveries are interpolated from the boiling-point equations. The criteria that SMCReporter uses to determine the equation selected (boiling-point group) depends on the boiling point of the relative-volatility internal standards being calculated.


Recovery(bp corrected) vs. Relative Volatility (Ln) -- Relative Volatility range(0.86 - 14999.00)

Compound	BP	RVW	Meas.,Recovery(%)		Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	106.27 ,	106.27	-2.250e-02	1.0589	0.83
fluorobenzene	85	3.5	103.83 ,	102.47			
1,4-difluorobenzene	88.5	3.83	104.67 ,	103.44			
1,4-difluorobenzene	88.5	3.83	104.67 ,	103.44	-2.265e-02	1.0645	1.07
o-xylene-d10	143	6.14	100.59 ,	101.57			
chlorobenzene-d5	131	6.27	102.52 ,	103.03			
o-xylene-d10	143	6.14	100.59 ,	101.57	4.601e-03	1.0144	0.76
chlorobenzene-d5	131	6.27	102.52 ,	103.03			
1,2-dibromoethane-d4	131	26	102.19 ,	102.70			
diethyl_ether-d10	35	32.5	103.24 ,	103.24			
1,2-dibromoethane-d4	131	26	102.19 ,	102.70	3.613e-02	0.9007	7.79
diethyl_ether-d10	35	32.5	103.24 ,	103.24			
tetrahydrofuran-d8	66	355	102.83 ,	102.83			
acetone-13C	57	600	120.17 ,	120.17			
tetrahydrofuran-d8	66	355	102.83 ,	102.83	0.6981	-3.158e+00	13.86
acetone-13C	57	600	120.17 ,	120.17			
1,4-dioxane-d8	101	5800	293.23 ,	291.20			
acetone-13C	57	600	120.17 ,	120.17	0.4738	-1.685e+00	61.73
1,4-dioxane-d8	101	5800	293.23 ,	291.20			
pyridine-d5	115	15000	252.95 ,	252.60			

Figure 19: Boiling points of the relative-volatility internal standards

Example 4: What are the boiling point effects on chlorobenzene-*d*$_5$? Chlorobenzene-*d*$_5$ has a 131 °C boiling point, which means the first boiling point equation in Figure 15 (values below 155 °C) should be used. We know the equation is a line (y = m × X+B) and we have the solutions for M and B (slope and intercept). Substitution gives

$$\text{BP recovery} = -3.964\times10^{-04}\times131 + 1.0470 = 1.0252$$

Determining Relative-Volatility Effects, Step 3: Determining the Recovery of Relative-Volatility Internal Standards that Reflect Relative-Volatility Effects

As noted in equation 2, the experimental recovery is a product of the recovery after boiling point effects and recovery after relative volatility effects. We have the experimental recovery and can determine the boiling-point effects from Figure 15 so we can now solve for the relative volatility recovery as

$$\text{RV}_{\text{recovery}} = \text{Experimental Measurement}_{\text{recovery}} \div \text{BP}_{\text{recovery}} \qquad \text{(Eq4)}$$

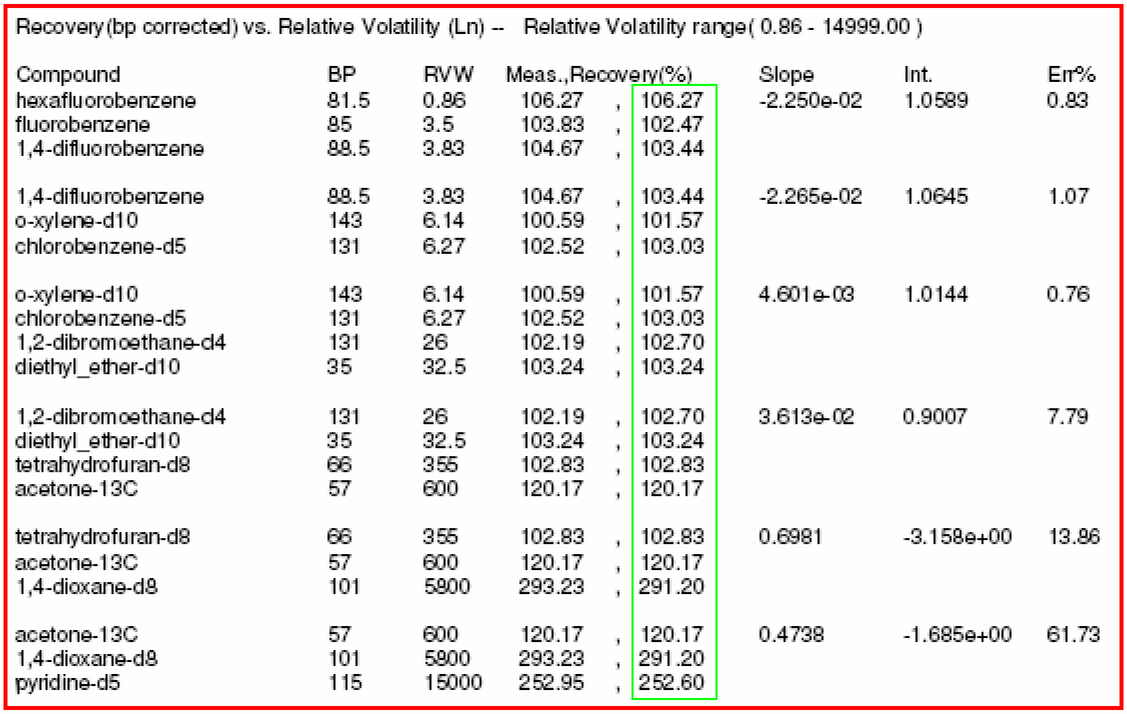
Using equation 4 the recovery of the relative volatility internal standards that reflect relative volatility effects are determined and listed in Figure 20 in the column “Recovery (%)”.

Example 5: What is the recovery that reflects relative volatility effects for internal standard, *o*-xylene-*d*$_{10}$? *o*-Xylene-*d*$_{10}$ has a boiling point of 143 °C which means the first BP equation (boiling point values below 155 ºC) is used to determine BP recovery. The equation is a line (y = m × X + B) and we have the solutions for m and B (slope and intercept) so substitution gives

$$\text{BP recovery} = -3.108\times10^{-04}\times143 + 1.0470 = 0.99031$$

We have already calculated the experimental recovery for *o*-xylene-*d*$_{10}$ giving

$$\text{RV recovery} = 1.0059 \div 0.99031 = 1.0157$$

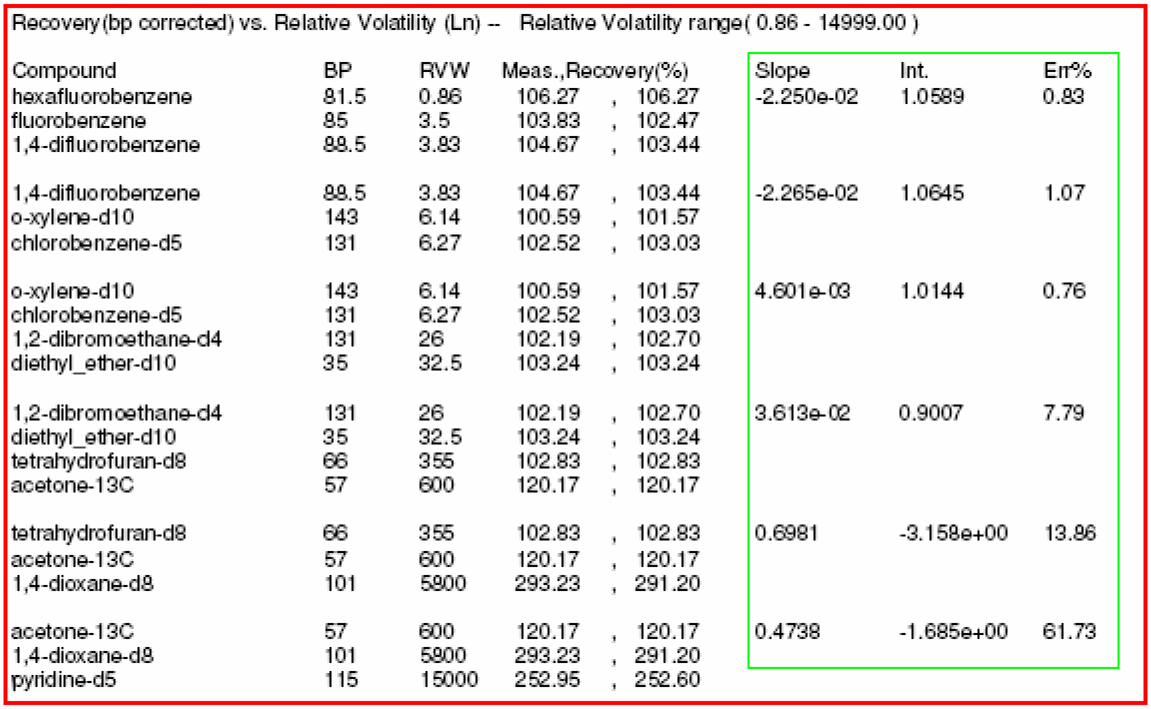


```
Recovery(bp corrected) vs. Relative Volatility (Ln) --   Relative Volatility range( 0.86 - 14999.00 )

Compound                BP     RVW    Meas.,Recovery(%)     Slope        Int.         Err%
hexafluorobenzene       81.5   0.86    106.27  ,  106.27    -2.250e-02   1.0589       0.83
fluorobenzene           85     3.5     103.83  ,  102.47
1,4-difluorobenzene     88.5   3.83    104.67  ,  103.44

1,4-difluorobenzene     88.5   3.83    104.67  ,  103.44    -2.265e-02   1.0645       1.07
o-xylene-d10            143    6.14    100.59  ,  101.57
chlorobenzene-d5        131    6.27    102.52  ,  103.03

o-xylene-d10            143    6.14    100.59  ,  101.57    4.601e-03    1.0144       0.76
chlorobenzene-d5        131    6.27    102.52  ,  103.03
1,2-dibromoethane-d4    131    26      102.19  ,  102.70
diethyl_ether-d10       35     32.5    103.24  ,  103.24

1,2-dibromoethane-d4    131    26      102.19  ,  102.70    3.613e-02    0.9007       7.79
diethyl_ether-d10       35     32.5    103.24  ,  103.24
tetrahydrofuran-d8      66     355     102.83  ,  102.83
acetone-13C             57     600     120.17  ,  120.17

tetrahydrofuran-d8      66     355     102.83  ,  102.83    0.6981       -3.158e+00   13.86
acetone-13C             57     600     120.17  ,  120.17
1,4-dioxane-d8          101    5800    293.23  ,  291.20

acetone-13C             57     600     120.17  ,  120.17    0.4738       -1.685e+00   61.73
1,4-dioxane-d8          101    5800    293.23  ,  291.20
pyridine-d5             115    15000   252.95  ,  252.60
```

Figure 20: Recovery of relative-volatility internal standards that reflect only relative volatility

Determining Relative-Volatility Effects, Step 4: Determine Relative-Volatility Effects as Functions of Recovery to Relative Volatility

Compensating the experimental recovery of the relative-volatility internal standards for boiling point effects predicted by the boiling point internal standards, results in recoveries that are attributed to relative volatility effects. Fig 21 shows that the relative volatility effects are described as five ranges in our analytical report example. Using the internal standards in each group, a line describing the relationship of the natural logarithm of relative volatility to recovery is determined. The line determinations require regression analyses and it is suggested to use spreadsheet functions to verify the slope, intercept, and standard error (1 sigma).



```
Recovery(bp corrected) vs. Relative Volatility (Ln) --   Relative Volatility range( 0.86 - 14999.00 )

Compound                BP     RVW     Meas.,Recovery(%)      Slope        Int.         Err%
hexafluorobenzene       81.5   0.86     106.27  ,  106.27     -2.250e-02   1.0589       0.83
fluorobenzene           85     3.5      103.83  ,  102.47
1,4-difluorobenzene     88.5   3.83     104.67  ,  103.44

1,4-difluorobenzene     88.5   3.83     104.67  ,  103.44     -2.265e-02   1.0645       1.07
o-xylene-d10            143    6.14     100.59  ,  101.57
chlorobenzene-d5        131    6.27     102.52  ,  103.03

o-xylene-d10            143    6.14     100.59  ,  101.57     4.601e-03    1.0144       0.76
chlorobenzene-d5        131    6.27     102.52  ,  103.03
1,2-dibromoethane-d4    131    26       102.19  ,  102.70
diethyl_ether-d10       35     32.5     103.24  ,  103.24

1,2-dibromoethane-d4    131    26       102.19  ,  102.70     3.613e-02    0.9007       7.79
diethyl_ether-d10       35     32.5     103.24  ,  103.24
tetrahydrofuran-d8      66     355      102.83  ,  102.83
acetone-13C             57     600      120.17  ,  120.17

tetrahydrofuran-d8      66     355      102.83  ,  102.83     0.6981       -3.158e+00   13.86
acetone-13C             57     600      120.17  ,  120.17
1,4-dioxane-d8          101    5800     293.23  ,  291.20

acetone-13C             57     600      120.17  ,  120.17     0.4738       -1.685e+00   61.73
1,4-dioxane-d8          101    5800     293.23  ,  291.20
pyridine-d5             115    15000    252.95  ,  252.60
```

Figure 21: Linear relationship of relative volatility to recovery determined from relative-volatility internal standards

Example 6: Derive the relative volatility function for the third relative volatility group. Using a Lotus spreadsheet the line is solved by the regression function. First create Range A (contains natural logarithms of 6.14, 6.27, 26, and 32.5) and Range B (recoveries 1.0157, 1.0303, 1.0270, and 1.0324). The Lotus functions are used to duplicate SMCReporter calculations as the following,

intercept = @regression(Range A, Range B, 1, 1) = 1.0144
slope = @regression(Range A, Range B, 101, 1) = 0.004601 = 4.601×10^{-3}
err = @regression(Range A, Range B, 2) = .0076

Determining Relative-Volatility Effects, Step 5: Graphic Display of Relative-Volatility Effects

The relative-volatility effects are displayed graphically as individual points (relative-volatility internal standards recovery and the logarithm of relative volatility values) as well as the lines that were determined for the five groups (Figure 22). The graph shows the data is largely uniform but the calculated error values tend to increase with larger values of relative volatility, which is common. Again, one of this method's attributes is that these errors will be propagated for all compound results. While the recoveries of the higher relative volatility compounds tend to vary greatest, being these compounds are very sensitive to minor experimental variations, the relative volatility corrections make these determinations accurate.

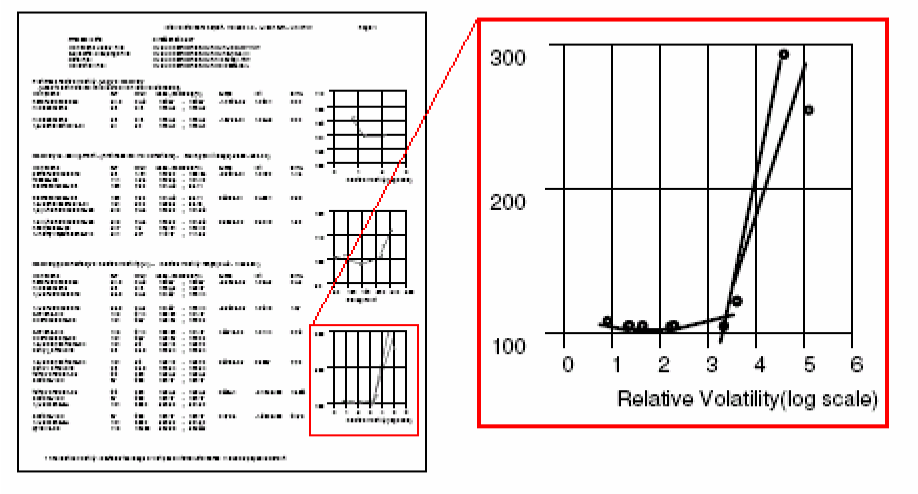


Figure 22: Graph of recovery as relates to relative volatility

Internal Standard Groups

Internal standards are added to each sample in order to calculate matrix effects on analytes as discussed in earlier sections. By calculating the effects as recovery, the measured response of an analyte at the GC/MS an accurate concentration (compensated for matrix effects) of the analyte is determined. The selection of what group of internal standards are used to measure matrix effects is based upon the chemical properties of the analyte.

What internal standards are contained in each boiling point or relative volatility group is identified by SMCReporter in the internal standard file. The program has a default internal standard file containing assignments as in the example internal standard report. However, the user can change internal standards and groupings from the default file. If the user is to change internal standards or groups the following should be considered:

1. There are no gaps. This typically means that the internal standards that define an upper limit of a group also define the next higher group.
2. An analyte does not have a property value that exceeds the upper range of the highest group. SMCReporter will substitute the upper limit of the highest group should its limit be exceeded.
3. Each boiling point and relative volatility group should have three or more internal standards.
4. Internal Standards should be used for only one property (not always possible due to limited selection of labeled compounds).

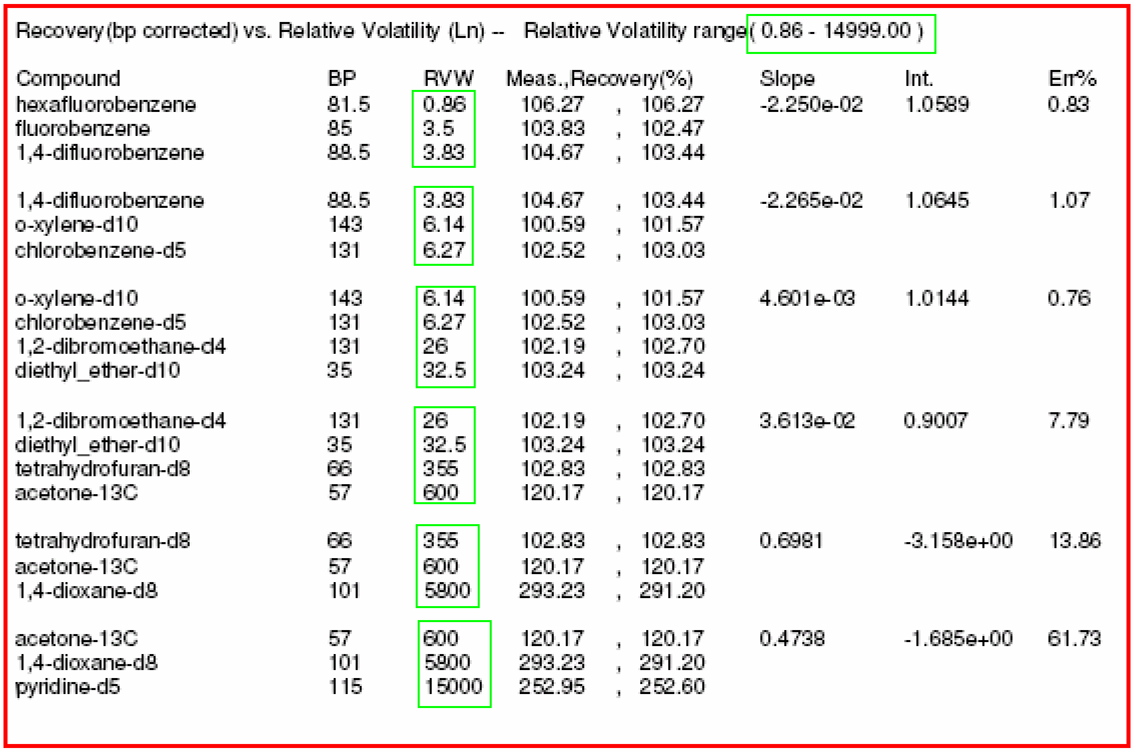
What is the Upper and Lower Limit of a Group?

SMCReporter uses the upper limits of groups as criteria for determining which group is used for a calculation of a matrix effect. The identification of a group's limits is based on how many internal standards populate a group. If there are only two internal standards in a group such as the example's first-pass internal standards, the upper and lower limits are simply the upper and lower relative volatility values of the internal standards. The upper and lower limit of a "property" group of three internal standards is taken to be the highest and lowest "property" value of the internal standards. If there are more than three internal standards in a group, the average of the upper two internal standards is taken as the upper limit and the average of the two lower internal standards is taken as the lower limit.

The Example's Relative-Volatility Limits of Relative-Volatility Groups

SMCReporter takes the natural logarithm of a compound's relative volatility value and tests it against the first RV-Group's upper limit, ln (3.83). If the value exceeds its range it tests the next group's upper limit, ln (6.27). The next group has four internal standards so its upper limit is the average of the two higher points, ln (26) and ln (32.5). This process is repeated until it finds a RV-Group that has an upper range limit that exceeds the compound's relative volatility and then that group is used to determine the compound's RVrecovery. If the natural logarithm of the compound's relative volatility exceeds the last group's upper limit, the upper limit is used.

The lower and upper limits for relative-volatility values are presented in the relative volatility display in the upper right hand corner (Figure 23) with the values 0.86-14999.

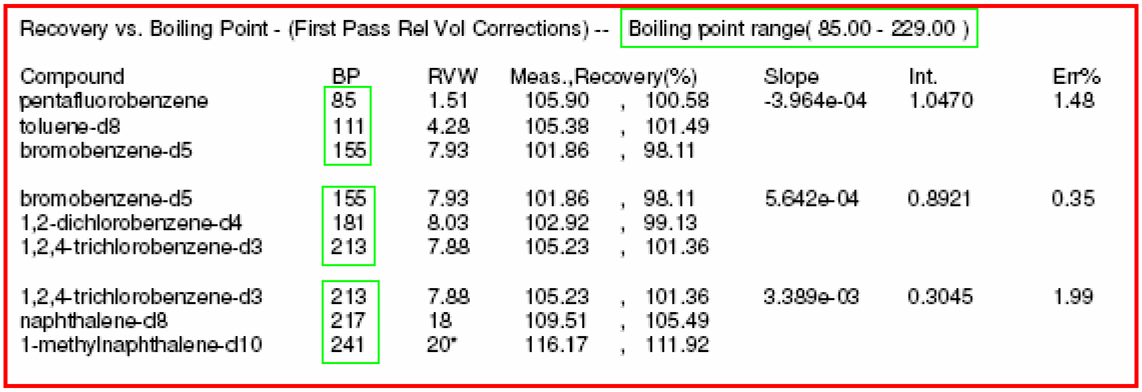


```
Recovery(bp corrected) vs. Relative Volatility (Ln) --   Relative Volatility range( 0.86 - 14999.00 )

Compound               BP      RVW     Meas.,Recovery(%)     Slope        Int.         Err%
hexafluorobenzene      81.5    0.86     106.27  ,  106.27    -2.250e-02   1.0589       0.83
fluorobenzene          85      3.5      103.83  ,  102.47
1,4-difluorobenzene    88.5    3.83     104.67  ,  103.44

1,4-difluorobenzene    88.5    3.83     104.67  ,  103.44    -2.265e-02   1.0645       1.07
o-xylene-d10           143     6.14     100.59  ,  101.57
chlorobenzene-d5       131     6.27     102.52  ,  103.03

o-xylene-d10           143     6.14     100.59  ,  101.57    4.601e-03    1.0144       0.76
chlorobenzene-d5       131     6.27     102.52  ,  103.03
1,2-dibromoethane-d4   131     26       102.19  ,  102.70
diethyl_ether-d10      35      32.5     103.24  ,  103.24

1,2-dibromoethane-d4   131     26       102.19  ,  102.70    3.613e-02    0.9007       7.79
diethyl_ether-d10      35      32.5     103.24  ,  103.24
tetrahydrofuran-d8     66      355      102.83  ,  102.83
acetone-13C            57      600      120.17  ,  120.17

tetrahydrofuran-d8     66      355      102.83  ,  102.83    0.6981       -3.158e+00   13.86
acetone-13C            57      600      120.17  ,  120.17
1,4-dioxane-d8         101     5800     293.23  ,  291.20

acetone-13C            57      600      120.17  ,  120.17    0.4738       -1.685e+00   61.73
1,4-dioxane-d8         101     5800     293.23  ,  291.20
pyridine-d5            115     15000    252.95  ,  252.60
```

Figure 23: Relative-volatility internal standard groupings

The Example’s Boiling-Point Limits of Boiling-Point Groups

SMCReporter records the upper and lower limits of the boiling point calculations (Figure 24). Boiling-point recovery = 100% for compounds with boiling points below 85 ºC and any compound that has a boiling point value greater than the upper limit will only be corrected as if its boiling point were at the upper limit (229 ºC). These limits can be changed in SMCReporter (in the surrogate file) but care should be taken as extrapolation that exceeds the default limits is not as reliable.



```
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) -- Boiling point range( 85.00 - 229.00 )

Compound                   BP    RVW   Meas.,Recovery(%)   Slope        Int.     Err%
pentafluorobenzene         85    1.51   105.90 , 100.58    -3.964e-04   1.0470   1.48
toluene-d8                 111   4.28   105.38 , 101.49
bromobenzene-d5            155   7.93   101.86 , 98.11

bromobenzene-d5            155   7.93   101.86 , 98.11     5.642e-04    0.8921   0.35
1,2-dichlorobenzene-d4     181   8.03   102.92 , 99.13
1,2,4-trichlorobenzene-d3  213   7.88   105.23 , 101.36

1,2,4-trichlorobenzene-d3  213   7.88   105.23 , 101.36    3.389e-03    0.3045   1.99
naphthalene-d8             217   18     109.51 , 105.49
1-methylnaphthalene-d10    241   20*    116.17 , 111.92
```

Figure 24: Boiling-point internal standard groupings

How SMCReporter Chooses a Group for Processing an Analyte

SMCReporter has an automated procedure for determining how an analyte or surrogate will be processed for reporting. Having the selection process automated makes review or reproducing results straightforward. SMCReporter follows a flowchart protocol for determining which groups (boiling point and relative volatility) are appropriate for calculating the recovery of an analyte. If the property has a value that is lower than the first group’s upper limit, the first group is used in the calculation. If the analyte’s property is greater than the first group’s upper limit then it is compared to the next group’s upper limit and so on until the first upper limit that exceeds the property value is found. If the property is greater than the last group then the upper limit of the highest group is substituted as the property value. If the property is lower than the lowest group’s lower limit and the property is a boiling point, no loss of analyte relating to boiling point is assumed so the recovery is 100 %. If the property is lower than the lowest group’s lower limit and the property is relative volatility, the group’s lower limit is substituted as the analyte’s relative volatility. SMCReporter does not extrapolate results but provides a conservative result instead. See Figure 25 for an illustration of the process for selecting the appropriate group among three groups.

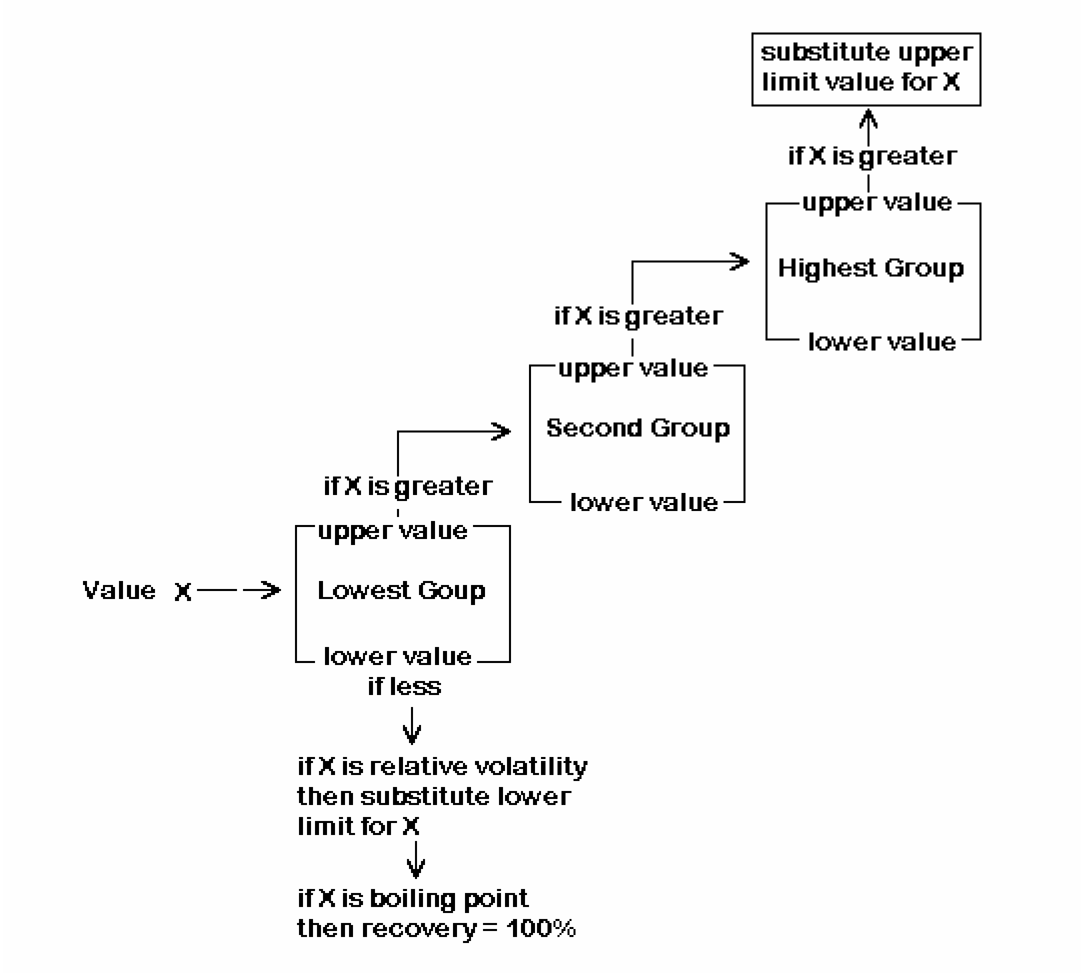


Figure 25: Scheme for selecting the internal standard group that a value, x, will be processed

Surrogate Report

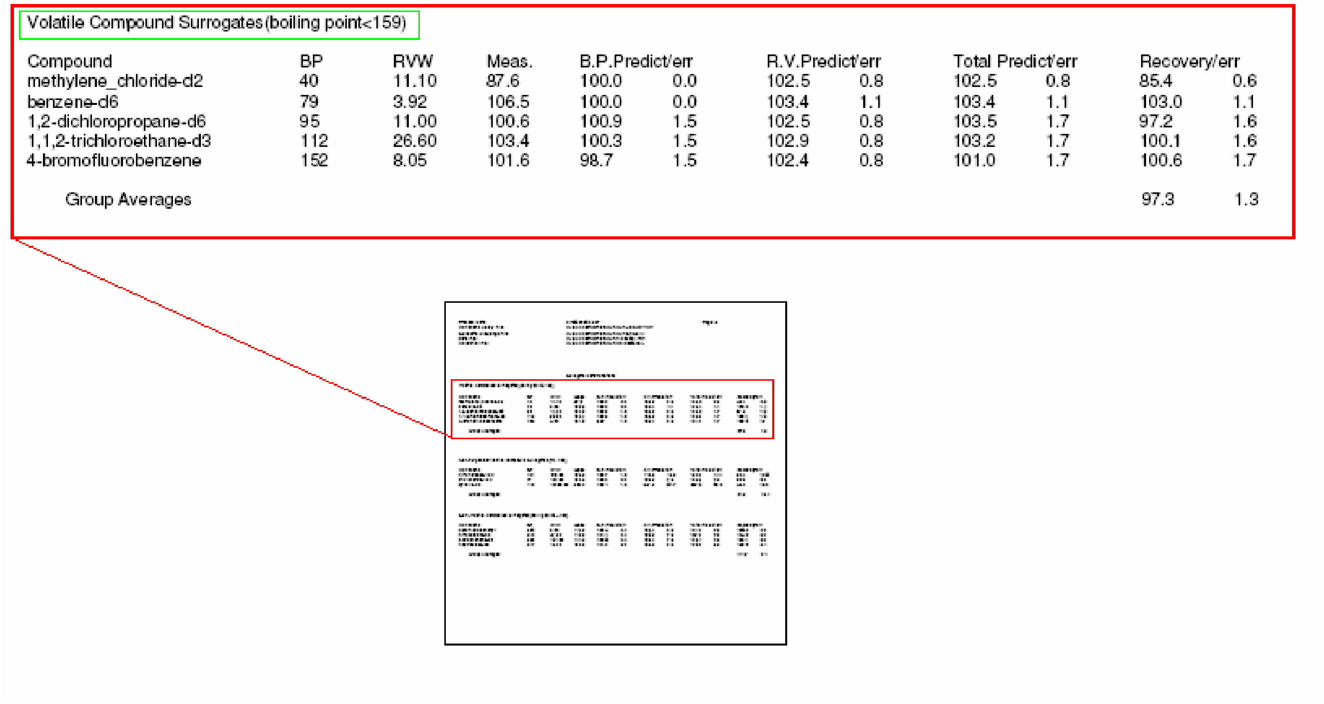
The last page of the analytical report is the surrogate report. Figure 4 presents the surrogate page generated for the example. This page is generated to provide an assessment of how well an analysis conformed to the predictions of the internal standard corrections.

Known amounts of surrogate compounds are added to each sample and standard. The experimental recovery of the surrogates is determined the same as for the internal standards. The internal standard predicted recovery of each surrogate compound is also calculated. Ideally the experimental recovery and the internal-standard predicted recovery are the same. How far the experimental recovery differs from the internal-standard predicted recovery is called ‘recovery’ in the surrogate report and is an estimate how accurate the method performed for a given analysis.

There are three types of surrogates that are used, volatile, non-purgeable, and semi-volatile. These classifications are based upon their chemical properties and make review of surrogate results easier to interpret. The demarcations between the groups in the example are the default values and can be changed in the internal standards file. Note: The limits to define a type are variables that can be changed in SMCReporter (File->Edit Surrogate File -> Surrogate Ranges).

Volatile Compound Surrogates

The volatile compounds are interpreted to be those compounds with boiling points less than 159 °C (see Figure 26) and have a relative volatility value of less than 100. These compounds collectively represent the analytes that fit within these criteria.



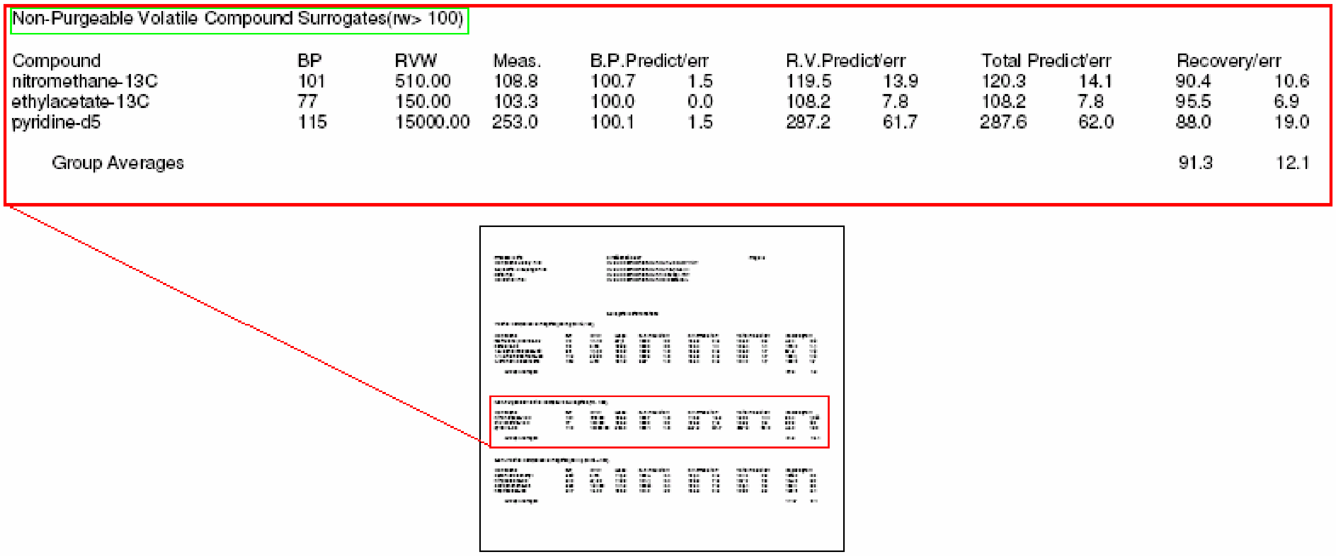
Volatile Compound Surrogates(boiling point<159)

Compound	BP	RVW	Meas.	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
methylene_chloride-d2	40	11.10	87.6	100.0	0.0	102.5	0.8	102.5	0.8	85.4	0.6
benzene-d6	79	3.92	106.5	100.0	0.0	103.4	1.1	103.4	1.1	103.0	1.1
1,2-dichloropropane-d6	95	11.00	100.6	100.9	1.5	102.5	0.8	103.5	1.7	97.2	1.6
1,1,2-trichloroethane-d3	112	26.60	103.4	100.3	1.5	102.9	0.8	103.2	1.7	100.1	1.6
4-bromofluorobenzene	152	8.05	101.6	98.7	1.5	102.4	0.8	101.0	1.7	100.6	1.7
Group Averages										97.3	1.3

Figure 26: Volatile compound surrogates

Non-Purgeable Compound Surrogates

Volatile compounds (boiling points < 159 °C) that have a strong affinity for water are called "non-purgeable" volatile compounds. RCRA methods manual, SW-846 uses the term "non-purgeable" to describe those volatile compounds that have a strong affinity for water. SMCReporter uses a default of relative volatility greater than 100 as the demarcation between "volatile" and "non-purgeable volatile" (see Figure 27). This value can be changed in the event that a different value is desired.



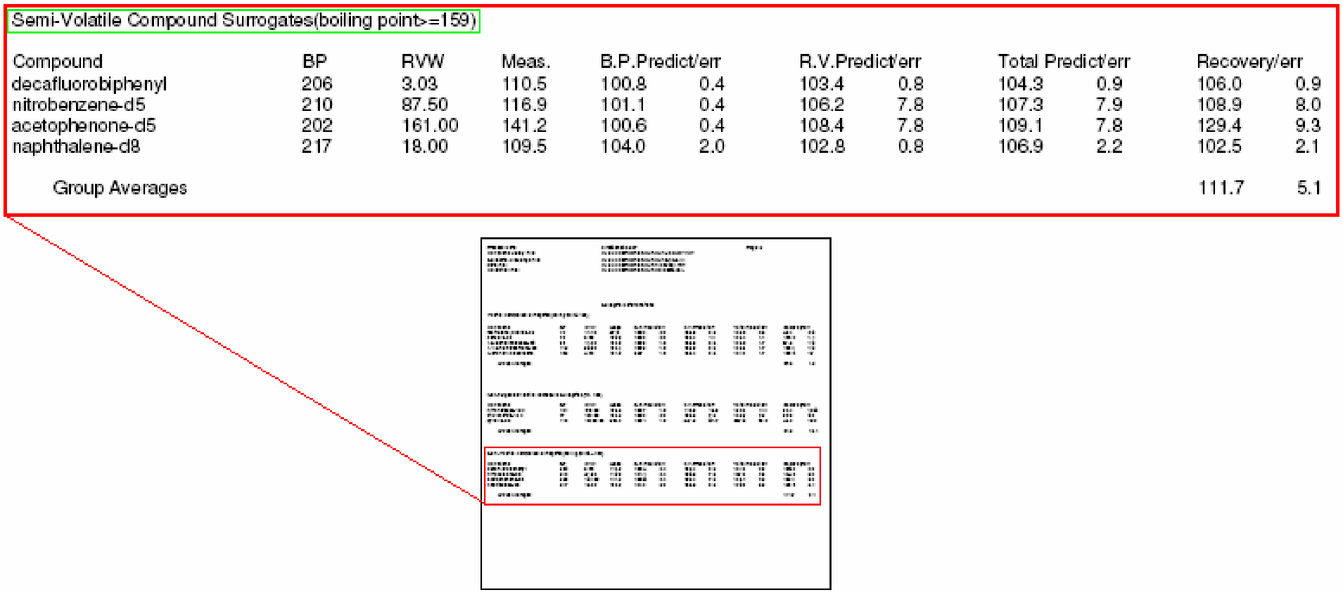
Non-Purgeable Volatile Compound Surrogates(rw> 100)

Compound	BP	RVW	Meas.	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
nitromethane-13C	101	510.00	108.8	100.7	1.5	119.5	13.9	120.3	14.1	90.4	10.6
ethylacetate-13C	77	150.00	103.3	100.0	0.0	108.2	7.8	108.2	7.8	95.5	6.9
pyridine-d5	115	15000.00	253.0	100.1	1.5	287.2	61.7	287.6	62.0	88.0	19.0
Group Averages										91.3	12.1

Figure 27: Non-purgeable compound surrogates

Semi-Volatile Compound Surrogates

Method 8261 includes additional compounds that are not always considered “volatile”. These compounds are also analyzed by other means after a solvent extraction procedure. SMCReporter categorizes these compounds as “semi-volatile” compounds and uses a boiling point of 159 °C or greater as the indicator (Figure 28). This surrogate grouping also includes compounds that are quite water soluble (nitrobenzene-*d*$_5$, acetophenone-*d*$_8$) and so that a review of this data needs to recognize the disparity in chemical properties.



Semi-Volatile Compound Surrogates(boiling point>=159)

Compound	BP	RVW	Meas.	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
decafluorobiphenyl	206	3.03	110.5	100.8	0.4	103.4	0.8	104.3	0.9	106.0	0.9
nitrobenzene-d5	210	87.50	116.9	101.1	0.4	106.2	7.8	107.3	7.9	108.9	8.0
acetophenone-d5	202	161.00	141.2	100.6	0.4	108.4	7.8	109.1	7.8	129.4	9.3
naphthalene-d8	217	18.00	109.5	104.0	2.0	102.8	0.8	106.9	2.2	102.5	2.1
Group Averages										111.7	5.1

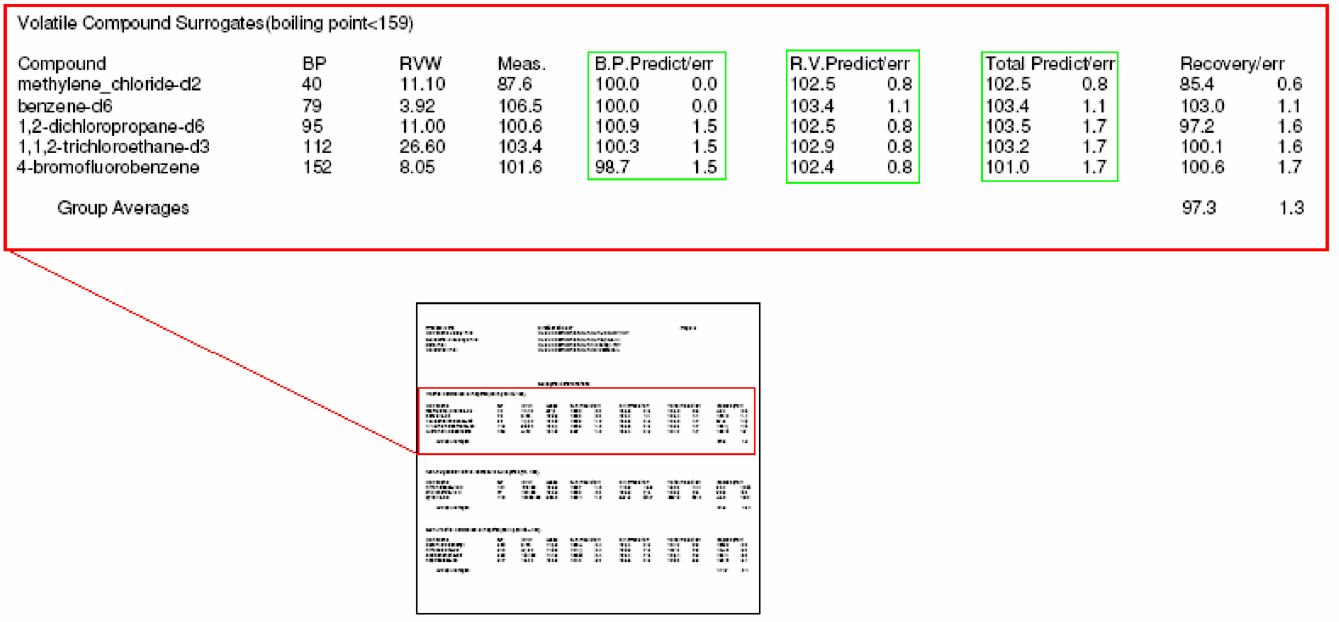
Figure 28: Semi-volatile compound surrogates

Review Surrogate Results

The data presented in the Surrogate report can be reproduced from the information in the internal standard report, the raw data file (to get a surrogate's experimental recovery) and the calibration curve (to get expected response of the surrogate). The three sections (volatile, non-purgeable, and semi-volatile) are determined in the same manor so we will discuss how the reproduce the volatile surrogate results. The volatile compound section of the surrogate report shown in Figure 29 shows the chemical properties of the surrogates as well as the experimentally measured recovery under the "Meas." column. The "Meas." column contains the experimental recovery data as discussed in the Internal Standard Report section.

Surrogate Predicted Recoveries

We can easily verify these calculations by looking at the surrogate's chemical properties and then interpolating from the expected recoveries from the internal standard solutions from the internal standard report.



Volatile Compound Surrogates(boiling point<159)

Compound	BP	RVW	Meas.	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
methylene_chloride-d2	40	11.10	87.6	100.0	0.0	102.5	0.8	102.5	0.8	85.4	0.6
benzene-d6	79	3.92	106.5	100.0	0.0	103.4	1.1	103.4	1.1	103.0	1.1
1,2-dichloropropane-d6	95	11.00	100.6	100.9	1.5	102.5	0.8	103.5	1.7	97.2	1.6
1,1,2-trichloroethane-d3	112	26.60	103.4	100.3	1.5	102.9	0.8	103.2	1.7	100.1	1.6
4-bromofluorobenzene	152	8.05	101.6	98.7	1.5	102.4	0.8	101.0	1.7	100.6	1.7
Group Averages										97.3	1.3

Figure 29: Internal standard derived recoveries

Example 7: We will verify the predicted results for benzene-d_6. Benzene-d6 has a boiling point of 79 °C which is below the lower limit of the boiling-point range (85 °C) and so 100% is the expected recovery relating to boiling point. Benzene-d_6 has a relative volatility of 3.92 which puts it in the range of the second relative volatility group (3.83 to 6.27). Solving the second group equation for the natural logarithm of 3.92 provides

$$\text{predicted recovery} = \ln(3.92) \times -.02265 + 1.0645 = 1.0336 = 103.36\ \%$$

Note: SMCReporter does not round numbers in calculations, only in displaying values. To always match exactly the SMCReporter value we need to use more significant numbers than shown in the internal standard report to get the same recovery.

Example 8: We will verify the predicted results for 4-bromofluorobenzene. First the predicted recovery based on its boiling point (152 °C) is determined using the first boiling point group equation (boiling points between 85 and 155 °C).

Boiling-point recovery = $152 \times -3.964 \times 10^{-4} + 1.0470 = 0.9867 = 98.7\%$

The relative volatility of 4-bromofluorobenzene is greater than the upper limit of the second group (6.27) and is less than the upper limit of the third group ($e^{\frac{1}{2}(\ln(26) + \ln(32.5)}$ = 28.93). Therefore the third relative volatility group is used for the calculation.

Relative-volatility recovery = $\ln(8.05) \times 0.004601 + 1.0144 = 1.024 = 102.4\%$

The total predicted recovery (boiling-point recovery × relative-volatility recovery) is

Total predicted recovery = $0.987 \times 1.024 = 1.0106 = 101.1\%$

Note: If you carried more significant numbers the total would be 1.0104 =101.0 as in Figure 29.

The error term for the total predicted recovery is calculated by propagating errors. The formula for this calculation is

Total error = total predicted recovery × ((boiling-point error ÷ boiling-point recovery) ^{2} + (relative-volatility error ÷ relative-volatility recovery) ^{2}) $^{0.5}$

Imputing the example values the equation becomes

Total error = $1.010 \times ((.015 \div 0.987)^2 + (.008 \div 1.024)^2)^{0.5} = .017 = 1.7\%$

Surrogate Recoveries

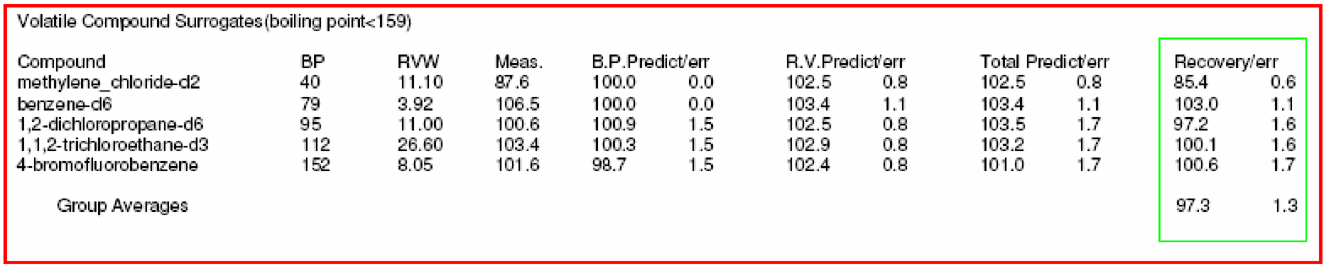
Surrogate data is reported to provide insight as to how the method including the internal standard data processing, have performed. In keeping with the RCRA format, surrogate data is interpreted as a “recovery” which is the experimentally measured amount divided by the amount expected to be seen. In method 8261, this assessment is performed as the comparison to the experimentally measured surrogate to its predicted recovery. The closer these values are to each other the more accurate the determination of the surrogate compound.

The surrogate recovery data are displayed by surrogate compound and average their class. The volatile compound classification (boiling point < 159 °C and relative volatility < 100) is seen in Figure 28. Each surrogate recovery is presented with its associated error term. The average of all of the surrogate recoveries is also presented with the average deviation.

Example 9: What is the surrogate recovery for 4-bromofluorobenzene? From the previous example we found the recovery predicted by the internal standards to be 101.0 ±1.7. The surrogate recovery is the experimentally measured recovery ÷ the internal standard predicted recovery. The surrogate recovery for 4-bromofluorobenzene is calculated as

$$\text{Surrogate recovery} = 1.016 \div 1.010 = 1.006 = 100.6\%$$

The associated error term is .017 ÷ 1.010 × 1.006 = .017 = 1.7% as shown in Figure 30.



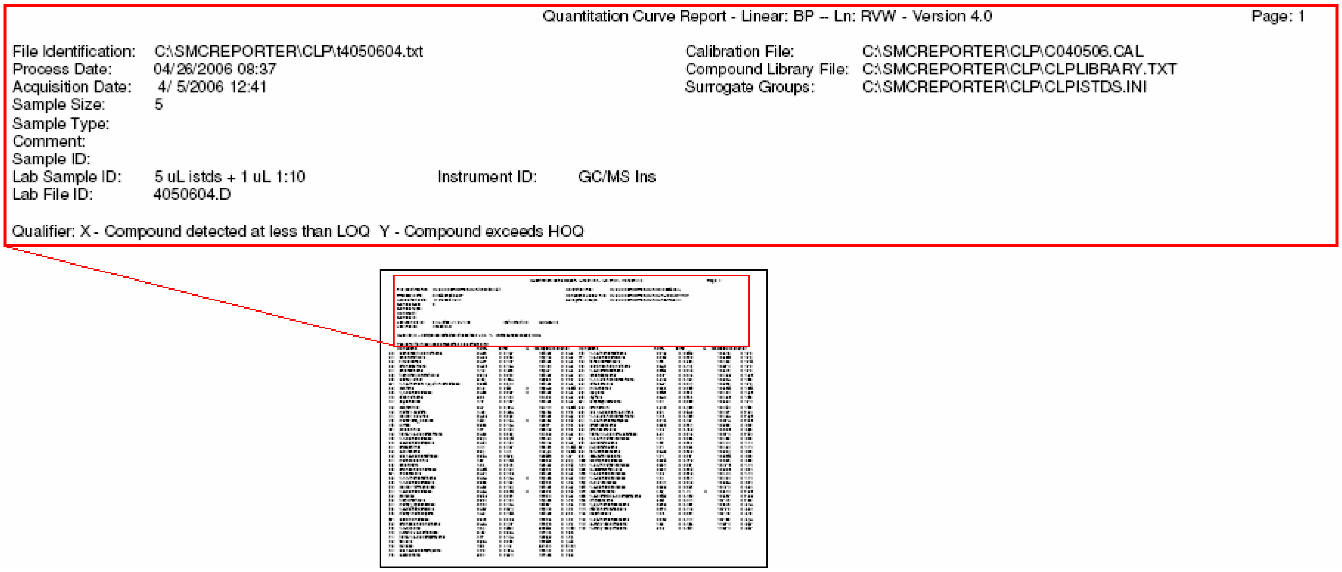
Volatile Compound Surrogates(boiling point<159)

Compound	BP	RVW	Meas.	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
methylene_chloride-d2	40	11.10	87.6	100.0	0.0	102.5	0.8	102.5	0.8	85.4	0.6
benzene-d6	79	3.92	106.5	100.0	0.0	103.4	1.1	103.4	1.1	103.0	1.1
1,2-dichloropropane-d6	95	11.00	100.6	100.9	1.5	102.5	0.8	103.5	1.7	97.2	1.6
1,1,2-trichloroethane-d3	112	26.60	103.4	100.3	1.5	102.9	0.8	103.2	1.7	100.1	1.6
4-bromofluorobenzene	152	8.05	101.6	98.7	1.5	102.4	0.8	101.0	1.7	100.6	1.7
Group Averages										97.3	1.3

Figure 30: Volatile surrogate recovery data

Quantitation Report

The quantitation report contains the analyte results processed by SMCReporter. The report has a header (Figure 31) that lists sources of data, selected options, and sample information. The analyte section lists results, confidence intervals, and the recovery predicted by the internal standards.

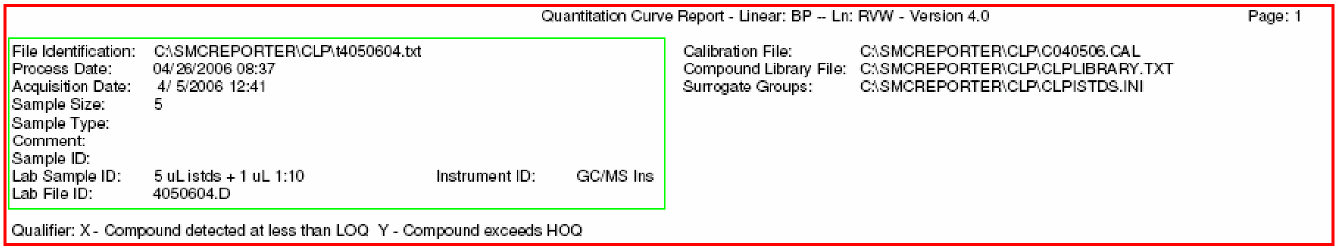


```
                                Quantitation Curve Report - Linear: BP -- Ln: RVW - Version 4.0                      Page: 1

File Identification:   C:\SMCREPORTER\CLP\t4050604.txt                       Calibration File:        C:\SMCREPORTER\CLP\C040506.CAL
Process Date:          04/26/2006 08:37                                      Compound Library File:   C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Acquisition Date:       4/ 5/2006 12:41                                      Surrogate Groups:        C:\SMCREPORTER\CLP\CLPISTDS.INI
Sample Size:           5
Sample Type:
Comment:
Sample ID:
Lab Sample ID:         5 uL istds + 1 uL 1:10        Instrument ID:     GC/MS Ins
Lab File ID:           4050604.D

Qualifier: X - Compound detected at less than LOQ  Y - Compound exceeds HOQ
```

Figure 31: Quantitation report header

Quantitation Report Header

The left side of the header posts the sample information (Figure 32). The top row identifies the pathway and SMCReporter format file containing raw data that was processed by SMCReporter. The Process Date on the next line identifies when the Quantitation Report was generated. The third line identifies the date the raw data file was created. The fourth line is for the sample size used and this amount was used to calculate concentrations. The next three lines are for user inputs. The Lab File ID is the raw data file that was used to generate the SMCReporter format file.



Quantitation Curve Report - Linear: BP -- Ln: RVW - Version 4.0 Page: 1

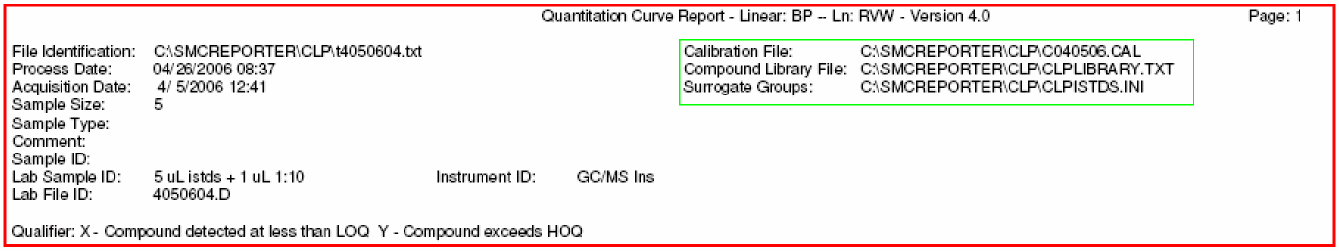
File Identification: C:\SMCREPORTER\CLP\t4050604.txt
Process Date: 04/26/2006 08:37
Acquisition Date: 4/ 5/2006 12:41
Sample Size: 5
Sample Type:
Comment:
Sample ID:
Lab Sample ID: 5 uL istds + 1 uL 1:10 Instrument ID: GC/MS Ins
Lab File ID: 4050604.D

Calibration File: C:\SMCREPORTER\CLP\C040506.CAL
Compound Library File: C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Surrogate Groups: C:\SMCREPORTER\CLP\CLPISTDS.INI

Qualifier: X - Compound detected at less than LOQ Y - Compound exceeds HOQ

Figure 32: Quantitation report sample information

The right-hand side of the header presents the calibration, library and internal standard files and their pathways (Figure 33). These files were used to process the report and these are also presented in the Internal Standard and Surrogate reports.



Quantitation Curve Report - Linear: BP -- Ln: RVW - Version 4.0 Page: 1

File Identification: C:\SMCREPORTER\CLP\t4050604.txt
Process Date: 04/26/2006 08:37
Acquisition Date: 4/ 5/2006 12:41
Sample Size: 5
Sample Type:
Comment:
Sample ID:
Lab Sample ID: 5 uL istds + 1 uL 1:10 Instrument ID: GC/MS Ins
Lab File ID: 4050604.D

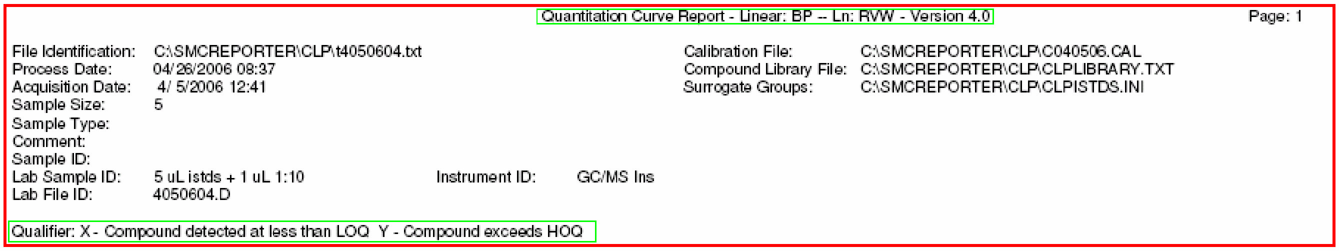
Calibration File: C:\SMCREPORTER\CLP\C040506.CAL
Compound Library File: C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Surrogate Groups: C:\SMCREPORTER\CLP\CLPISTDS.INI

Qualifier: X - Compound detected at less than LOQ Y - Compound exceeds HOQ

Figure 33: Files used in quantitation of sample file

The center of the top line identifies if chemical properties were treated as a value or the natural log of a value (Figure 34). These options exist in SMCReporter for unique applications. At the bottom left is a list of active qualifiers.

The ‘Y’ qualifier identifies when amount of an analyte detected by the GC/MS exceeded the upper limit of the calibration curve (Figure 34). This is a warning the value may not be reliable. The upper limit for an analyte is defined as its calibration curve average response factor times its highest mass standard in the curve. The ‘X’ qualifier is for the instance where the analyte was detected below the lower limit of the calibration curve. The lower limit for an analyte is defined as its calibration curve average response factor times its lowest standard mass in the curve.

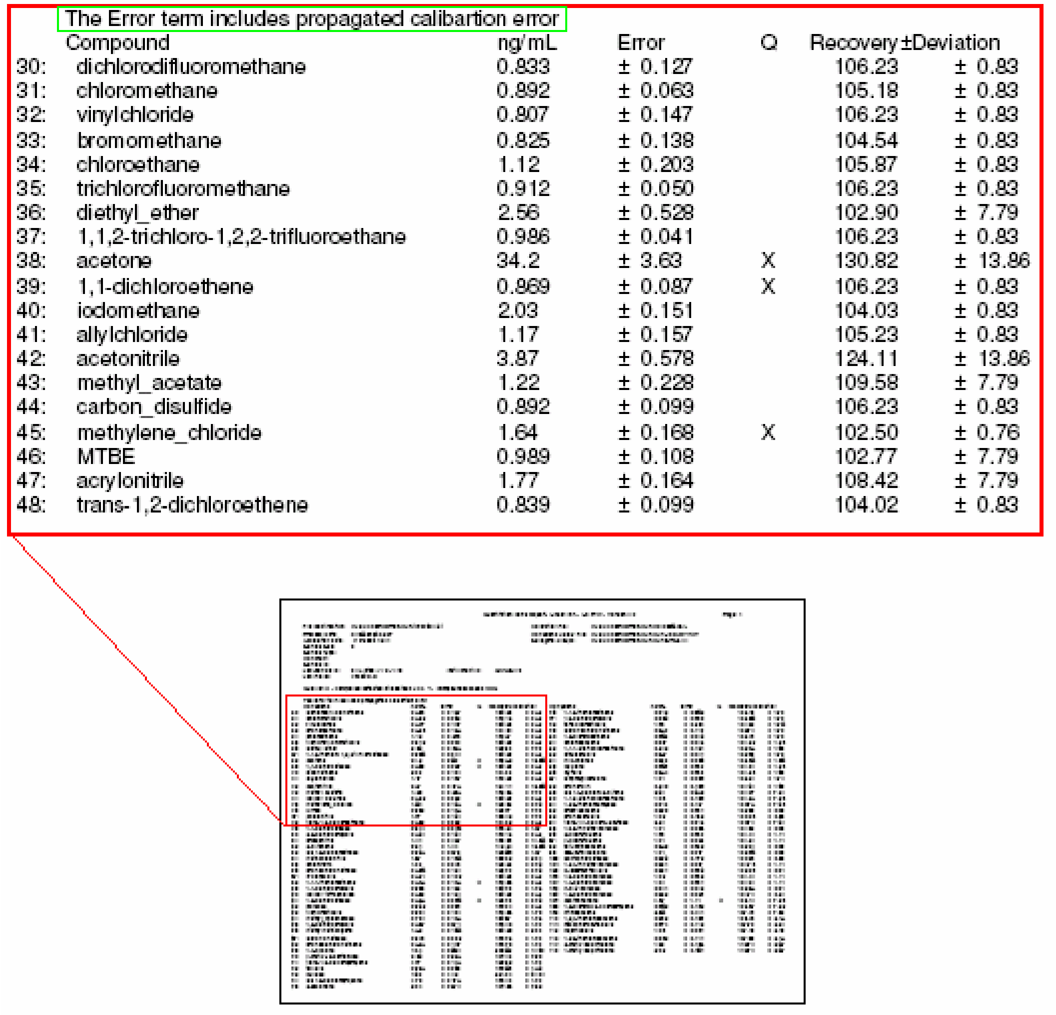


```
                                   Quantitation Curve Report - Linear: BP -- Ln: RVW - Version 4.0                    Page: 1

File Identification:  C:\SMCREPORTER\CLP\t4050604.txt                           Calibration File:         C:\SMCREPORTER\CLP\C040506.CAL
Process Date:         04/26/2006 08:37                                          Compound Library File:    C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Acquisition Date:      4/ 5/2006 12:41                                          Surrogate Groups:         C:\SMCREPORTER\CLP\CLPISTDS.INI
Sample Size:          5
Sample Type:
Comment:
Sample ID:
Lab Sample ID:        5 uL istds + 1 uL 1:10         Instrument ID:    GC/MS Ins
Lab File ID:          4050604.D

Qualifier: X - Compound detected at less than LOQ  Y - Compound exceeds HOQ
```

Figure 34: Result qualifiers

Compound Quantitation Results

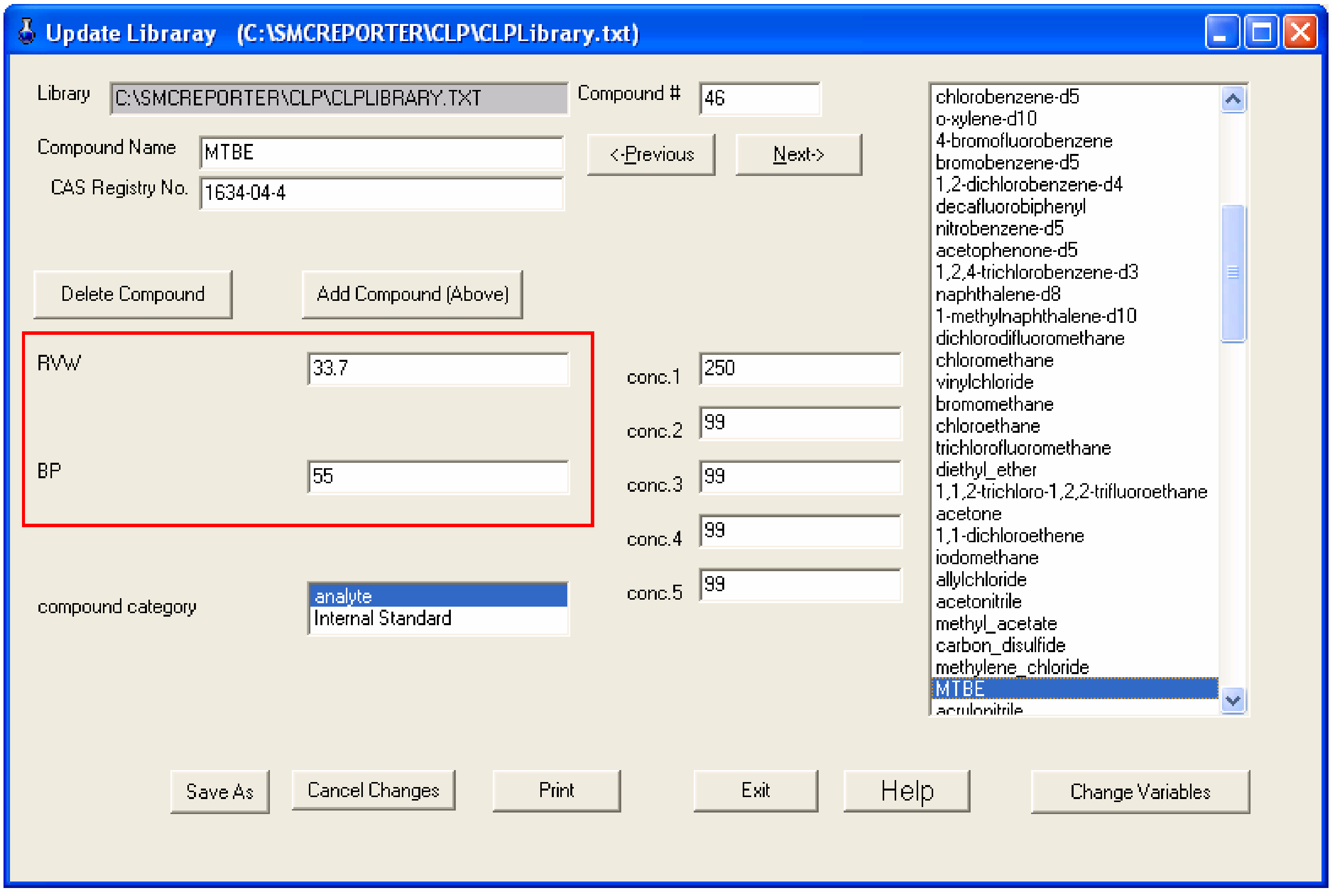
The analyte list and results are presented in the quantitation report (Figure 35). How this data is determined depends on how the report was defined during the data processing. This example includes propagation of calibration errors (highlighted in Figure 35). The quantitation report presents the analytes, their measured concentration (with error), and their recovery (with error) determined from the internal standards.



```
      The Error term includes propagated calibartion error
      Compound                                 ng/mL     Error        Q    Recovery ±Deviation
30:   dichlorodifluoromethane                  0.833     ± 0.127             106.23    ± 0.83
31:   chloromethane                            0.892     ± 0.063             105.18    ± 0.83
32:   vinylchloride                            0.807     ± 0.147             106.23    ± 0.83
33:   bromomethane                             0.825     ± 0.138             104.54    ± 0.83
34:   chloroethane                             1.12      ± 0.203             105.87    ± 0.83
35:   trichlorofluoromethane                   0.912     ± 0.050             106.23    ± 0.83
36:   diethyl_ether                            2.56      ± 0.528             102.90    ± 7.79
37:   1,1,2-trichloro-1,2,2-trifluoroethane    0.986     ± 0.041             106.23    ± 0.83
38:   acetone                                  34.2      ± 3.63       X      130.82    ± 13.86
39:   1,1-dichloroethene                       0.869     ± 0.087      X      106.23    ± 0.83
40:   iodomethane                              2.03      ± 0.151             104.03    ± 0.83
41:   allylchloride                            1.17      ± 0.157             105.23    ± 0.83
42:   acetonitrile                             3.87      ± 0.578             124.11    ± 13.86
43:   methyl_acetate                           1.22      ± 0.228             109.58    ± 7.79
44:   carbon_disulfide                         0.892     ± 0.099             106.23    ± 0.83
45:   methylene_chloride                       1.64      ± 0.168      X      102.50    ± 0.76
46:   MTBE                                     0.989     ± 0.108             102.77    ± 7.79
47:   acrylonitrile                            1.77      ± 0.164             108.42    ± 7.79
48:   trans-1,2-dichloroethene                 0.839     ± 0.099             104.02    ± 0.83
```

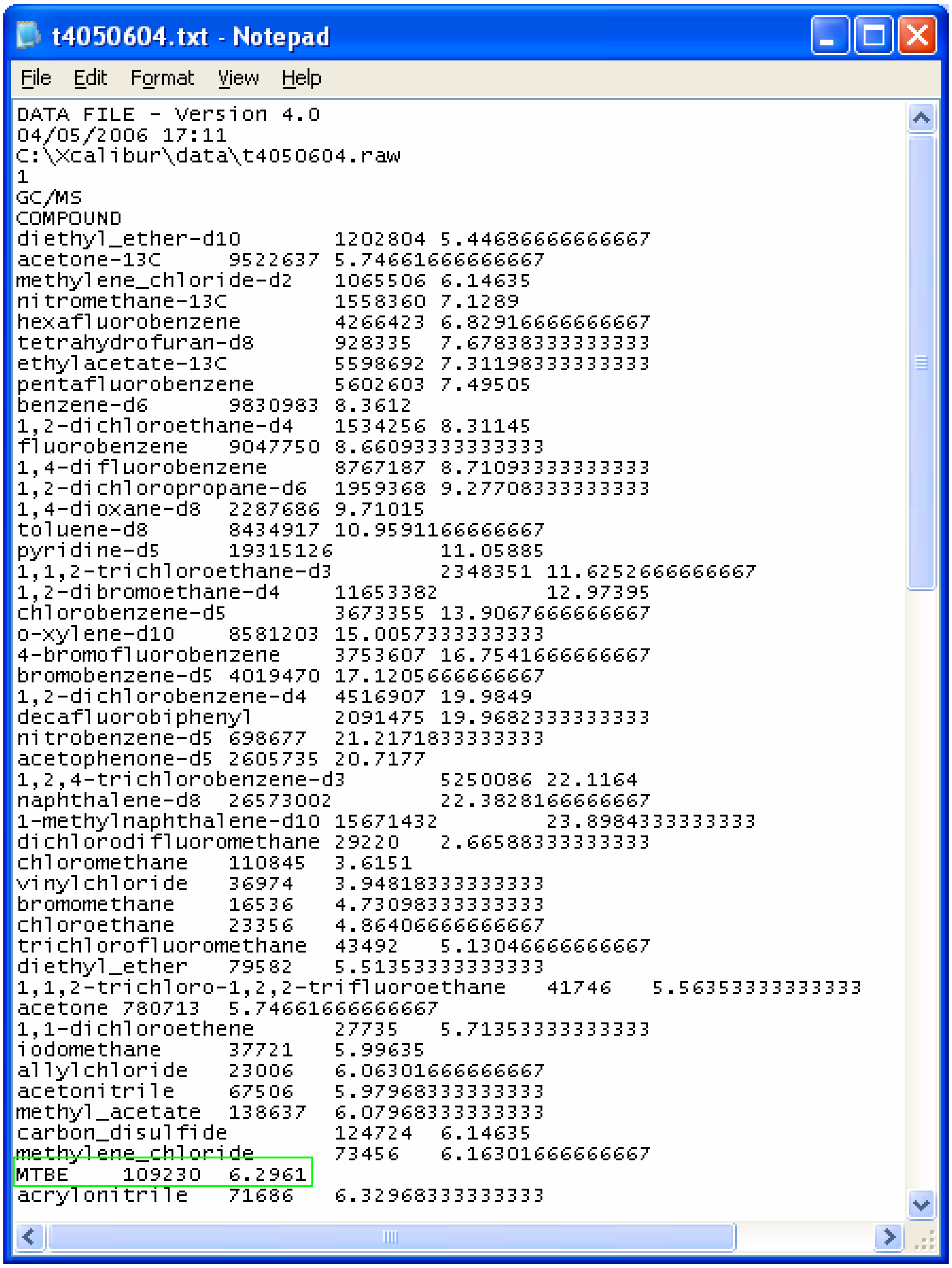
Figure 35: Analyte results

Running SMCReporter V4.0 and the presentation, “Creating the Calibration Curve and Generating Method 8261 Quantitation Reports through SMCReporter V4.0” provides the information necessary to reproduce the quantitation results for each analyte (available at http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm#calibration).We can reproduce all of the data shown in the quantitation report by looking at the library for each analyte’s relative volatility and boiling point (Figure 36), the internal standard report for determining recovery of each analyte (Figure 3), looking at the calibration curve for response factor and calibration error (Figure 38), and looking at the raw data for each compound’s response (Figure 37).



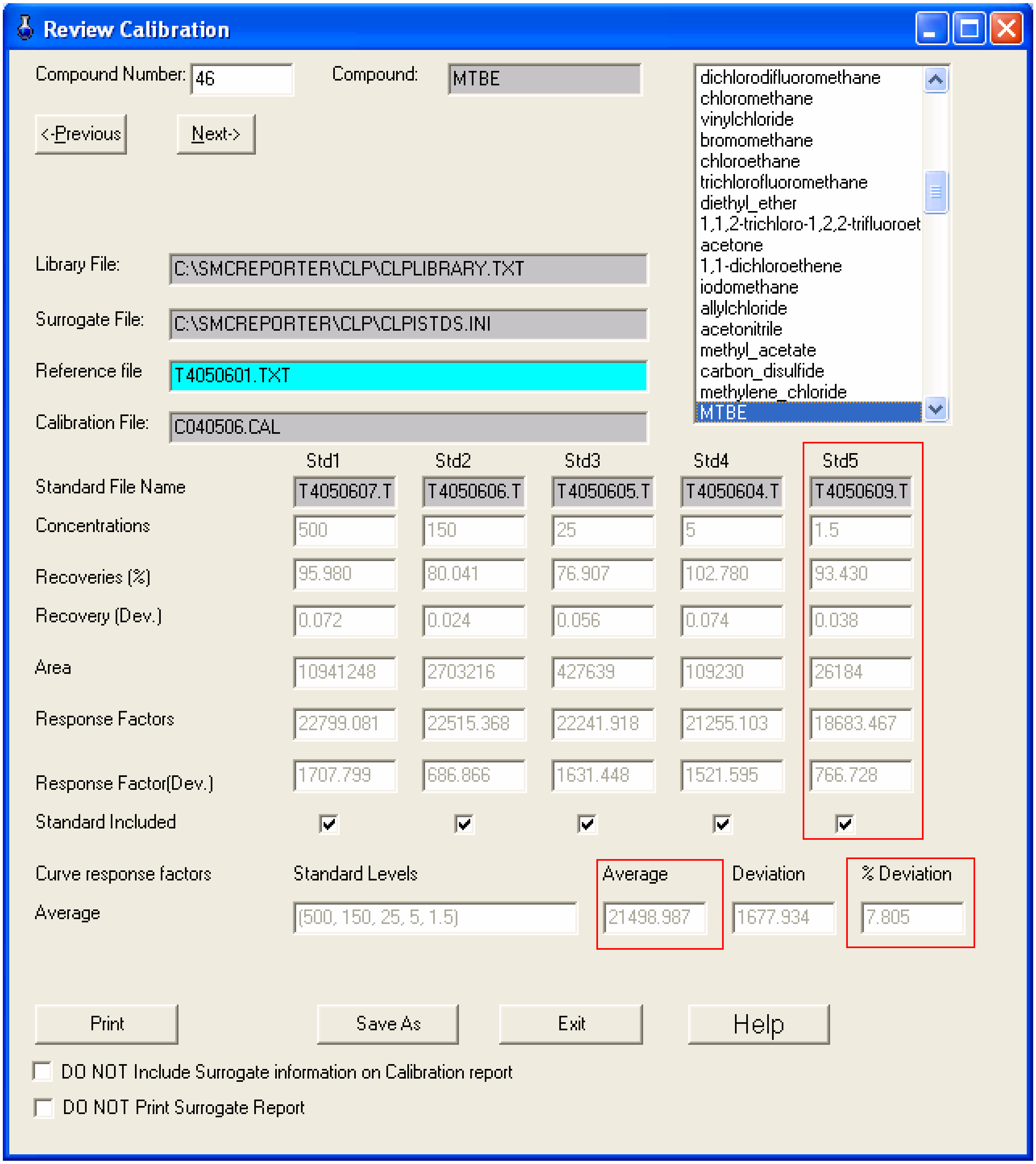
Library C:\SMCREPORTER\CLP\CLPLIBRARY.TXT
Compound # 46
Compound Name MTBE
CAS Registry No. 1634-04-4
RVW 33.7
BP 55
conc.1 250
conc.2 99
conc.3 99
conc.4 99
conc.5 99
compound category analyte

Figure 36: Relative-volatility and boiling-point values for MTBE



```
DATA FILE - Version 4.0
04/05/2006 17:11
C:\Xcalibur\data\t4050604.raw
1
GC/MS
COMPOUND
diethyl_ether-d10       1202804 5.44686666666667
acetone-13C     9522637 5.74661666666667
methylene_chloride-d2   1065506 6.14635
nitromethane-13C        1558360 7.1289
hexafluorobenzene       4266423 6.82916666666667
tetrahydrofuran-d8      928335  7.67838333333333
ethylacetate-13C        5598692 7.31198333333333
pentafluorobenzene      5602603 7.49505
benzene-d6      9830983 8.3612
1,2-dichloroethane-d4   1534256 8.31145
fluorobenzene   9047750 8.66093333333333
1,4-difluorobenzene     8767187 8.71093333333333
1,2-dichloropropane-d6  1959368 9.27708333333333
1,4-dioxane-d8  2287686 9.71015
toluene-d8      8434917 10.9591166666667
pyridine-d5     19315126        11.05885
1,1,2-trichloroethane-d3        2348351 11.6252666666667
1,2-dibromoethane-d4    11653382        12.97395
chlorobenzene-d5        3673355 13.9067666666667
o-xylene-d10    8581203 15.0057333333333
4-bromofluorobenzene    3753607 16.7541666666667
bromobenzene-d5 4019470 17.1205666666667
1,2-dichlorobenzene-d4  4516907 19.9849
decafluorobiphenyl      2091475 19.9682333333333
nitrobenzene-d5 698677  21.2171833333333
acetophenone-d5 2605735 20.7177
1,2,4-trichlorobenzene-d3       5250086 22.1164
naphthalene-d8  26573002        22.3828166666667
1-methylnaphthalene-d10 15671432        23.8984333333333
dichlorodifluoromethane 29220   2.66588333333333
chloromethane   110845  3.6151
vinylchloride   36974   3.94818333333333
bromomethane    16536   4.73098333333333
chloroethane    23356   4.86406666666667
trichlorofluoromethane  43492   5.13046666666667
diethyl_ether   79582   5.51353333333333
1,1,2-trichloro-1,2,2-trifluoroethane   41746   5.56353333333333
acetone 780713  5.74661666666667
1,1-dichloroethene      27735   5.71353333333333
iodomethane     37721   5.99635
allylchloride   23006   6.06301666666667
acetonitrile    67506   5.97968333333333
methyl_acetate  138637  6.07968333333333
carbon_disulfide        124724  6.14635
methylene_chloride      73456   6.16301666666667
MTBE    109230  6.2961
acrylonitrile   71686   6.32968333333333
```

Figure 37: Integrated area for each compound from GC/MSD



Compound Number: 46

Compound: MTBE

dichlorodifluoromethane
chloromethane
vinylchloride
bromomethane
chloroethane
trichlorofluoromethane
diethyl_ether
1,1,2-trichloro-1,2,2-trifluoroet
acetone
1,1-dichloroethene
iodomethane
allylchloride
acetonitrile
methyl_acetate
carbon_disulfide
methylene_chloride
MTBE

Library File: C:\SMCREPORTER\CLP\CLPLIBRARY.TXT

Surrogate File: C:\SMCREPORTER\CLP\CLPISTDS.INI

Reference file: T4050601.TXT

Calibration File: C040506.CAL

	Std1	Std2	Std3	Std4	Std5
Standard File Name	T4050607.T	T4050606.T	T4050605.T	T4050604.T	T4050609.T
Concentrations	500	150	25	5	1.5
Recoveries (%)	95.980	80.041	76.907	102.780	93.430
Recovery (Dev.)	0.072	0.024	0.056	0.074	0.038
Area	10941248	2703216	427639	109230	26184
Response Factors	22799.081	22515.368	22241.918	21255.103	18683.467
Response Factor(Dev.)	1707.799	686.866	1631.448	1521.595	766.728
Standard Included	☑	☑	☑	☑	☑

Curve response factors	Standard Levels	Average	Deviation	% Deviation
Average	(500, 150, 25, 5, 1.5)	21498.987	1677.934	7.805

☐ DO NOT Include Surrogate information on Calibration report

☐ DO NOT Print Surrogate Report

Figure 38: Calibration data for MTBE

The information presented in Figures 36-38 and the Internal Standard Report (Figure 3) accompanying in quantitation report (Figure 2) provides the information necessary to reproduce the analytical results.

Example 10: To reproduce the MTBE results the first step is to calculate the recovery of MTBE using the Internal Standard Report. From Figure 37 we find the boiling point of MTBE is 55 °C which is below the boiling point threshold (85 °C) for calculating boiling point recoveries with internal standards and so the boiling point recovery for MTBE is determined to be 100%. The relative volatility of MTBE is 33.7, which falls in the fourth relative volatility group (see Figure 24). Using the line described for group 4 the recovery relating to the relative volatility of MTBE is

$$\text{relative-volatility recovery} = \ln(33.7) \times .03613 + 0.9007 = 1.0277 = 102.77$$

The relative volatility error is .0779
And the error term is

$$\text{total recovery error} = 1.0277 \times ((0 \div 1)^2 + (.0779 \div 1.0277)^2)^{0.5} = .0779 = 7.79\%$$

The raw data response for MTBE is 109230 (area) and the response factor for MTBE in the calibration curve is 21498.987 area/ng. Therefore amount of MTBE in ngs detected by the GC/MS is

$$109230 \text{ area} \div 21498.987 \text{ area/ng} = 5.081\text{ng}$$

The response factor err is 7.805% and so the error associated with determining the amount of MTBE seen by the GC/MS is

$$5.081 \text{ ng} \times 0.07805 = 0.397 \text{ ng}$$

Note: The limit of quantitation is lowest mass in the calibration curve is the limit of quantitation (LOQ) and equal 1.5 ng (the lowest standard amount for MTBE in Figure 39). Had the mass detected by the GC/MS not been 5.081 and had been less than 1.5 ng, an ‘X’ would have been placed in the qualifier column (Q) for MTBE.

The final concentration of MTBE in the water takes into account the internal standard determined recovery of MTBE and is

$$\text{concentration} = 5.081 \text{ ng} \div 5 \text{ mL} \div 1.0277 = 0.989 \text{ ng/mL}$$

The error term is

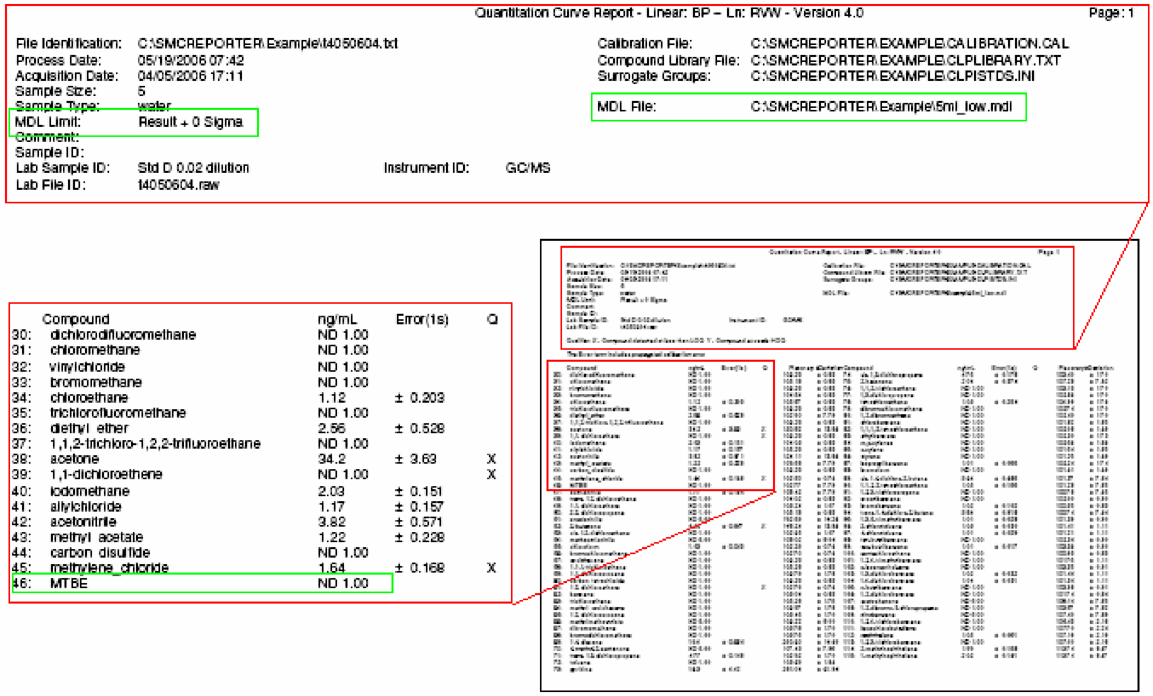
$$\text{Concentration error} = 0.989 \times ((0.397 \div 5.081)^2 + (.0779 \div 1.0277)^2)^{0.5} = .1076 = 0.108\text{ng/mL}$$

Reporting Limits

There is the option within the SMCReporter program to put reporting limits (as concentration) on the results by compound. This is a convenient tool to prevent reporting values that are of no interest to the data user. The reporting limits are saved as a file and referenced in each quantitation report for documentation. The reporting limit files have an extension ‘.MDL’ to identify their purpose. A reporting limit file can be used in two ways, the MDL option and the CRQL option.

Reporting Limits-MDL Option

The ‘MDL’ reporting limit is one option that SMCReporter can use for reporting limits. There are two types, the first is the ‘MDL’ option that uses the value in a *.mdl file as the lowest value reported. Any concentration below that value (including zero) will be replaced by the reporting limit with a qualifier. See Figure 39.



Quantitation Curve Report - Linear: BP – Ln: RVW - Version 4.0 Page: 1

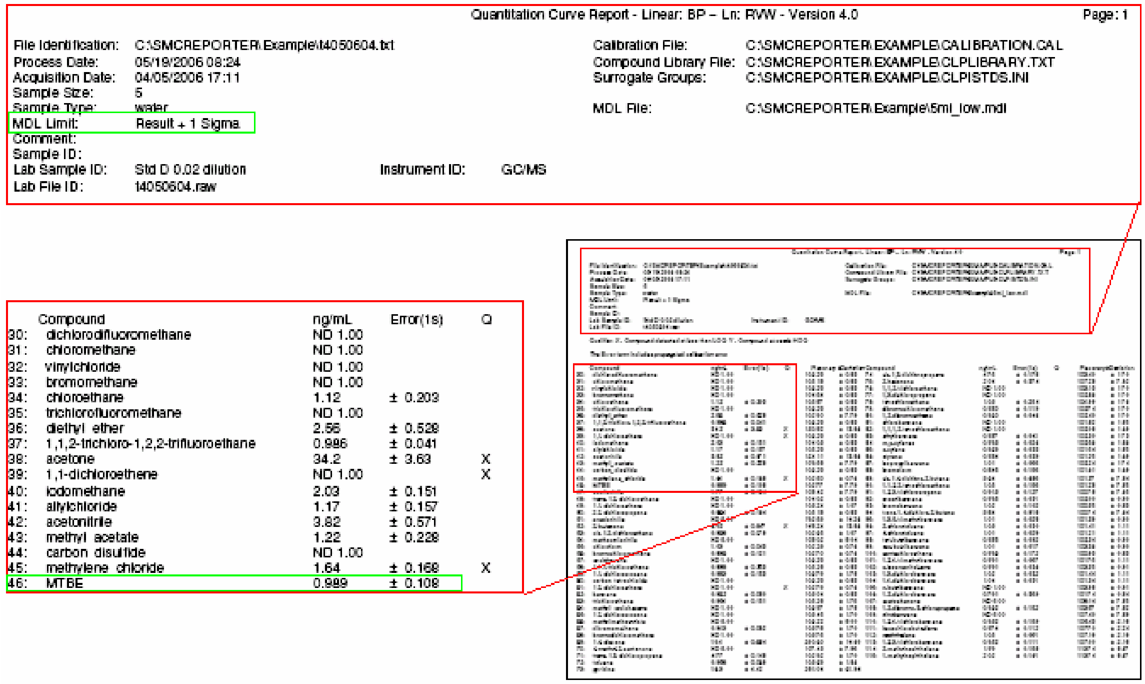
File Identification: C:\SMCREPORTER\Example\t4050604.txt
Process Date: 05/19/2006 07:42
Acquisition Date: 04/05/2006 17:11
Sample Size: 5
Sample Type: water
MDL Limit: Result + 0 Sigma
Comment:
Sample ID:
Lab Sample ID: Std D 0.02 dilution
Instrument ID: GC/MS
Lab File ID: t4050604.raw

Calibration File: C:\SMCREPORTER\EXAMPLE\CALIBRATION.CAL
Compound Library File: C:\SMCREPORTER\EXAMPLE\CLPLIBRARY.TXT
Surrogate Groups: C:\SMCREPORTER\EXAMPLE\CLPISTDS.INI
MDL File: C:\SMCREPORTER\Example\5ml_low.mdl

	Compound	ng/mL	Error(1s)	Q
30:	dichlorodifluoromethane	ND 1.00		
31:	chloromethane	ND 1.00		
32:	vinylchloride	ND 1.00		
33:	bromomethane	ND 1.00		
34:	chloroethane	1.12	± 0.203	
35:	trichlorofluoromethane	ND 1.00		
36:	diethyl ether	2.56	± 0.528	
37:	1,1,2-trichloro-1,2,2-trifluoroethane	ND 1.00		
38:	acetone	34.2	± 3.63	X
39:	1,1-dichloroethene	ND 1.00		X
40:	iodomethane	2.03	± 0.151	
41:	allylchloride	1.17	± 0.157	
42:	acetonitrile	3.82	± 0.571	
43:	methyl acetate	1.22	± 0.228	
44:	carbon disulfide	ND 1.00		
45:	methylene_chloride	1.64	± 0.168	X
46:	MTBE	ND 1.00		

Figure 39: Reporting limits using MDL reporting option

Note that the selection of a reporting limit is identified in the sample header (Figure 39 top). The file used to determine the limits by compound is also listed on the right side of the header. The result for MTBE now differs from the report where no report limits were used (Figure 35) as the reporting limit (1 ng/mL) is greater than the determined concentration (0.989 ± 0.108). There is a reporting option with the MDL-file limit in that an additional confidence that a value is below a reporting limit can be added. With this option the result plus error value can be combined to test if the result should be reported.



```
                                    Quantitation Curve Report - Linear: BP – Ln: RVW - Version 4.0                    Page: 1

File Identification:  C:\SMCREPORTER\Example\t4050604.txt                  Calibration File:        C:\SMCREPORTER\EXAMPLE\CALIBRATION.CAL
Process Date:         05/19/2006 08:24                                     Compound Library File:   C:\SMCREPORTER\EXAMPLE\CLPLIBRARY.TXT
Acquisition Date:     04/05/2006 17:11                                     Surrogate Groups:        C:\SMCREPORTER\EXAMPLE\CLPISTDS.INI
Sample Size:          5
Sample Type:          water                                                MDL File:                C:\SMCREPORTER\Example\5ml_low.mdl
MDL Limit:            Result + 1 Sigma
Comment:
Sample ID:
Lab Sample ID:        Std D 0.02 dilution          Instrument ID:    GC/MS
Lab File ID:          t4050604.raw
```

```
    Compound                                   ng/mL      Error(1s)    Q
30:  dichlorodifluoromethane                   ND 1.00
31:  chloromethane                             ND 1.00
32:  vinylchloride                             ND 1.00
33:  bromomethane                              ND 1.00
34:  chloroethane                              1.12       ± 0.203
35:  trichlorofluoromethane                    ND 1.00
36:  diethyl  ether                            2.56       ± 0.529
37:  1,1,2-trichloro-1,2,2-trifluoroethane     0.986      ± 0.041
38:  acetone                                   34.2       ± 3.63       X
39:  1,1-dichloroethene                        ND 1.00                 X
40:  iodomethane                               2.03       ± 0.151
41:  allylchloride                             1.17       ± 0.157
42:  acetonitrile                              3.82       ± 0.571
43:  methyl  acetate                           1.22       ± 0.228
44:  carbon  disulfide                         ND 1.00
45:  methylene  chloride                       1.64       ± 0.169      X
46:  MTBE                                      0.989      ± 0.108
```

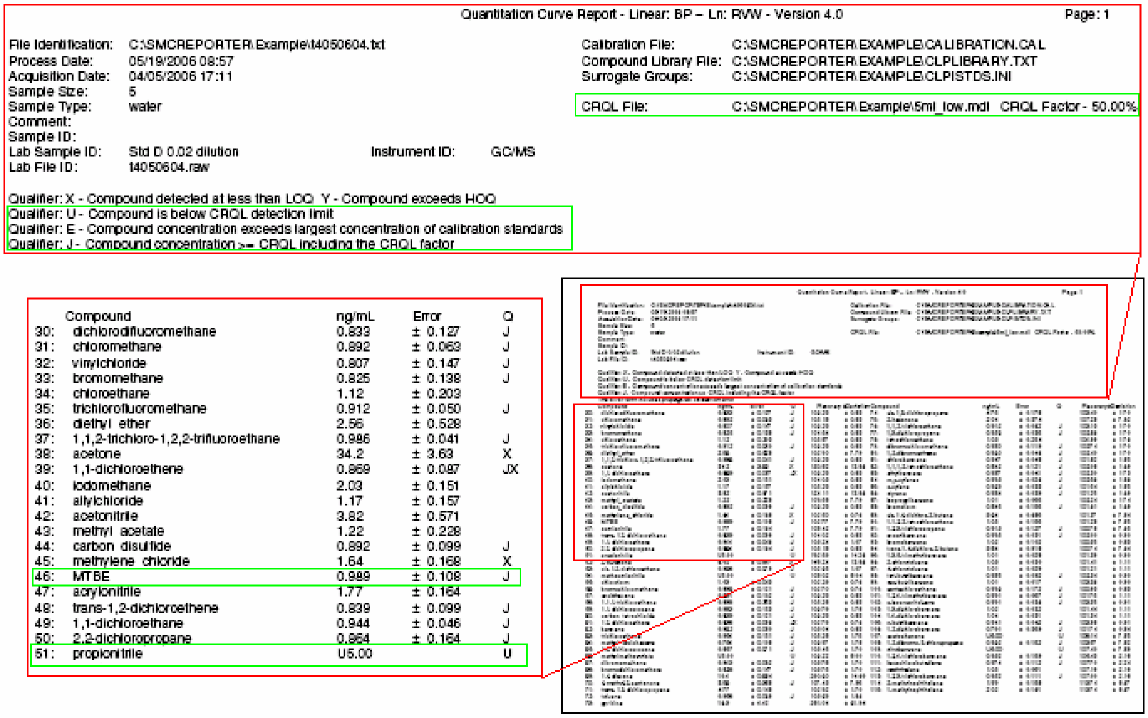
Figure 40: Reporting limits using MDL reporting option with one sigma confidence

Figure 40 demonstrates the quantitation report when one sigma confidence is used to determine reporting limits. Note the one sigma option is identified in the header (left side). The reported value for MTBE is no longer the 'ND 1.00' as seen in Figure 40 but is now 0.989 ± 0.108 as the concentration plus error value exceed the MDL value of 1.

Reporting Limits-CRQL Option

The second kind of reporting limit supports Superfund's Contract Laboratory Program (CLP). With this style of reporting limits the reports are consistent with the CLP reporting requirements. When this kind of reporting is used it is noted in the quantitation header (right hand side Figure 42). Also the use of different qualifiers is identified in the lower left-hand side of the header. With this style of reporting a 'U' replaces the 'not detected' (ND) and is entered in the qualifier column.

There is an option with SMCReporter to report concentrations lower than the normal CRQL limit. This option is for all compounds to be reported as a percentage of the CRQL limit percentage is identified in the header (middle of right side). Anytime an analyte is detected between the normal CRQL and the 'optional' lower limit, a 'J' qualifier signifies the occurrence. For instance the MTBE concentration in the example is below the CRQL of 1.0, but it is reported as 0.9890 ± 0.108 with a 'J' qualifier (Figure 41).



Quantitation Curve Report - Linear: BP – Ln: RVW - Version 4.0 Page: 1

File Identification: C:\SMCREPORTER\Example\t4050604.txt
Process Date: 05/19/2006 08:57
Acquisition Date: 04/05/2006 17:11
Sample Size: 5
Sample Type: water
Comment:
Sample ID:
Lab Sample ID: Std D 0.02 dilution Instrument ID: GC/MS
Lab File ID: t4050604.raw

Calibration File: C:\SMCREPORTER\EXAMPLE\CALIBRATION.CAL
Compound Library File: C:\SMCREPORTER\EXAMPLE\CLPLIBRARY.TXT
Surrogate Groups: C:\SMCREPORTER\EXAMPLE\CLPISTDS.INI

CRQL File: C:\SMCREPORTER\Example\5ml_low.mdl CRQL Factor - 50.00%

Qualifier: X - Compound detected at less than LOQ Y - Compound exceeds HOQ
Qualifier: U - Compound is below CRQL detection limit
Qualifier: E - Compound concentration exceeds largest concentration of calibration standards
Qualifier: J - Compound concentration >= CRQL including the CRQL factor

	Compound	ng/mL	Error	Q
30:	dichlorodifluoromethane	0.833	± 0.127	J
31:	chloromethane	0.892	± 0.063	J
32:	vinylchloride	0.807	± 0.147	J
33:	bromomethane	0.825	± 0.138	J
34:	chloroethane	1.12	± 0.203	
35:	trichlorofluoromethane	0.912	± 0.050	J
36:	diethyl ether	2.56	± 0.528	
37:	1,1,2-trichloro-1,2,2-trifluoroethane	0.986	± 0.041	J
38:	acetone	34.2	± 3.63	X
39:	1,1-dichloroethene	0.869	± 0.097	JX
40:	iodomethane	2.03	± 0.151	
41:	allylchloride	1.17	± 0.157	
42:	acetonitrile	3.82	± 0.571	
43:	methyl acetate	1.22	± 0.228	
44:	carbon disulfide	0.892	± 0.099	J
45:	methylene chloride	1.64	± 0.168	X
46:	MTBE	0.989	± 0.108	J
47:	acrylonitrile	1.77	± 0.164	
48:	trans-1,2-dichloroethene	0.839	± 0.099	J
49:	1,1-dichloroethane	0.944	± 0.046	J
50:	2,2-dichloropropane	0.864	± 0.164	J
51:	propionitrile	U5.00		U

Figure 41: Reporting limits using CRQL reporting option with 50% threshold

Summary

The analytical reports generated by SMCReporter incorporate internal standard determined recoveries that reflect analyte boiling point and relative volatilities. All of the data used to generate the report is identified or there is a link to where the data would be found (such as calibration curve data). Options that an analyst can use will be identified in the report when selected and can be verified by tracking the data process.

References

[1]Hiatt, M.H., “Vacuum Distillation Coupled with Gas Chromatography/Mass Spectrometry for the Analysis of Environmental Samples”, Analytical Chemistry, Vol. *67*, No. 22, p. 4044-4052, 1995

[2]Hiatt, M.H., Farr, C.M, “Volatile Organic Compound Determinations Using Surrogate-Based Correction for Method and Matrix Effects”, Analytical Chemistry, Vol. 67, No. 2, p. 426-433, January 15, 1995