USER'S GUIDE FOR

SURROGATE MATRIX NORMALIZATION

ADD-ON FOR AGILENT CHEMSTATION

(SMCREPORTER)

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SECTION 1
INTRODUCTION

1.1 System Purpose

Smcreporter is an add-on program adapted to Agilent ChemStation (ChemStation) software for gas chromatograph/mass spectrometer (GC/MS) applications. It is intended to simplify and standardize EPA method 8261 surrogate matrix normalization for volatile organic compounds in a variety of environmental matrices (a description of method 8261 is available at http://www.epa.gov/sw-846/pdfs/8261.pdf). The program allows all method 8261 functions to be accessed from the Agilent ChemStation Enhanced Data Analysis menu.

1.2 Document Organization

This User's Guide is intended to enable users to access functions of the Smcreporter application. Use of the application to perform Method 8261 normalization will be described in detail. Technically knowledgeable users will still access all other ChemStation functions as usual.

Section 2 – System Overview – describes technical details of Smcreporter. This section includes system requirements and a discussion of essential concepts for use of the application.

Section 3 – System Operation – provides a description of the software user interface as currently implemented and a step-through list for performing Method 8261 normalization in the ChemStation Enhanced Data Analysis screen.

1.3 User Profile

Users of this system are expected to be experienced technical personnel, familiar with GC/MS, microcomputers and Windows operating systems. They should be familiar with method 8261 procedures and concepts.

1.4 Conventions

To help the user to easily interpret information in this manual, certain conventions will be used:

- When indicating information to be entered from the keyboard, text will be shown in `COURIER` font. Specific keys will be identified by label, enclosed in angle brackets. For

example, `Type this.<Enter>` means to type in the phrase: Type this. Then press the Enter key.

- Nested menu selections will be separated by a vertical bar (|). File | Exit means to select the 'File' menu option in the top-level menu, then select 'Exit' from the next menu.
- The standard DOS directory and file conventions will be used.

SECTION 2
SYSTEM OVERVIEW

2.1 System Requirements

Smcreporter was written and tested using ChemStation product number G1701BA version B.00.00 and G1701CA version C.00.00. It has been demonstrated to work for stand-alone data analysis on PCs using Windows 98 and Windows NT version 4 operating systems. It is designed to work only under the Enhanced Data Analysis mode of Agilent ChemStation.

Systems used to run Smcreporter along with ChemStation must meet the following minimum requirements:

- Windows NT 4.0 operating system
- Pentium 166 MHz
- Super VGA display (800 x 600 resolution)
- 1.2 GB hard disk,
- CD-ROM drive
- 48 MB RAM for a 2D single instrument configuration, plus 8 MB RAM for every additional instrument configured

2.2 Essential Concepts

The purpose of Smcreporter is to simplify the application of Method 8261 surrogate matrix normalization computations to ChemStation data. Method 8261 provides a basis to determine the concentration of volatile organic compounds (VOCs) in various matrices. The method is described in an on-line EPA document – Volatile Organic Compounds by Vacuum Distillation in Combination With Gas Chromatography/Mass Spectrometry (VD/GC/MS), available at http://www.epa.gov/epaoswer/hazwaste/test/ txup4b.htm. The experimental basis of the method is explained in previous publications.[1,2] The method will be broadly discussed and terminology

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[1] Hiatt, M.H; Farr C.M. Volatile Organic Compound Determinations Using Surrogate-Based Correction for Method and Matrix Effects, Analytical Chemistry, 1995, 67, 426-433.

[2] Hiatt, M.H. Vacuum Distillation Coupled with Gas Chromatography/Mass Spectrometry for the Analysis of Environmental Samples, Analytical Chemistry, 1995,

introduced in section 2.3.1.

2.2.1 Basis and Terminology

Method 8261 employs an instrument calibration using spiked samples of VOCs to calculate analyte recoveries from vacuum distillation and cryogenic trapping. VOCs used in spiked samples are referred to as surrogates. By introducing known amounts of surrogates into field samples, the sample analyte recoveries can be calculated based on the measured recovery of the surrogates.

The physical properties of interest for recovery of VOCs by vacuum distillation and cryogenic trapping are relative volatility[1] and boiling point. In keeping with other publications, the following terms will be used:

- Relative volatility describes the potential of a compound to be extracted from a matrix.
- Relative volatility surrogates (-surrogates) are compounds used to assess relative volatility effects on analyte recoveries.
- Boiling point describes the potential of a compound to condense.
- Boiling point surrogates (-surrogates) are compounds used to assess condensation effects on analyte recoveries.

2.2.1.1 The 8261 Library

For each ChemStation quantitation library (ChemStation 'Method'), Smcreporter maintains a library (8261 library) of compounds and parameters necessary for Method 8261 calculations. The ChemStation quantitation library and 8261 library contain the same set of compounds and must remain synchronized. The 8261 library is updated each time the quantitation library is edited (see section 3.1.2.2). The 8261 library contains the following for each compound (information not currently used is shown as 'not required'):

- Compound name
- Relative volatility with respect to water
- Boiling Point
- Relative volatility with respect to octanol (not required)
- Whether the compound is a surrogate or an analyte
- Octanol-water partition coefficient (not required)

67, 4044-4052.

- Concentration (ng) of the compound in spiked calibration samples (1-5 sample concentrations).

In Smcreporter, these values are entered and maintained in the 8261 library using the Edit 8261 Library dialog box (Figure 6).

The 8261 library is maintained in a file called lib8261.ini, located in a subdirectory – 8261dir – under the ChemStation method directory. See Appendix 4 for a discussion of .ini files and their use in this application.

2.2.1.2 Surrogates

Surrogate compounds are selected to cover the range of relative volatilities and boiling points for analytes being measured. There are four classes of surrogate compounds:

- First pass surrogates attempt to estimate the effects of relative volatility on compound recoveries, as independently of boiling point effects as possible. First pass surrogates should have low boiling points (< 100°C) to minimize any boiling point effects.
- Boiling point surrogates reflect the effect of boiling point on compound recovery.
- Relative volatility surrogates estimate the effect of relative volatility on compound recovery.
- Check surrogates are used as quality assurance checks on the Method 8261 calculations.

First pass, boiling point, and relative volatility surrogates are grouped in smaller ranges to more accurately depict the expected recovery of compounds. Linear regressions are used to characterize recoveries for each surrogate grouping.

Surrogate groups are maintained using the Surrogate Data dialog box (section 3.1.2.7). In the Surrogate Data dialog box, all compounds selected as surrogates in the 8261 library are listed.

Smcreporter requires that there be at least three first pass surrogates. Select first pass surrogates by indicating 'Yes' in the 'First Pass?' list box. First pass surrogates are first ordered by increasing relative volatility, then automatically assigned to groups of two. Table 1 shows example first pass surrogates and groupings.

Table 1 - First Pass Surrogate Groups

Compounds	Group	Relative Volatility Range
Hexafluorobenzene / Fluorobenzene	1	0.86 - 3.5
Fluorobenzene / 1,2-dichloroethane-d4	2	3.5 - 20
1,2-dichloroethane-d4 / Teterahydrofuran	3	20 - 355

In Table 1, there are four first pass surrogates defined to cover the range of relative volatilities from 0.86 to 355. Note that adjacent groups share compounds. The high relative volatility for the first group becomes the low relative volatility for the second group, etc. First pass surrogates must be selected to cover the range of relative volatilities for boiling point surrogates.

Boiling point and relative volatility surrogates are manually assigned to groups in the Surrogate Data form, using the 'Boiling Point Group' and 'Relative Volatility Group' check boxes. There must be at least three compounds per group and at least two groups for each surrogate type. Up to six groups can be defined. Table 2 shows example groups.

Table 2 - Example Surrogate Groupings

Group	Boiling Point	Relative Volatility
1	Pentafluorobenzene (85) Toluene-d8 (111) Bromobenzene-d5 (155)	Hexafluorobenzene (0.86) Fluorobenzene (3.5) 1,4-difluorobenzene (3.83)
2	Bromobenzene-d5 (155) 1,2-dichlorobenzene-d4 (181) 1,2,4-trichlorobenzene-d3 (213)	Fluorobenzene (3.5) 1,4-difluorobenzene (3.83) O-xylene-d10 (6.14) Chlorobenzene-d5 (6.27)
3	1,2,4-trichlorobenzene-d3 (213) Naphthalene-d8 (217) 1-methylnaphthalene-d10 (245)	O-xylene-d10 (6.14) Chlorobenzene-d5 (6.27) 1,2-dibromoethane-d4 (26) 1,1,2-trichloroethane-d3 (26.6)

4		1,2-dibromoethane-d4 (26) 1,1,2-trichloroethane-d3 (26.6) Tetrahydrofuran-d8 (355) Acetone-c13 (600)
5		Tetrahydrofuran-d8 (355) Acetone-c13 (600) 1,4-dioxane-d8 (5800) Pyridine-d5 (15000)

Notice that the groups are defined so that there are one or two compounds common to adjacent groups. There cannot be any gap between groups. In the Surrogate Data form, check two group boxes for compounds that are shared; i.e., check boxes 4 and 5 for Tetrahydrofuran-d8.

Linear regressions determined by each group are used to calculate expected recoveries for compounds. The selection of limits for the regression lines affects which regression will be used to calculate recoveries. Some care must be taken in the selection of surrogate groups to ensure that the desired regression is used. The algorithm for selecting regressions is included in Appendix 3.

SECTION 3
SYSTEM OPERATION

3.1 Smcreporter Operation

3.1.1 Starting Smcreporter

All start-up procedures for Smcreporter are handled by ChemStation macros from a modified Enhanced Data Analysis main menu (Figure 1). An option – Method8261 – is added to the Enhanced Data Analysis main menu. All ChemStation Smcreporter routines are called using drop-down menu options from Method8261. All other Enhanced Data Analysis main menu options are still available and work as before.

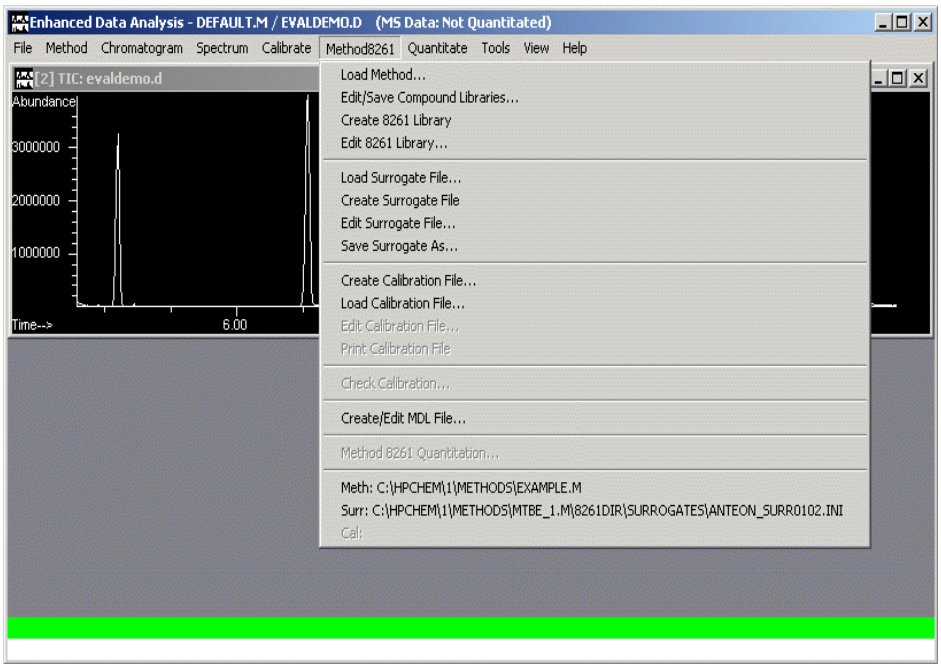


Figure 1 - Enhanced Data Analysis Method 8261 Menu

3.1.2 Method 8261 Menu

The Method 8261 drop-down menu in the Enhanced Data Analysis menu of ChemStation is shown in Figure 1. Each menu option will be explained in detail in sections 3.1.2.1 to 3.1.2.15. Available functions are divided into six groups. Menu selections are enabled or disabled based on options selected. To begin, only the 'Load Method...' and 'Load Calibration File...' options are enabled. At the bottom of the menu, current selections for the ChemStation method directory, and the surrogate, and calibration files are displayed.

3.1.2.1 Load Method

This menu option allows the selection of a ChemStation method directory as the current quantitation library for Smcreporter. Selection of a method for Smcreporter does not change the active method in ChemStation (as Method | Load Method does).

When this option is selected, a browse folder dialog box will be displayed as shown in Figure 2. Since a ChemStation method is a directory rather than a file, this dialog box allows selection of a directory. The topmost directory shown is the parent directory of the current Smcreporter method. The dialog's scroll bar allows access to the computer's full directory structure.

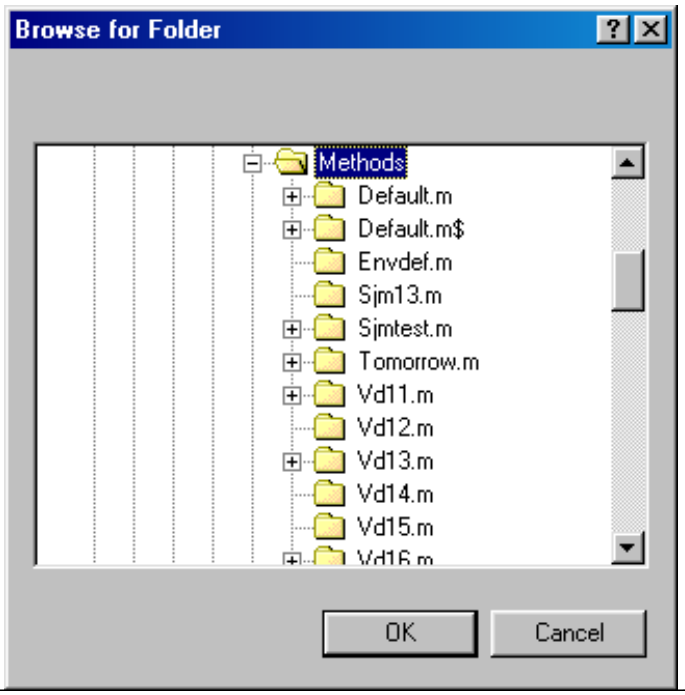


Figure 2 - Browse Folder Dialog Box

After the method is selected, the full path will be displayed on the 'Meth:' line at the bottom of the Method 8261 menu (see Figure 1). The menu options 'Edit/Save Compound Libraries...', 'Create 8261 Library', 'Edit 8261 Library...', 'Load Surrogate File...', 'Create Surrogate File', 'Create/Edit MDL File...' will be enabled as these menu options are dependent on having a method loaded. Options dependent on a calibration file – 'Edit Calibration File...', 'Print Calibration File', 'Check Calibration...', and 'Method 8261 Quantitation...' – will be disabled.

3.1.2.2 Edit / Save Compound Libraries

This option is used to edit the ChemStation quantitation library and maintain synchronization between the quantitation library and the 8261 library. The quantitation library is edited in much the same manner as the Calibrate | Edit Compounds menu option, then the 8261 library is updated and both libraries are saved to disk.

NOTE: Selecting Calibrate | Edit Compounds directly will not maintain the synchronization of the libraries. DO NOT use this option when editing quantitation libraries used in method 8261 calculations.

The function used to edit quantitation libraries in ChemStation is a 'black box' – it edits the quantitation library, but provides no details of what has been done. After the quantitation library has been edited in ChemStation, there is no way to tell if a compound was renamed or added. The input dialog box shown in Figure 3 informs the user that renaming compounds must be done separately from all other quantitation library changes. It also queries the user as to what types of changes will be made so that the 8261 library can be updated appropriately.

NOTE: Information in the 8261 library file may be corrupted if the user renames and adds compounds in one operation, or indicates one operation and performs the other.

To edit and save the quantitation and 8261 libraries:

- Complete the dialog shown in Figure 3. Select one of the radio buttons. If the top button is selected, rename existing compounds only. If the second button is selected, compounds may be added, deleted, and rearranged in the same operation and in any sequence.

  Press "OK" to continue, or "Cancel" to end compound editing and return to ChemStation.

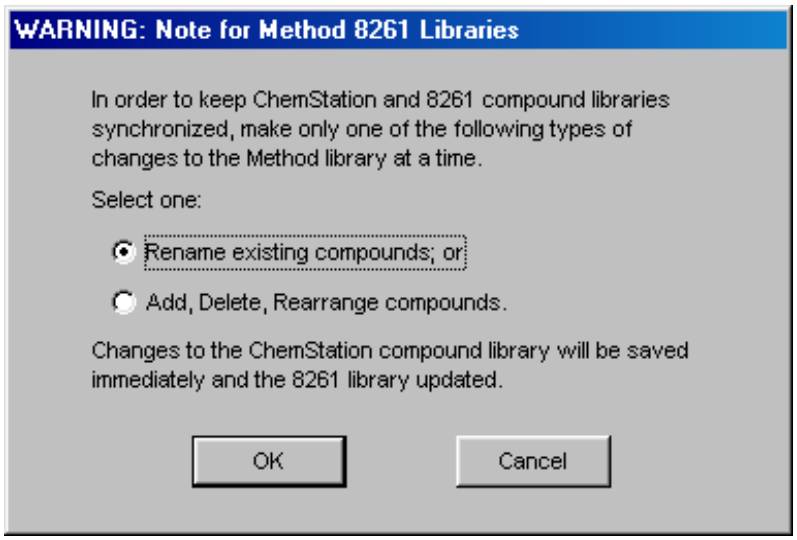


Figure 3 - Input Dialog for Compound Editing

- Following the input dialog, the 'Edit Compounds' dialog will be displayed (Figure 4). This is the same ChemStation dialog used in the Calibrate | Edit Compounds menu option. It is assumed that ChemStation users are familiar with ChemStation functions, so editing the quantitation library in ChemStation will not be explained here.

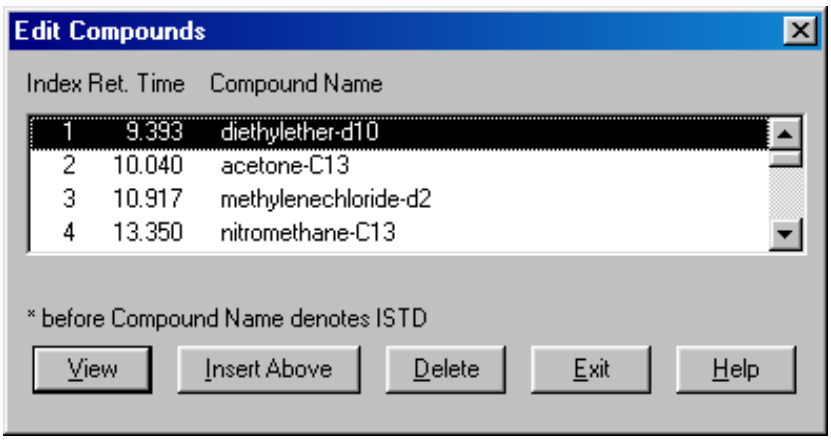


Figure 4 - ChemStation Edit Compounds Dialog

- After the quantitation library is edited, changes will be saved and the 8261 library updated. A 'Save Method As' dialog will be shown (Figure 5). The currently selected quantitation library (labeled as 'Meth:' in the Method 8261 menu) is shown as the default directory. To save the changes as a new method, enter a new directory name.
  Press "OK" to save changes.

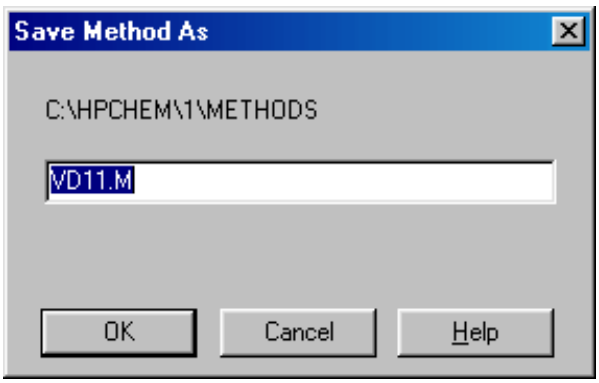


Figure 5 - Save Method As Dialog

  Press "Cancel" only if no changes were made in the 'Edit Compounds' dialog (the 'Save Method As' dialog will be displayed even if no changes were made).

- After a method directory has been specified, the quantitation library and the 8261 library will be updated and saved to disk. A message box will be displayed with the message: "About to update the Method 8261 Library." Click "OK". Wait until another message box indicates "Method 8261 Library has been updated." This may take a while depending on the changes made and the hardware speed. Be patient. Click "OK" to close the second message box and return to ChemStation.

  NOTE: The Edit / Save Compound Libraries option attempts to carry over as much information as possible from the 8261 library. After editing a method, check the 8261 library (using the Edit 8261 Library option, section 3.1.2.4) to make sure all information is correct and to add necessary information for any new compounds.

3.1.2.3 Create 8261 Library

Use this option to create an 8261 library (lib8261.ini) for a ChemStation method where the 8261 library does not exist. This option will create a library with default values for the compound entries (boiling point, relative volatility, concentrations). These defaults values (999 for boiling point and relative volatility, and 99 for concentrations) are primarily flags to indicate that real values need to be entered. By modifying existing libraries as explained in section 3.1.2.2, and saving to a new method directory, any existing data in the Method 8261 library will be transferred to the new library.

A new session of ChemStation will be opened to create the 8261 library. The new library will be created in the \8261dir directory of the current method shown at the bottom of the Method 8261 menu. An existing library file will be saved as 'lib8261.sav'. A message box will be displayed with the message: "About to update the Method 8261 Library." Click "OK". Wait until another message box indicates "Method 8261 Library has been updated." Click "OK" to close the second message box and return to ChemStation.

3.1.2.4 Edit 8261 Library

This option allows the user to enter compound specific data regarding boiling point, relative volatility, concentrations, etc. into the Method 8261 library. The dialog box for data entry is shown in Figure 6.

The full path name of the current 8261 library is shown in the 'Library' edit box. This box is read-only. Select this box and scroll right to see the full name.

The 'Compound Name' box displays the compound currently selected for updating. This box is read-only. Select a different compound from the list box at the right of the form. Or, enter the compound number (the compound's sequential number in the compound list) in the 'Record #' box. Press `<Tab>` rather than `<Enter>` to accept the entry. Compounds may also be sequentially accessed using the Next and Previous buttons, or `<Alt-N>` and `<Alt-P>`.

Enter the relative volatility to water and the boiling point in the appropriate boxes. A negative number is not allowed for the relative volatility as calculations use the natural log (ln). The relative volatility-organic and the octanol-water partition coefficient are not currently used.

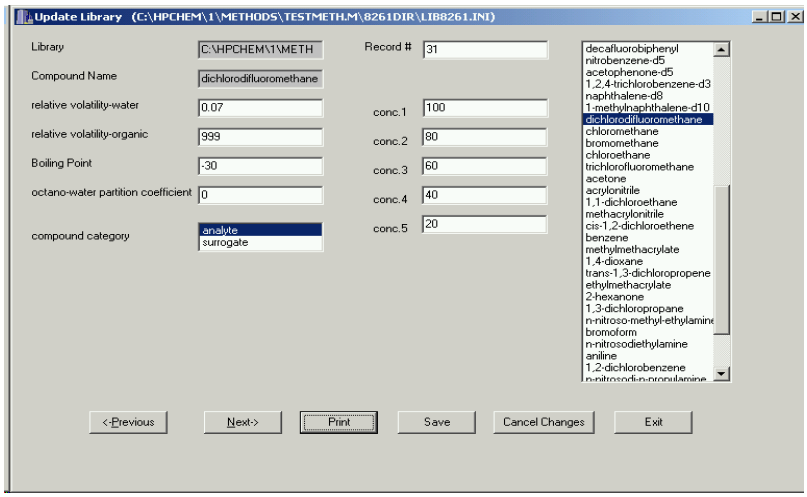


Figure 6 - Edit 8261 Library Dialog Box

In the 'Compound Category' selection list, indicate whether the current compound is an analyte or a surrogate compound. The selected choice is highlighted in blue.

The boxes labeled 'Conc1' through 'Conc5' are for recording various concentrations of analytes and surrogates in spiked samples used for instrument calibration. All samples are spiked with surrogates at a constant concentration (ng); thus, only one box ('Conc1') will be displayed for surrogate compounds. For analytes, boxes are provided for up to five different sample concentrations.

Any changes made to a compound are saved in memory when the user selects another compound. Prior to selecting another compound, the "Cancel Changes" button can be used to restore original compound entries.

Any changes must be saved before they will be applied to later data processing. The "Save" button will write all changes to the compound library file.

The "Print" button prints a listing of the compound library and all compound entries as shown in Appendix 6.

The "Exit" button exits the form. If there are any unsaved changes, the user will be prompted to

save or cancel changes on exit.

3.1.2.5 Load Surrogate File

This option allows the selection of a surrogate file to be used in Method 8261 calibrations and calculations. Surrogate files contain all compounds identified as surrogates in the 8261 library file. Surrogates may be selected and grouped in various ways, thus, there may be numerous surrogate files associated with a library file. The surrogate files are stored in a directory (8261dir\ Surrogates) under the appropriate method directory.

When this option is selected, a file open dialog box will be displayed as shown in Figure 7. The default directory for the surrogate file is 8261dir\Surrogates under the currently selected 8261 method file.

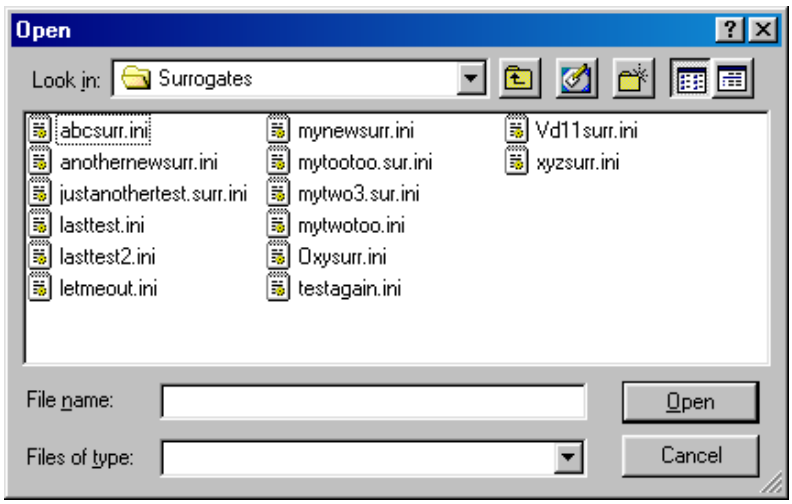


Figure 7 - File Open Dialog Box

When a file is selected, the full path will be displayed on the line labeled 'Surr:' at the bottom of the Method 8261 menu (see Figure 1). Menu options that are dependent on a surrogate file – 'Edit Surrogate File...', 'Save Surrogate As...', and 'Create Calibration File...' – will be enabled.

3.1.2.6 Create Surrogate File

This option creates a new surrogate file from the currently selected 8261 method file. As this option populates fields with default values, it will often be better to save an existing surrogate file under a new name (see section 3.1.2.8).

A file open dialog box (Figure 7) will be displayed. Enter a new file name for the surrogate file. You will be prompted for another file name if the file already exists. A message box will indicate that the file has been created.

3.1.2.7 Edit Surrogate File

This option is used to identify and group specific surrogates to be used in Method 8261 calculations. Before the Edit Surrogate File dialog box (Figure 8) is displayed, several checks of the surrogate file are performed:

- The surrogate groupings in the file are checked. If a problem grouping is found, a message box alerts the user.
- The Method 8261 library and the surrogate library must be synchronized. That is, they must include the same set of compounds and in the same order. Method 8261 library compounds can be renamed, added, deleted, or reordered using the 'Edit/Save Compound Libraries...' menu option (see section 3.1.2.2). If a compound mismatch is found, a warning message box is displayed. The Method 8261 library compound name is shown on the left, the surrogate file compound name on the right. If the compound has been renamed in one file, clicking the 'Yes' button will update the surrogate compound name to match the Method 8261 library name. If the compounds are different, and one has not been renamed, the surrogate file must be recreated (see section 3.1.2.6). A printout is produced showing surrogate file compounds on the left side and associated Method 8261 library compounds on the right (see Appendix 12). The printout includes surrogate settings and will assist in resolving problems between the libraries.

In the Edit Surrogate File dialog box, the currently selected surrogate file is shown in the 'Surrogate Library' edit box. This is a read-only box. The user may scroll through the box to see the entire file name and path.

The current compound is identified in the 'Compound Name' box. This box is read-only. The surrogate number shown in the 'surrogate number' box is the sequence number of the selected

surrogate in the surrogate file. This number may or may not correspond to the sequence number of the surrogate compound in the 8261 library file; i.e., if a compound is the second compound in the library, but the first surrogate, it will have surrogate number 1 and compound library number 2. Surrogate compounds can be selected by entering the surrogate file or the 8261 library file sequence number, or by using the Next button (or <Alt-N>) or Previous button (or <Alt-P>) . Press <Tab> to accept the entry.

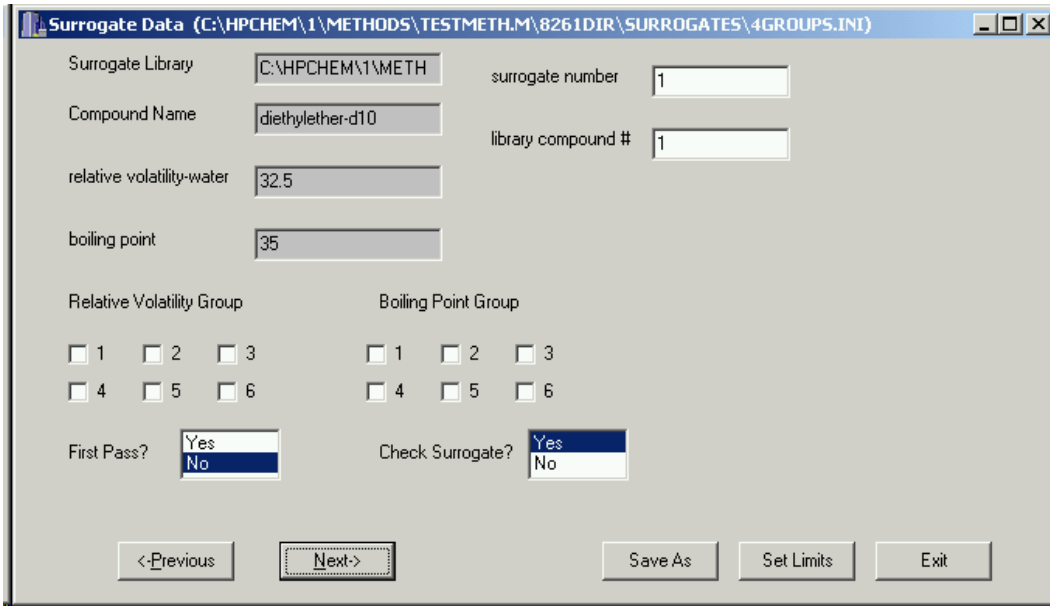


Figure 8 - Edit Surrogate File Dialog Box

The relative volatility and boiling point are displayed for reference – they are important in determining surrogate groupings. These are read-only boxes. These values are changed by editing the 8261 library (see section 3.1.2.4).

All changes made to the current surrogate compound are saved in memory when the user selects a different surrogate.

In the Edit Surrogate File dialog box, place a checkmark in each group the compound belongs to. A compound may belong to one or two groups. Remember that the groups shown in Tables 1 and 2 share some compounds. These shared compounds determine the endpoints for regression lines

representing expected recoveries over the group interval. However, the only programmatic requirement for surrogate groups is that they must contain at least three compounds. Ordinarily, a compound should not be both a boiling point and a relative volatility surrogate.

First pass surrogates are used to estimate the effects of relative volatility on boiling point surrogates. First pass surrogates should have boiling points below 100°C to minimize any boiling point effects. They must be selected to cover the full range of relative volatilities for the boiling point surrogates. Select between three and five first pass surrogates by highlighting 'Yes' (in blue) in the 'First Pass?' box.

Check surrogates are surrogates that will be added to samples as a check on the Method 8261 calculations. These compounds are not ordinarily included in other surrogate groups. Select check surrogates by highlighting 'Yes' (in blue) in the 'Check Surrogate?' box.

The Set Limits button is used to define minimum and maximum limits for calculations. Experience using the Method 8261 normalization algorithm has shown that it is possible to have negative recoveries, especially near the minimum and maximum surrogate limits. For this reason, the user may specify limits to boiling points and relative volatilities used in calculations. The Surrogate Limits dialog box (Figure 9) is displayed when the Set Limits button is pressed. The use of this dialog will be explained using data in Table 2:

- The range of boiling point group 1 is 85 to 155. The user may specify a minimum boiling point from 85 to 155. Because group 1 has three points (see Appendix 3 for rules concerning endpoints of regressions), the default minimum for group 1 is 85. If a compound's boiling point is below the user-specified minimum, the predicted recovery will be 1 (100%).
- The range of boiling point group 3 is 213 to 245. The user may specify a maximum boiling point in that range. The default maximum boiling point is always the average of the two highest boiling points, thus the default maximum for group 3 is 231. If a compound's boiling point is greater than the maximum limit, the predicted recovery will be the specified maximum endpoint of the group 3 regression line.

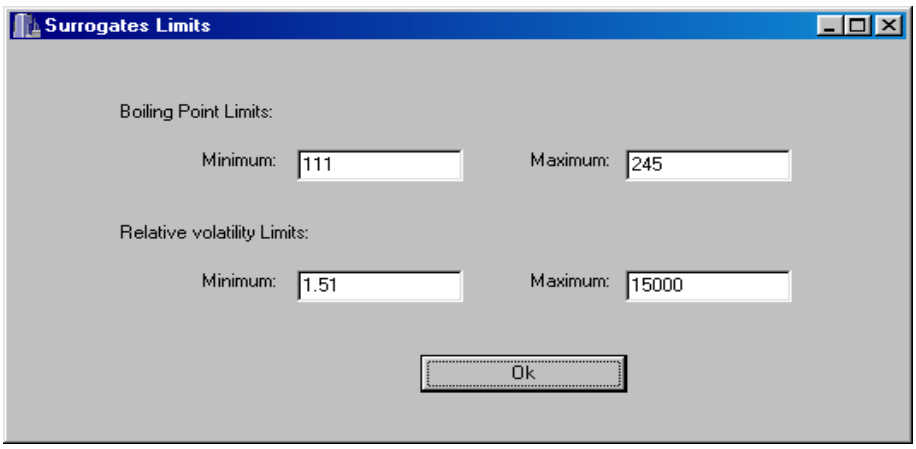


Figure 9 - Surrogate Limits Dialog Box

- The range of relative volatility group 1 is 0.86 to 3.83. The minimum relative volatility must be within that range. Because this is a three-point line, the default is 0.86. Relative volatilities below the user-defined value, will have a predicted recovery equal to the specified minimum endpoint of group 1.
- The range of relative volatility group 5 is 355 to 15000. The maximum endpoint must be within that range. The default maximum is always the log average of the two highest relative volatilities:

$$e^{\frac{\ln(5800)+\ln(15000)}{2}} = 9327.38.$$

  The predicted relative volatility for compounds greater than the maximum will be the specified maximum endpoint of the group 5 regression.

All changes must be saved before they can be used in any further processing. Any changes made during the edit session are saved to memory only. To save changes to the current surrogate file, click the Save As button.

Except when first creating a surrogate file, it is recommended that any changes to a surrogate file be saved to a different file name. After a surrogate file has been used for sample quantitations, it should be maintained on disk. If the surrogate file is edited, save it to another file name by selecting the "Save As" button. A 'Save As' dialog box will be shown. The current surrogate file name may be selected (although it is strongly discouraged). A dialog will warn that the current file will be overwritten. The user may elect to proceed (Yes button) or enter another file name

(No button).

Exit the form by clicking "Exit". If there are any changes, a prompt will be displayed to save or cancel changes.

3.1.2.8 Save Surrogate As

This option allows the user to save the current surrogate file with a new name. This minimizes changes required when slight modifications are desired in a surrogate file.

- A message will be displayed confirming that you have the desired surrogate file selected.
- A standard file save dialog box will allow you to choose the new file name. If the file already exists, you will be prompted to confirm overwriting the existing file.

3.1.2.9 Create Calibration File

A calibration must be performed before a quantitation on environmental samples can be done. The calibration consists of measuring known samples, calculating recoveries versus a selected sample (the 'surrogate reference'), and estimating the effects of boiling point and relative volatility on the recovery. The result is a set of response factors (area counts/ng) that can be applied to field samples.

In creating a calibration file, the user selects a set of known samples and a surrogate reference. When the 'Create Calibration File' option is selected, a message box will be shown confirming the surrogate file that will be used for the calibration. Click the Cancel button if the desired surrogate file is not shown. Load the desired file using the 'Load Surrogate File' option (see section 3.1.2.5). The form for creating a calibration file is shown in Figure 10.

The top two fields - 'Compound Library:' and 'Surrogate Library:' are read-only. They confirm the libraries that will be used in calibration calculations.

To complete this form and create a calibration file:

- Select between one and five standard samples to process. Click the "Add Standard" button. This will display a browse folder dialog (Figure 2). Select a data directory. The directory must contain a quantitation file (the sample must have been quantitated using the Quantitate|Calculate main menu option) for the selected method. This file must have the ChemStation default name, which consists of the method name (OXY_MORN is the

method name for the compound library shown in Figure 10), with a '.res' extension.

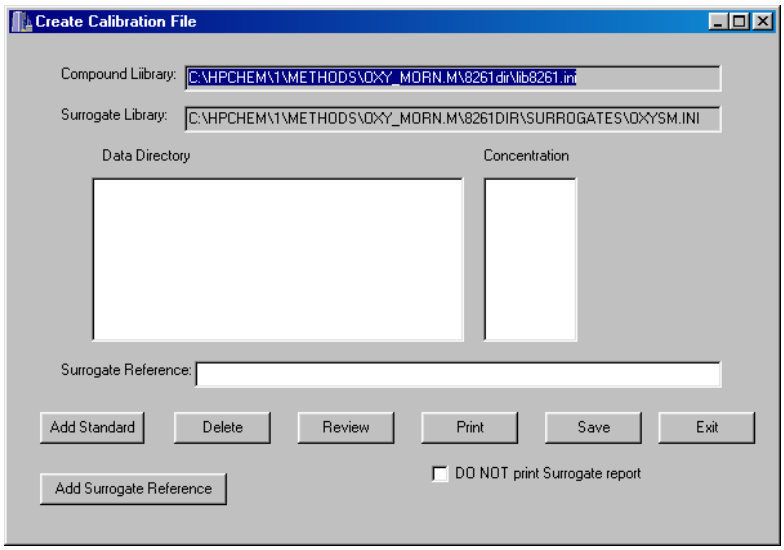


Figure 10 - Create Calibration File Dialog Box

- The standard level dialog box shown in Figure 11 will be displayed. This dialog is used to select the appropriate concentration (ng) for the sample. The radio buttons correspond to the standard concentrations entered in the compound edit screen (Figure 6). Select a standard concentration or a dilution of standard concentration 1. Enter the dilution factor if a dilution is used.

  NOTE: A dilution is ordinarily indicated by a fraction less than one. However, the dilution factor edit box will accept numbers greater than one. This allows preparation of calibration samples with higher concentrations than concentration 1, but bypasses inputting individual concentrations for each compound (see section 3.1.2.4) – substantially reducing inputs.

- Control will return to the create calibration file dialog on exiting the standard level dialog. The data directory and concentration selected will be displayed in the 'Data Directory' and 'Concentration' list boxes.
- After all standards have been chosen, select a surrogate reference. Click the "Add Surrogate Reference" button or simply click inside the 'Surrogate Reference:' edit box. A browse folder dialog will be displayed to select the surrogate reference.

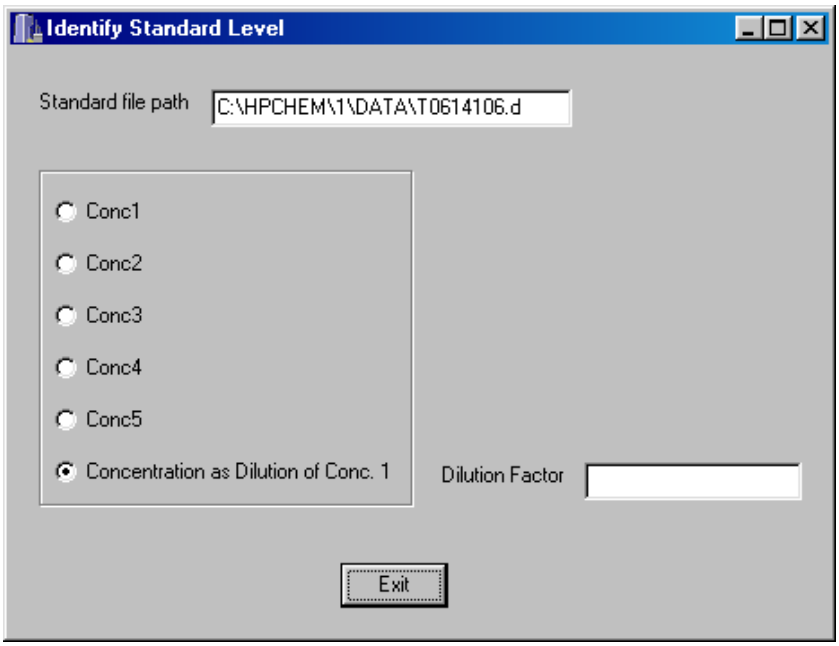


Figure 11 - Standard Level Selection Dialog Box

- A standard can be deleted from the list by highlighting the desired entry and clicking the "Delete" button.
- To perform calculations and review the results of the calibration, click "Review". The results of the calibration will be shown in an edit calibration dialog box (Figure 12). This dialog is explained in detail in section 3.1.2.11.
- Click "Print" to print a record of the calibration shown. To suppress printing of a surrogate report for each standard used, check the 'DO NOT print Surrogate report' box. See Appendices 6 and 7 for explanations of the calibration report and the surrogate report.
- Press "Save" to save the calibration to a file. <u>There is no automatic saving of the calibration information</u>. The file selection is accomplished using a standard file save dialog box.
- Click "Exit" to close this form. The user will not be prompted to save the current calibration.

3.1.2.10 Load Calibration File

This option allows the selection of a previously saved calibration file to be used in Method 8261 calculations. The calibration file contains the response factors for each compound in the method. The calibration files are stored in a directory (8261dir\Calibration) under the appropriate method directory.

When this option is selected, a standard file open dialog box will be displayed. The default directory for the calibration file is 8261dir\Calibration under the currently selected 8261 method file.

When a file is selected, the full path will be displayed on the line labeled 'Cal:' at the bottom of the Method 8261 menu (see Figure 1). The 'Edit Calibration File...', 'Print Calibration File', 'Check Calibration...', and 'Method 8261 Quantitation...' menu options will be enabled. All method and surrogate options will be disabled. The 'Create/Edit MDL File...' option and the 'Meth:' and 'Surr:' file listings will also be disabled.

3.1.2.11 Edit Calibration File

The results of a calibration, or a saved calibration file, can be viewed using the edit calibration dialog (Figure 12). This dialog allows the user to review and select calibration samples to be used in determining the final response factor. It also displays important calibration statistics for each compound in the compound method library.

To complete this form and determine response factors for each compound:

- Select the desired compound by entering the record number in the Record Number box, using the Previous (`<Alt-P>`) and Next (`<Alt-N>`) buttons to navigate the compound list, or select the compound from the list box in the upper right corner of the form. The current compound will be shown in the Compound edit box.
- Information for each standard solution used in the calibration will be displayed in separate columns. Review the information shown for each standard solution. To exclude a standard solution from the final calculations, uncheck the check box in the standard column. The average response factor, deviation and percent deviation for the compound (shown in the bottom row of edit boxes) will be updated as boxes are checked or unchecked.
- Click the Save As button to save changes. It is suggested that changes be saved to a

different calibration file. A standard file save box will be displayed. The current calibration file may be selected – a warning will be displayed about overwriting the file.

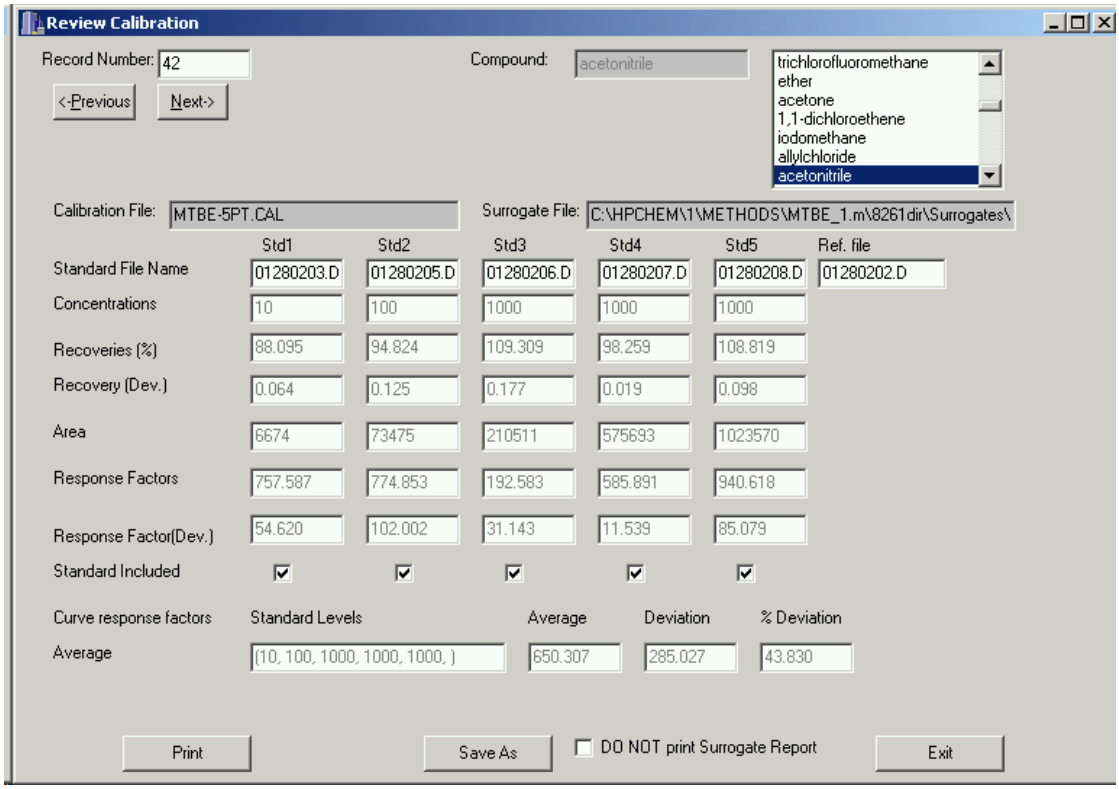


Figure 12 - Edit Calibration File Dialog Box

- Click the Print button to print the calibration results (Appendix 7). A surrogate report (Appendix 8) will be printed for each sample, unless the DO NOT print Surrogate Report check box is checked..
- Click the Exit button to close the form. If any changes have been made, a prompt will be displayed to save or discard changes.

The 'Calibration File:' box shows the name of the calibration file displayed. The names of each standard directory and the surrogate reference directory are shown on the next row. It may be necessary to scroll right to see the full directory name.

The concentrations (ng) of the compound in the standard solutions are shown in the 'Concentrations' row.

The 'Area' row contains the area counts for the compound from the quantitation result file in the data directory indicated.

The row labeled 'Average' shows the average response factor for the columns selected. The text box under 'Standard Levels' lists of the analyte amounts for the selected columns. The average (mean), deviation (standard deviation), and percent deviation (the standard deviation as a percent of the average) are shown for the selected samples.

3.1.2.12 Print Calibration File

Selecting this option prints a report listing response factors for all compounds in the Method 8261 library. An example report is included in Appendix 7.

3.1.2.13 Check Calibration

The 'Check Calibration' menu option compares response factors for a given quantitation with those for the selected calibration file. To perform a check calibration:

- Select a data folder from a browse folders dialog box (Figure 2). The data folder must have been quantitated using ChemStation (the folder contains a .res file for the current method).
- The check calibration standard dialog box (Figure 13) will be displayed. The edit boxes on the left side of this form are all read-only and indicate selected files.
- Enter a concentration for the check standard file. If the concentration is a dilution, enter the dilution factor.
- Check the 'DO NOT Print Surrogate Report' checkbox if a surrogate report for the selected check standard is not desired.
- Click "Print" to receive a printout of the results. A check calibration report is included in Appendix 10.
- Select "Review" to display the check calibration review dialog (Figure 14). This dialog operates like dialogs previously explained in sections 3.1.2.4 and 3.1.2.11. The response and deviation listed under the calibration file are those listed in the calibration file. The check standard concentration, area counts, and response are listed under the check

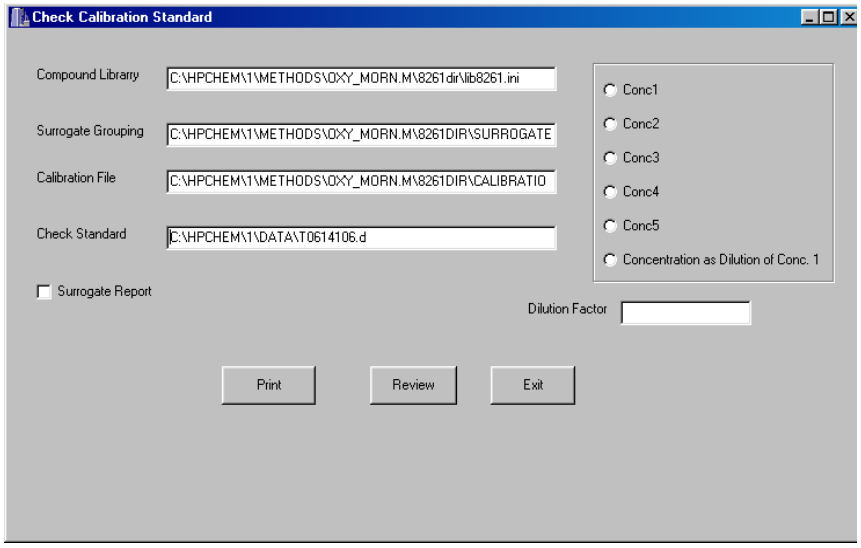


Figure 13 - Check Calibration Standard Dialog

standard file. The difference percent is the difference between the calibration response factor and the response factor calculated for the check standard. The "Print" button is the same as "Print" on the check calibration standard form.

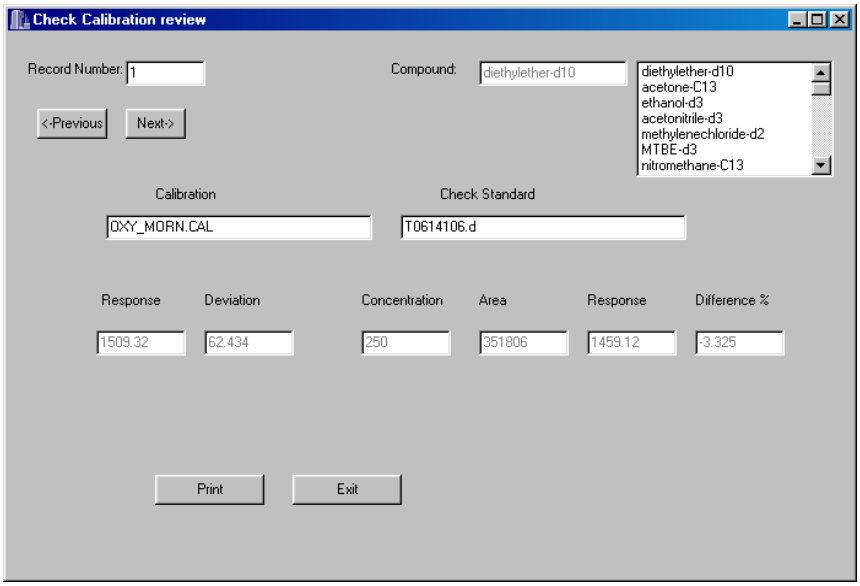


Figure 14 - Check Calibration Review Dialog

- Click "Exit" to exit the form.

3.1.2.14 Create/Edit MDL File

This option allows the user to manage files to apply minimum detectable levels (MDL) to Method 8261 calculations. When this option is selected, the Edit MDL Dialog shown in Figure 15 will be displayed. Only compounds listed as analytes in the 8261 library are listed in this dialog.

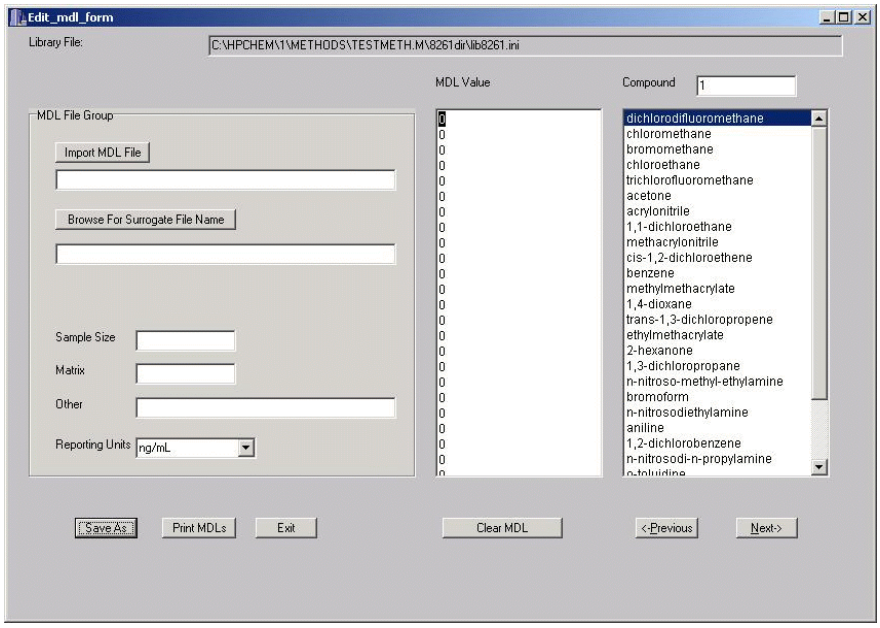


Figure 15 - Edit MDL Dialog

To complete this dialog:

- The Library File edit box displays the current 8261 library file. It is read-only.
- An existing MDL file can be loaded by clicking the "Import MDL File"button. An Open File Dialog will be presented to select the MDL file. If an existing file is imported, all other edit boxes in the MDL File Group (the grouped edit boxes on the left of the dialog) will be filled automatically.
  Otherwise:
- Click the "Browse For Surrogate File Name" button to select the surrogate file used in

calculating MDLs. An Open File Dialog will be displayed. This is a required field.

- Enter the sample size used in calculating MDLs. This is a required field.
- Enter the appropriate matrix. This is strictly a comment field, but is required for complete documentation.
- Any further comments can be entered in the 'Other' field.
- Select the appropriate reporting units from the drop-down list box.
- Navigation among compounds in this dialog is accomplished using the "Next" and "Previous" buttons, entering a compound number in the 'Compound' edit box, or selecting a compound in the compound list box.
- MDLs are entered using the text box labeled 'MDL Value'. MDLs can be entered by placing the cursor on the appropriate line and entering a value from the keyboard.

  Values may also be cut (Ctrl-C) and pasted (Ctrl-V) from a text file, or from a Microsoft Excel spreadsheet (values from any other spreadsheet should be exported to a text editor before cutting and pasting). The text file format must be a value followed by an endline; for example:

  2.45
  3.67
  5.00
  etc.

  Values are associated with compounds strictly on a positional basis; i.e. the first value will be associated with the first compound, the second value with the second compound, etc. Enter a zero (0) for any compounds which do not have an MDL.

  Always check the MDL file.

- The "Clear MDL" button is used to reset all MDLs to zero.
- Click the "Save As" button to save all information to a data file. A Save As Dialog will be displayed.
- The "Print" button will print a listing of compounds and MDLs (see Appendix 11 for an example listing).
- Click "Exit" to close this dialog and return to ChemStation.

3.1.2.15 Method 8261 Quantitation

This final processing option is used to apply Method 8261 calculations to samples. Up to 20 sample files can be processed at one time, using the selected method, surrogates, and calibration file. The Process Files dialog box (Figure 16) allows selection of multiple files. To complete file processing:

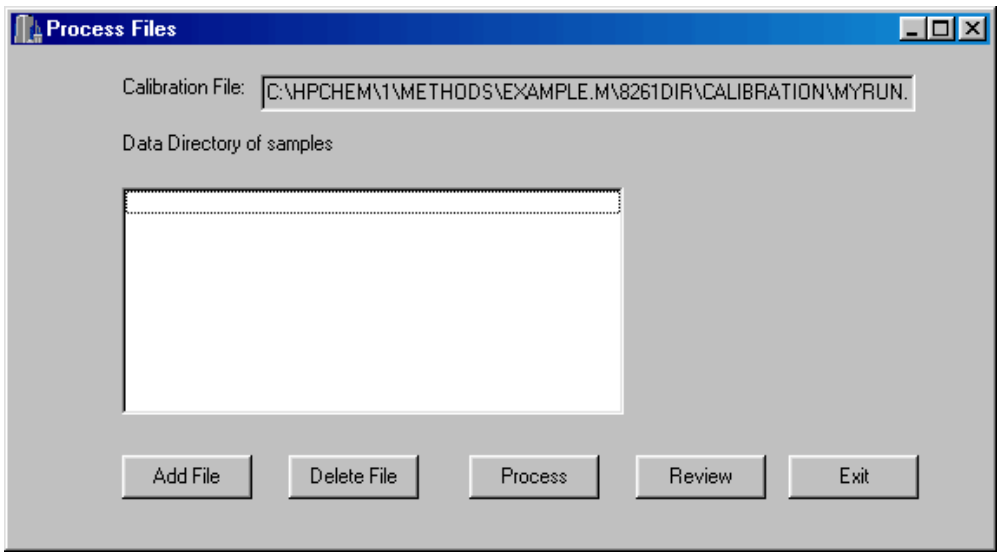


Figure 16 - Process Files Dialog Box

- Click the "Add File" button. A browse folder dialog (Figure 2) will be shown to allow selection of a data directory. Following selection of a data directory, the file processing input dialog box (Figure 17) will be displayed.
  - The current sample file name is displayed in a read-only field.
  - Use the 'List MDL' radio buttons to select whether to apply MDLs to final calculations. The default in 'No'. The 'Reporting Limits (Number of Standard Deviations)' drop-down list and the 'Browse for MDL File' button and edit box are not displayed. If 'Yes' is selected, these fields will be displayed. Click the 'Browse for MDL File' button to display an Open File dialog. Select how to apply reporting limits in the quantitation report. A value of '0' will display any concentrations below the MDL as not detectable (ND). Selecting a number from 1 to 3 will only indicate ND if the measured value plus the number of standard deviations chosen is less than the MDL. The reporting units, sample size, matrix

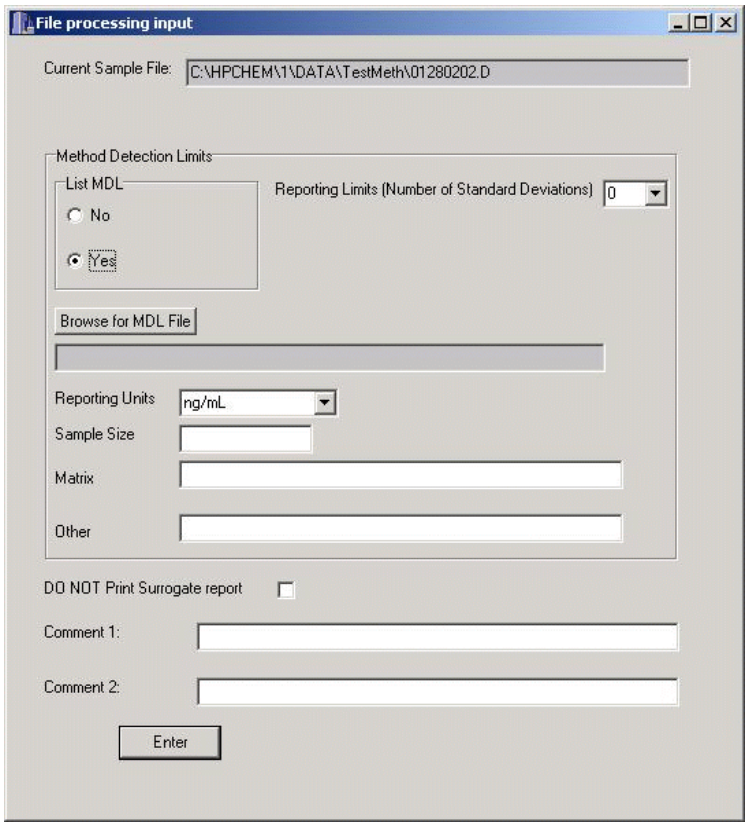


Figure 17 - File Processing Input Dialog

and 'Other' fields will be automatically filled when an MDL file is selected.

- Select the reporting units from the drop-down list box.
- Enter the sample size (milliliters or grams). This is a required field.
- Enter the matrix type.
- The 'Other' and comment fields can be used for any documentation or notes associated with the quantitation.
- Check the 'DO NOT Print Surrogate report' check box if a surrogate report is not desired.
- Press "Enter" to return to the process files dialog.

- Repeat the steps above to enter up to 100 files to process. To remove a file from the list, highlight the file and press "Delete File".
- Press "Process" to perform Method 8261 calculations for all selected files. For each data

file, a text file will be created in the data directory. This file will have the name of the calibration file followed by a sequence number. The file extension is .prn. For example, when quantitating data in the sludge.d directory with the sludge-5pt.cal calibration file, the calibration results will be saved in the sludge-5pt1.prn file in the sludge.d directory. Results for each file will also be printed. See Appendix 9 for a sample report.

- Select "Review" to display a report for a selected sample. Select a sample in the Process Files dialog list box. If a sample is not selected, "Review" will display the first file in the list. This report is displayed in Notepad and can be saved as a file using the Files | Save As menu option, otherwise the file is saved as sample.prn in the 8261 directory. This default file is overwritten each time the review option is used. This is a semicolon delimited text file. See Appendix 10 for a sample report.
- Click "Exit" to return to ChemStation.

APPENDIX 1
INSTALLED PROGRAM FILES

The program files installed by Smcreporter are listed below, sorted by version and directories.

Directory	Version B	Version C
Install Directory\Msmacros	A1cr.mac A1create.mac A1getres.mac A1load.mac A1Mchng.mac A1rdres.mac A1Setup.mac A1applic.mac A1autoed.mac A1autorn.mac A1autocr.mac A1Upmenu.mac Smcreporter.exe Methapp.exe Loadfile.exe	A1cr.mac A1create.mac A1getres.mac A1load.mac A1Mchng.mac A1rdres.mac A1Setup.mac A1applic.mac A1Upmenu.mac Smcreporter.exe Methapp.exe Loadfile.exe
Install Directory\Msexe[1]	Enhmsbar.mac Envcomm.mac	A1autoed.mac A1autorn.mac A1autocr.mac Enhmsbar.mac Envcomm.mac

Window System32 directory (This is OS specific and is determined by InstallShield)	Borlndmm.dll Cp3245mt.dll Dclusr40.bpl Vcl40.bpl Vclx40.bpl	Borlndmm.dll Cp3245mt.dll Dclusr40.bpl Vcl40.bpl Vclx40.bpl

1 Enhmsbar.mac and envcomm.mac replace existing macros with the same names. The original macros are renamed enhmsbar.bac and envcomm.bac. Following an uninstall, they must be manually restored to .mac.

APPENDIX 2
VERIFYING SMCREPORTER INSTALLATION

Verification of the installation consists of performing a calibration and checking the calibration against a calibration file included in the installation.

- The Method 8261 menu (Figure 1) will initially have only one option: 'Load Method'.
  - Click 'Load Method'. A browse folder dialog box will be displayed.
  - Select the 'Example.m' directory. The path will depend on what directory was entered for the ChemStation data directory during installation. For example, if the data directory was entered as "c:\hpchem\1\data", the full path of example.m will be "c:\hpchem\1\methods\ example.m". All default paths specified below assume the initial data directory given in this example.
- Click 'Load Surrogate File' and select 'oxysm.ini' as the surrogate file. The default path will be "c:\hpchem\1\methods\8261dir\surrogates\oxysm.ini".
- Click 'Create Calibration File'.
  - The Create Calibration File dialog box will be displayed (Figure 10).
  - Press "Add Standard" and select 'Example1.d' as the standard directory. The default path is "c:\hpchem\1\data\example1.d".
  - The Standard Level Selection dialog (Figure 11) will be displayed. Select 'Conc1' as the standard concentration for Example1. Press "Exit".
  - Press "Add Standard" again and select 'Example2.d'. The default path is "c:\hpchem\1\data\example2.d".
  - Select 'Concentration as Dilution of Conc1'. Enter 0.6 for the 'Dilution Factor'. Press "Exit".
  - Press "Add Surrogate Reference" and select 'Example3.d' as the surrogate reference file. The default path is "c:\hpchem\1\data\example3.d".
  - Press "Review". An Edit Calibration dialog box will be displayed. A warning message will be displayed: "Negative response factor OR surrogate measured recovery greater than 500%... Proceed?" Click the 'Yes' button to proceed. (At other times, pay attention to this message and check the indicated .log file to help pinpoint possible data problems.)
  - Press "Save As". A file open dialog box will be displayed. Enter a new unique name for the calibration. Calibration files are stored in a subdirectory under the current method. Thus, the default calibration directory is: "c:\hpchem\1\methods\

example.m\8261dir\calibration".
- Click 'DO NOT print Surrogate report'.
- Press "Print".
- Press "Exit".

- Click 'Load Calibration File' and select '2runs.cal' as the calibration file. The default path is "c:\hpchem\1\methods\8261dir\calibration\2runs.cal'.
- Select 'Edit Calibration File'.
  - On the Edit Calibraton dialog box (Figure 10), check 'DO NOT print Surrogate Report'.
  - Click the "Print" button. A calibration report for 2runs.cal will be printed.
  - Press "Exit".

The calibration reports for 2runs.cal and the new calibration should match. If not, contact Steven McLemore – Anteon Corporation – at (702) 784-8324 or mclemore.steven@epa.gov.

APPENDIX 3
REGRESSION SELECTION ALGORITHM

For each surrogate group, a regression line is calculated. The independent variable (x) is the value of the appropriate physical property (boiling point or relative volatility). The following procedure is used to determine the appropriate regression to calculate the expected recovery for a compound:

- For each line, determine the absolute minimum and maximum group surrogate values.
- For each line, determine the limits of the regression line.
  - For a group of three surrogates, the limits are the two extreme values (limits equal absolute minimum and maximum)..
  - For groups of four or more surrogates, the lower limit is the average of the two lowest values and the upper limit is the average of the two highest values (limits are different than absolute minimum and maximum).

1) Start with group 1.
2) If the compound value is less than the lower limit of group 1, assign the group 1 regression.
3) If group is 1, go to step 6.
4) If the value is less than the group absolute minimum, assign the previous group regression.
5) If the value is less than the group lower limit, assign the current group regression.
6) If the value falls within the group limits, assign the group regression.
7) Go to the next group.
8) If the group number is less than or equal to the highest group, go to step 4.
9) If the value is greater than the group's upper limit, use the last group regression.

APPENDIX 4
WINDOWS INITIALIZATION FILE (INI) FORMAT

This section explains the Windows initialization file (.ini) format. An INI file is simply a text file. However, it has a structure which allows Windows to find data in it. It can be thought of as a three-field data table, where the first two fields are keys. The first key is called the 'Application' or 'Section' (in the rest of this document, 'section' will be used). The second key is simply called the 'Key'. The third field is the 'Value'.

Here is an example INI file (taken from the 8261lib.ini file).

```
[compound1]
name=diethylether-d10
bp=35
rvW=32.5
cmpndType=surrogate
```

The word in brackets is the section field. Each word on the left of an equal sign is a key, and the words to the right of the equal signs are the values.

Keys must be unique within a given section, but they may be duplicated in two or more sections. If the INI file is edited manually (using Notepad or another text editor), non-unique keys could be created. Windows will simply use the first one it finds and ignore the rest.

INI files were used because they are part of the Windows Application Programming Interface (API). Windows provides functions to access them quickly and easily. The Windows application programming interface (API) functions that allow reading and writing of INI files are GetPrivateProfileString( ) and WritePrivateProfileString( ). They are implemented in ChemStation macro language as GetIniString$( ) and SetIniString( ), and in C++Builder as TiniFile::ReadString() and TIniFile::WriteString(). Use of these functions is documented on the Web, or through ChemStation or C++Builder online documentation.

INI files do have some important limitations:

- When reading an INI file, a default value is specified to return in case the keys provided are not found. This means that the INI file operations work just fine, even if the INI file

does not exist. The API functions which retrieve data from INI files do not even tell the calling function whether the value it is returning came from the INI file, or is simply a copy of the default value.

- INI files cannot be over 64 KB in length.

APPENDIX 5
METHOD 8261 CALCULATIONS

1. Quantitative Analysis – Calibration

An instrument calibration must be performed before any quantitation of environmental samples. Spiked samples are used for the calibration. Following measurement of the samples[3], the calibration involves the following steps to calculate response factors (area counts/ng) for each compound in the sample: estimate relative volatility effects on boiling point surrogates using first pass surrogates(f); calculate boiling point ( ) and relative volatility ( ) effects on surrogate recoveries; combine these effects to estimate total recoveries of compounds; and, finally, calculate a response factor for each compound based on area counts, mass of the compound present, and the estimated recovery. This section presents a step-wise approach to the calculations.

In the following discussion, various variables will be introduced. These variables may be associated with first pass, relative volatility, or boiling point surrogates. Subscripts will be used to clarify the distinction. For example, equation 1 is used to calculate the relative recovery (R). R_f is used for a relative recovery associated with first pass surrogates, R for relative volatility surrogates, and R for boiling point surrogates.

- Select results of 1 to 5 spiked samples, of various concentrations, as calibration files. Select a spiked sample file as a 'surrogate reference'. The surrogate reference represents 100% recovery of target compounds.
- First pass surrogates:
  - For each first pass surrogate, calculate the relative recovery (R_f) as:

    Equation 1

$$R = \frac{a_s / c_s}{a_r / c_r}$$

[3] Hiatt, M.H. Method 8261: Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectrometry (VD/GC/MS), Draft Update IVB of SW-846 On-line, URL: http://www.epa.gov/epaoswer/hazwaste/ test/txup4b.htm.

where
R = relative recovery
a_s = sample area counts
c_s = sample amount (ng)
a_r = reference area counts
c_r = reference amount (ng).

- Arrange first pass surrogates in order of relative volatility.
- For each adjacent pair of first pass surrogates, calculate a linear regression slope (m_f), intercept (b_f), and associated standard error ($lstderr_f$):

Equation 2

$$m = \frac{n\sum xy - \left(\sum x \sum y\right)}{n\sum x^2 - \left(\sum x\right)^2}.$$

Equation 3

$$b = \frac{\left(\sum y \sum x^2\right) - \left(\sum x \sum xy\right)}{n\sum x^2 - \left(\sum x\right)^2}.$$

Equation 4

$$lstderr = \sqrt{\left[\frac{1}{n(n-2)}\right]\left[n\sum y^2 - \left(\sum y\right)^2 - \frac{\left[n\sum xy - \sum x \sum y\right]^2}{n\sum x^2 - \left(\sum x\right)^2}\right]}$$

= 0 for first pass surrogates (two first pass surrogates determine a line)

where
n = the number of points determining the line
x = ln rw (natural log of relative volatility) for points determining the line
y = relative recovery (R_f) for first pass surrogates determining the line.

lstderr is a measure of the error in the relative recovery, predicted from the regression, for each natural log of relative volatility (ln rw).

- Boiling point surrogates:
  - For each boiling point surrogate, calculate the relative recovery (R - Equation 1).
  - For each boiling point surrogate, determine the first pass predicted recovery (Rp_f) from the first pass regressions above:

    Equation 5

    $$Rp_f = \ln rw \times m_f + b_f$$

    where
    rw = surrogate relative volatility
    Use the slope and intercept for the calculated line segment that includes the given ln rw. Do not extrapolate lines. Set the relative volatility equal to the nearest endpoint if it is outside the range of first pass relative volatilities.

  - For each boiling point surrogate, calculate the first pass adjusted relative recovery (Ra) as:

    Equation 6

    $$Ra_\beta = \frac{R_\beta}{Rp_f}$$

  - For each boiling point surrogate group, calculate a linear regression (m, b, and lstderr) as in Equations 2,3, and 4 above:
    where
    x = boiling point for each surrogate in the group
    y = Ra for each surrogate in the group.
    These linear regressions will yield a predicted recovery for any compound based on that compound's boiling point.

- Relative volatility surrogates:
  - For each relative volatility surrogate, calculate the relative recovery (R - Equation 1).
  - For each relative volatility surrogate, determine the boiling point predicted

recovery (Rp) from the boiling point regressions above:

Equation 7

$$Rp_\beta = bp \times m_\beta + b_\beta$$

where
bp = surrogate boiling point. **Note:** If bp exceeds the maximum boiling point for the surrogate file(see section 3.1.2.7), set bp equal to the maximum value.

The slope and intercept are for the calculated line segment that includes the given bp. Rp = 1 for boiling points less than the surrogate file minimum. These boiling points will ordinarily be less than 100°C and it is assumed that boiling point effects will be negligible.

- For each relative volatility surrogate, calculate the boiling point adjusted relative recovery (Ra) as:

  Equation 8

  $$Ra_\alpha = \frac{R_\alpha}{Rp_\beta}$$

- For each relative volatility surrogate group, calculate a linear regression (m, b, and lstderr) as in Equations 2,3, and 4 above:
  where
  x = ln rw for each surrogate in the group
  y = Ra for each surrogate in the group.

- For each surrogate and analyte in the sample:
  - Calculate the boiling point predicted recovery (Rp - Equation 7) and the relative volatility predicted recovery (Rp - Equation 9) :

    Equation 9

    $$Rp_\alpha = \ln rw \times m_\alpha + b_\alpha$$

where:
rw = relative volatility of the compound
The slope and intercept are for the calculated line segment that includes the given ln rw. If rw is less than the surrogate file minimum relative volatility, set rw equal to the minimum value. If rw is greater than the surrogate file maximum relative volatility, set rw equal to the maximum value.

- Calculate the total predicted recovery (R_T) as:

  Equation 10

  $$R_T = Rp_\beta \times Rp_\alpha$$

- The total predicted recovery deviation (Rdev) is calculated as:

  Equation 11

  $$Rdev = \sqrt{\left(\frac{lstderr_\beta}{Rp_\beta}\right)^2 + \left(\frac{lstderr_\alpha}{Rp_\alpha}\right)^2} \times R_T$$

  where
  lstderr and lstderr = regression standard errors for the boiling point and relative volatility predicted recoveries

- Calculate a response factor (RF) as:

  Equation 12

  $$RF = \frac{a}{R_T \times c}$$

  where

a = area counts
c = amount of compound (ng) in the spiked sample.
The response factor is the expected area counts/ng for this compound.

- The response factor deviation (RFdev) is:

  Equation 13

$$RFdev = \left(\frac{Rdev}{R_T} \right) RF$$

2. Quantitative Analysis - Sample Corrections

Following the instrument calibration, field samples can be corrected for boiling point and relative volatility effects (hopefully, independent of matrix effects). The end result is a corrected concentration (ng/volume) for each analyte in the sample. This section explains all calculations.

- For each surrogate, calculate the relative recovery using the average response factor from the calibration samples rather than a surrogate reference:

  Equation 14

$$R = \frac{a_s}{c_s \times \overline{RF}}$$

  where
  $\overline{RF}$ = average calibration response factor for the compound.

- Generate linear regressions to predict recoveries adjusted for boiling point and relative volatility, as shown above for calibrations (use Equation 14 everywhere Equation 1 is referenced in the calibration).
- For each analyte in the sample, calculate a total predicted recovery (R_T) from the regressions in the step above.
- For each analyte, calculate the recovered concentration (C) as:

Equation 15

$$C = \frac{a_s}{\overline{RF} \times R_T \times s}$$

where
s = sample size.

- The concentration deviation is calculated as:

Equation 16

$$Cdev = C\left(\frac{Rdev}{R_T}\right)$$

3. Quantitative Analysis - Check Calibration

A check calibration is performed to compare response factors from a sample run with those calculated by a calibration. This aids in determining the quality of the data. A check calibration consists of the following:

- Calculate response factors (RF) for each compound in a sample using the same procedures shown for a calibration above. Use Equation 14 in place of Equation 1 to calculate relative recoveries..
- The percent difference (%Diff) between the calibration and sample response factors is given by:

Equation 17

$$\%Diff = \left(\frac{RF_{check} - \overline{RF}}{\overline{RF}}\right) \times 100$$

where
RF_{check} = response factor for the sample file.

APPENDIX 6
SAMPLE 8261 COMPOUND LIBRARY LISTING

The following page is a sample listing of the 8261 compound library. This listing is printed from the compound edit dialog box (Figure 6) "Print" button. The columns and rows of this listing contain the following items:

- The compound number (N) in the 8261 library is equivalent to the position of the compound in the ChemStation quantitation library.
- The compound name (Name).
- The compound type (Type) – surrogate or analyte.
- The rest of the row lists the relative volatility – water (Rvw), boiling point (Bp), relative volatility – organic (Rvo), and partition coefficient (PartCoef.).. 999's in this row are default values meaning there has been no user entry made.
- The next row (C1 - C5) lists the calibration concentrations prepared for this compound. 99s in this row are default values. Surrogates are present at the same concentration in all samples, thus all entries are the same for surrogates.

Page: 1

Compound Library C:\HPCHEM\1\METHODS\TESTMETH.M\8261dir\lib8261.ini
Process Date: 5/28/2002 11:47:17 AM

N	Name	Type	Rvw C1	Bp C2	Rvo C3	PartCoef. C4	C5
1	diethylether-d10	Surrogate	32.50	35.00	999.00	0.00	
			250.00	250.00	250.00	250.00	250.00
2	acetone-C13	Surrogate	600.00	56.00	999.00	0.00	
			3100.00	3100.00	3100.00	3100.00	3100.00
3	methylenechloride-d2	Surrogate	11.10	40.00	999.00	0.00	
			250.00	250.00	250.00	250.00	250.00
4	nitromethane-C13	Surrogate	510.00	101.00	999.00	0.00	
			650.00	650.00	650.00	650.00	650.00
5	hexafluorobenzene	Surrogate	0.86	81.50	999.00	0.00	
			250.00	250.00	250.00	250.00	250.00
6	teterahydrofuran-d8	Surrogate	355.00	66.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
7	ethylacetate-c13	Surrogate	150.00	77.00	999.00	999.00	
			2500.00	2500.00	2500.00	2500.00	2500.00
8	pentafluorobenzene	Surrogate	1.51	85.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
9	benzene-d6	Surrogate	3.92	79.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
10	1,2-dichloroethane-d4	Surrogate	20.00	84.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
11	Fluorobenzene	Surrogate	3.50	85.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
12	1,4-difluorobenzene	Surrogate	3.83	88.50	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
13	1,2-dichloropropane-d6	Surrogate	11.00	95.00	999.00	999.00	
			200.00	200.00	200.00	200.00	200.00
14	1,4-dioxane-d8	Surrogate	5800.00	101.00	999.00	999.00	
			2400.00	2400.00	2400.00	2400.00	2400.00
15	toluene-d8	Surrogate	4.28	111.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
16	pyridine-d5	Surrogate	15000.00	115.00	999.00	999.00	
			12500.00	12500.00	12500.00	12500.00	12500.00
17	1,1,2-trichloroethane-d3	Surrogate	26.60	112.00	999.00	999.00	
			200.00	200.00	200.00	200.00	200.00
18	1,2-dibromoethane-d4	Surrogate	26.00	131.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
19	chlorobenzene-d5	Surrogate	6.27	131.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
20	o-xylene-d10	Surrogate	6.14	143.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
21	4-bromofluorobenzene	Surrogate	8.05	152.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
22	bromobenzene-d5	Surrogate	7.93	155.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
23	aniline-13C6	Surrogate	13700.00	184.00	999.00	999.00	
			12800.00	12800.00	12800.00	12800.00	12800.00
24	1,2-dichlorobenzene-d4	Surrogate	8.03	181.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
25	decafluorobiphenyl	Surrogate	3.03	206.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
26	nitrobenzene-d5	Surrogate	87.50	210.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
27	acetophenone-d5	Surrogate	161.00	202.00	999.00	999.00	
			1040.00	1040.00	1040.00	1040.00	1040.00
28	1,2,4-trichlorobenzene-d3	Surrogate	7.88	213.00	999.00	999.00	
			250.00	250.00	250.00	250.00	250.00
29	naphthalene-d8	Surrogate	18.00	217.00	999.00	999.00	
			500.00	500.00	500.00	500.00	500.00
30	1-methylnaphthalene-d10	Surrogate	67.00	245.00	999.00	0.00	
			1050.00	1050.00	1050.00	1050.00	1050.00
31	dichlorodifluoromethane	Analyte	0.07	-30.00	999.00	0.00	
			100.00	80.00	60.00	40.00	20.00
32	chloromethane	Analyte	1.37	-24.00	999.00	999.00	
			100.00	80.00	60.00	40.00	20.00
33	bromomethane	Analyte	1.82	4.00	999.00	999.00	
			100.00	80.00	60.00	40.00	20.00
34	chloroethane	Analyte	1.01	12.00	999.00	999.00	
			100.00	80.00	60.00	40.00	20.00
35	trichlorofluoromethane	Analyte	0.20	24.00	999.00	999.00	
			100.00	80.00	60.00	40.00	20.00

APPENDIX 7
CALIBRATION REPORT

The calibration report is printed from the create calibration or review calibration forms (Figures 10 and 12), or from the 'Print Calibration File' option of the Method 8261 menu. A sample calibration report is included in this appendix. It shows the response factors (area counts/ng) for each compound in the calibration standard samples.

The report header lists:

- The calibration file, if the calibration has been saved.
- The date and time the report was printed.
- The surrogate file.
- The 8261 library file.
- The file names for the standard samples included in the calibration.
- The surrogate reference file.

For 1 to N compounds, the report shows:

- Compound name and the concentrations (ng) of the compound in each standard sample.
- For each calibration standard sample, the response factor (resp) and the recovery percent deviation (%dev).
- The average response factor (Ave), standard deviation of the response factors (dev), and percent standard deviation (rel dev).

Calibration Curve Report

Page: 1

Calibration File: A:\MTBE-5PTEDITED.CAL
Process Date: 5/30/2002 10:06:42 AM
Surrogate Groupings File: C:\HPCHEM\1\METHODS\MTBE_1.m\8261dir\Surrogates\surr0102.ini
Compound Library File: C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini
Files: C:\HPCHEM\1\DATA\aJANUARY\01280203.D, C:\HPCHEM\1\DATA\aJANUARY\01280205.D, C:\HPCHEM\1\DATA\aJANUARY\01280206.D, C:\HPCHEM\1\DATA\aJANUARY\01280207.D, C:\HPCHEM\1\DATA\aJANUARY\01280208.D,

Reference File: C:\HPCHEM\1\DATA\aJANUARY\01280202.D

	compound(concentartions)	Standard1 resp(%dev)	Standard2 resp(%dev)	Standard3 resp(%dev)	Standard4 resp(%dev)	Standard5 resp(%dev)	Results Ave	dev	rel dev
1	diethylether-d10 (250,250,250,250,250)	2013.74(4.4%)	1839.34(2.5%)	1910.58(3.6%)	1867.33(1.7%)	3200.52(11.2%)	2166.30	581.93	26.9%
2	acetone-C13 (3100,3100,3100,3100,3100)	1115.43(6.4%)	1060.88(12.5%)	1209.20(17.7%)	1067.35(1.9%)	1012.44(9.8%)	1093.06	74.47	6.8%
3	methylenechloride-d2 (250,250,250,250,250)	1119.29(2.6%)	1206.63(1.4%)	1240.04(3.2%)	1178.22(2.6%)	1884.52(2.9%)	1325.74	315.49	23.8%
4	nitromethane-C13 (650,650,650,650,650)	3619.30(6.3%)	3491.60(12.5%)	3097.90(17.2%)	2687.06(2.0%)	1806.43(38.5%)	2940.46	731.37	24.9%
5	hexafluorobenzene (250,250,250,250,250)	6289.85(0.0%)	6288.96(0.2%)	6283.32(0.8%)	6289.80(0.0%)	6372.23(4.6%)	6304.83	37.77	0.6%
6	teterahydrofuran-d8 (250,250,250,250,250)	1402.18(4.4%)	1370.78(2.5%)	1286.12(3.6%)	1319.52(1.7%)	1490.32(11.2%)	1373.78	79.10	5.8%
7	ethylacetate-c13 (2500,2500,2500,2500,2500)	905.71(4.4%)	881.99(2.5%)	817.83(3.6%)	776.08(1.7%)	939.77(11.2%)	864.28	66.46	7.7%
8	pentafluorobenzene (250,250,250,250,250)	9078.88(0.1%)	9224.13(0.8%)	8934.80(0.8%)	9062.77(0.2%)	9458.63(9.1%)	9151.84	199.82	2.2%
9	benzene-d6 (250,250,250,250,250)	15320.70(2.6%)	15325.47(1.4%)	15062.32(3.4%)	15476.62(2.3%)	23243.86(2.8%)	16885.79	3557.39	21.1%
10	1,2-dichloroethane-d4 (250,250,250,250,250)	6868.13(2.6%)	6794.14(1.4%)	6576.10(3.2%)	6614.75(2.6%)	7275.04(2.9%)	6825.63	279.06	4.1%
11	Fluorobenzene (250,250,250,250,250)	16033.03(0.1%)	16065.74(0.8%)	16209.97(0.8%)	16034.85(0.2%)	13655.66(10.0%)	15599.85	1089.27	7.0%
12	1,4-difluorobenzene (250,250,250,250,250)	15135.76(0.1%)	15106.98(0.8%)	14982.32(0.8%)	15134.17(0.2%)	17202.86(10.2%)	15512.42	947.09	6.1%
13	1,2-dichloropropane-d6 (200,200,200,200,200)	3980.37(2.5%)	3850.96(1.6%)	3892.06(3.1%)	3871.56(2.6%)	3464.12(13.6%)	3811.82	200.52	5.3%
14	1,4-dioxane-d8 (2400,2400,2400,2400,2400)	72.87(6.3%)	54.40(12.5%)	76.44(17.2%)	61.65(2.0%)	66.43(39.9%)	66.36	8.79	13.2%
15	toluene-d8 (250,250,250,250,250)	13839.92(2.6%)	13863.53(1.6%)	13641.46(3.4%)	13910.66(2.3%)	19389.69(9.6%)	14929.05	2495.69	16.7%
16	pyridine-d5 (12500,12500,12500,12500,12500)	98.00(6.5%)	328.99(12.7%)	142.52(17.9%)	312.45(2.1%)	281.97(40.6%)	232.79	105.28	45.2%
17	1,1,2-trichloroethane-d3 (200,200,200,200,200)	5504.68(4.4%)	5470.47(2.6%)	5488.66(3.6%)	5602.02(1.7%)	5622.76(24.6%)	5537.72	69.62	1.3%
18	1,2-dibromoethane-d4 (250,250,250,250,250)	783.52(2.7%)	790.19(1.7%)	792.76(3.4%)	773.46(2.8%)	749.81(16.1%)	777.95	17.41	2.2%
19	chlorobenzene-d5 (250,250,250,250,250)	7322.73(2.7%)	7166.30(1.6%)	7456.34(3.4%)	7339.50(2.8%)	7367.07(12.4%)	7330.39	105.21	1.4%
20	o-xylene-d10 (250,250,250,250,250)	16650.37(2.8%)	17065.66(1.7%)	16298.05(3.7%)	16606.83(2.5%)	16560.03(12.4%)	16636.19	276.43	1.7%
21	4-bromofluorobenzene (250,250,250,250,250)	5868.20(2.8%)	5865.63(1.6%)	5732.90(3.6%)	5799.23(2.9%)	5671.93(13.2%)	5787.58	85.28	1.5%
22	bromobenzene-d5 (250,250,250,250,250)	6700.99(2.8%)	6565.06(1.7%)	6673.87(3.6%)	6600.52(2.9%)	6374.49(13.2%)	6582.99	128.73	2.0%
23	aniline-13C6 (12800,12800,12800,12800,12800)	22.02(6.9%)	33.33(13.3%)	9.16(20.3%)	26.86(7.1%)	22.41(20.3%)	22.75	8.86	38.9%

APPENDIX 8
SURROGATE REPORT

The surrogate report depicts the calibration 'curves' (set of linear regressions) for a sample. These curves characterize the boiling point and relative volatility effects for sample surrogates. The two pages of a surrogate report are explained in this appendix, along with sample calculations based on equations in Appendix 5.

Page 1 of the surrogate report includes the following:

- The report header lists:
  - The report date and time.
  - The 8261 library file.
  - The surrogate data file.
  - The sample data path – the actual data file is the path name + '\results.ini'. The Method 8261 program creates results.ini. This file contains area counts.
  - The surrogate reference data path – the actual data file is the path name + '\results.ini'.

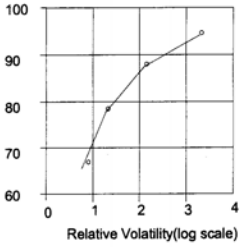
- First pass surrogates
  - The first pass surrogate groupings are shown. First pass surrogate groupings always consist of two surrogates. In this example, there are four first pass surrogates comprising three first pass groups. The surrogates are listed, followed by the boiling point (BP) and relative volatility-water (rw).
  - The measured recovery (Meas.) is calculated as shown in Appendix 5, Equation 1 or 14 (depending on whether the surrogate reports is for a calibration or a quantitation - this example report is from a quantitation, so Equation 14 is used), with the final result expressed as a percent. For hexafluorobenzene:
    - a_s (from c:\hpchem\1\data\aJanuary\01280205.D\results.ini) = 1045950
    - c_s (from lib8261.ini) = 250
    - $\overline{RF}$ = 6304.83 (the average response factor for hexafluorobenzene - shown in the Calibration Report - Appendix 6).

$$66.36 = \frac{1045950/250}{6304.83} \times 100$$

Process Date:	5/30/2002 10:22:29 AM	Surrogate Report - Page: 1
Compound Library File:	C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini	
Surrogate Groupings File:	C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\SURROGATES\SURR0102.INI	
Data File:	C:\HPCHEM\1\DATA\TestMeth\01280205.D	
Calibration File:	A:\MTBE-5PTEDITED.CAL	

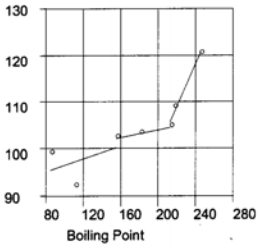
First Pass relative Volatility (Log) vs. Recovery
(Used to Estimate Rel vol effects on BP Surrogates)

Compound	BP	rw	Meas.,	Recovery(%)	Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	66.36	, 66.36	8.279e-02	0.6761	0.00
Fluorobenzene	85	3.5	77.98	, 77.98			
Fluorobenzene	85	3.5	77.98	, 77.98	5.458e-02	0.7114	0.00
1,2-dichloroethane-d4	84	20	87.49	, 87.49			
1,2-dichloroethane-d4	84	20	87.49	, 87.49	2.317e-02	0.8055	0.00
teterahydrofuran-d8	66	355	94.16	, 94.16			



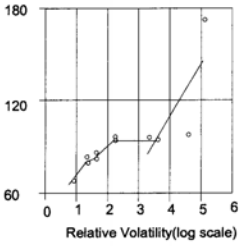
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) -- Boiling point range(85.00 - 231.00)

Compound	BP	rw	Meas.,	Recovery(%)	Slope	Int.	Err%
pentafluorobenzene	85	1.51	70.16	, 98.79	6.627e-04	0.8983	6.55
toluene-d8	111	4.28	72.67	, 91.90			
bromobenzene-d5	155	7.93	84.15	, 102.07			
bromobenzene-d5	155	7.93	84.15	, 102.07	4.046e-04	0.9575	0.12
1,2-dichlorobenzene-d4	181	8.03	84.96	, 102.97			
1,2,4-trichlorobenzene-d3	213	7.88	86.04	, 104.41			
1,2,4-trichlorobenzene-d3	213	7.88	86.04	, 104.41	4.659e-03	6.247e-02	1.63
naphthalene-d8	217	18	94.36	, 108.56			
1-methylnaphthalene-d10	245	67	108.56	, 120.23			



Recovery(bp corrected) vs. Relative Volatility (Log) -- Relative Volatility range(0.86 - 9327.38)

Compound	BP	rw	Meas.,	Recovery(%)	Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	66.36	, 66.36	9.140e-02	0.6788	3.23
Fluorobenzene	85	3.5	77.98	, 81.68			
1,4-difluorobenzene	88.5	3.83	74.59	, 77.94			
Fluorobenzene	85	3.5	77.98	, 81.68	4.124e-02	0.7468	2.91
1,4-difluorobenzene	88.5	3.83	74.59	, 77.94			
o-xylene-d10	143	6.14	83.83	, 84.42			
chlorobenzene-d5	131	6.27	79.23	, 80.42			
o-xylene-d10	143	6.14	83.83	, 84.42	7.577e-02	0.6861	2.46
chlorobenzene-d5	131	6.27	79.23	, 80.42			
1,2-dibromoethane-d4	131	26	93.24	, 94.65			
1,1,2-trichloroethane-d3	112	26.6	89.65	, 92.18			
1,2-dibromoethane-d4	131	26	93.24	, 94.65	-3.195e-04	0.9359	1.42
1,1,2-trichloroethane-d3	112	26.6	89.65	, 92.18			
teterahydrofuran-d8	66	355	94.16	, 94.16			
acetone-C13	56	600	92.76	, 92.76			
teterahydrofuran-d8	66	355	94.16	, 94.16	0.1618	-1.011e-01	30.89
acetone-C13	56	600	92.76	, 92.76			
1,4-dioxane-d8	101	5800	92.62	, 95.96			
pyridine-d5	115	15000	166.74	, 171.10			



- The slope, intercept (Int.), and regression error express as a percent (Err%) are calculated for each first pass group using X = measured recovery (not as a percent) and Y = ln(rw). Since the linear regression has only two points, the error is 0.
  NOTE: There is a distortion in the graphs introduced by the fact that results in this report are expressed in percent, but actual calculations are not.
- The predicted recovery (Recovery(%)) is predicted from the curve (Appendix 5, Equation 5). Since hexafluorobenzene is an endpoint of the curve, the predicted recovery is the same as the measured recovery.

- Boiling point surrogates
  - For pentafluorobenzene, the measured recovery is:

$$70.16 = \frac{1605270/250}{9151.84} \times 100$$

  - The predicted recovery is the measured recovery divided by the predicted recovery for pentafluorobenzene using the first pass curves (Appendix 5, Equations 5 and 6). Use the regression for first pass group 1, as the relative volatility of 1.51 falls within that group:

$$98.79 = \frac{70.16}{\ln 1.51 \times (0.08279) + 0.6761}$$

  - The slope, intercept, and regression error are calculated for each boiling point group defined in the surrogate file. X = predicted recovery (not percent) and Y = boiling point (BP).

- Relative volatility surrogates
  - For hexafluorobenzene, the measured recovery is 66.36.
  - The predicted recovery is the measured recovery divided by the predicted recovery for hexafluorobenzene using the boiling point curve. In Appendix 5, it is noted that for boiling points less than the lowest boiling point surrogate (in this case, 85°C), the predicted recovery is 1 (100%). Thus the predicted recovery for hexafluorobenzene (bp 81.5°C) is the same as the measured recovery.

- Pyridine-d5 has a boiling point of 115°C. The predicted recovery for pyridine-d5, using the first boiling point group, is:

$$171.10 = \frac{166.74}{115 \times (0.0006627) + 0.8983}$$

- The slope, intercept, and regression error are calculated for each relative volatility group defined in the surrogate file. X = predicted recovery (not percent) and Y = ln rw.

Page 2 of the surrogate report shows predicted results for check surrogates. It includes the following information:

- The report header lists:
  - The report date and time.
  - The 8261 library file.
  - The surrogate data file.
  - The sample data path – the actual data file is the path name + '\results.ini'.
  - The calibration file.

- The check surrogates are grouped by physical properties. For each check surrogate, the following information is shown:
  - Compound name
  - Boiling point
  - Relative volatility-water
  - The relative recovery (Recovery) is based on the sample area counts and the calibration response factor. For nitromethane-C13, the calibration response factor is shown in Appendix 6:

$$111.7 = \frac{2135560 / 650}{2940.46} \times 100$$

  - The boiling point predicted recovery and error (B.P. Predict/err) are found using boiling point group one:

$$96.5 = \left(101 \times 0.0006627 + 0.8983\right) \times 100$$

Page: 2

Process Date:	7/24/2002 4:06:57 PM
Compound Library File:	C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini
Surrogate Groupings File:	C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\SURROGATES\ANTEON_SURR0102.INI
Data File:	C:\HPCHEM\1\DATA\aJANUARY\01280205.D
Calibration File:	C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\CALIBRATION\MTBE-5PT.CAL

Check Surrogate Determinations

Volatile Compound Surrogates(boiling points<159 and rw<100)

Compound	BP	RW	Recovery	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
diethylether-d10	35	32.50	76.8	100.0	0.0	93.5	1.4	93.5	1.4	82.2	1.2
methylenechloride-d2	40	11.10	76.0	100.0	0.0	86.9	2.5	86.9	2.5	87.5	2.5
benzene-d6	79	3.92	70.3	100.0	0.0	80.3	2.9	80.3	2.9	87.5	3.2
1,2-dichloropropane-d6	95	11.00	83.7	96.1	6.6	86.8	2.5	83.4	6.2	100.4	7.4
4-bromofluorobenzene	152	8.05	85.4	99.9	6.6	84.4	2.5	84.3	6.1	101.3	7.3
Group Averages										91.8	4.3

Non-Purgeable Volatile Compound Surrogates(boiling points<159 and rw>100)

Compound	BP	RW	Recovery	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
nitromethane-C13	101	510.00	111.7	96.5	6.6	90.8	30.9	87.6	30.4	127.5	44.2
ethylacetate-c13	77	150.00	94.9	100.0	0.0	93.4	1.4	93.4	1.4	101.5	1.5
pyridine-d5	115	15000.00	166.7	97.5	6.6	137.8	30.9	134.3	31.4	124.1	29.1
Group Averages										117.7	24.9

Semi-Volatile Compound Surrogates(boiling points>158)

Compound	BP	RW	Recovery	B.P.Predict/err		R.V.Predict/err		Total Predict/err		Recovery/err	
aniline-13C6	184	13700.00	181.6	103.2	0.1	137.8	30.9	142.2	31.9	127.7	28.6
decafluorobiphenyl	206	3.03	81.1	104.1	0.1	78.0	3.2	81.2	3.4	99.9	4.1
nitrobenzene-d5	210	87.50	91.6	104.2	0.1	93.4	1.4	97.4	1.5	94.0	1.4
acetophenone-d5	202	161.00	115.8	103.9	0.1	93.4	1.4	97.1	1.5	119.3	1.8
naphthalene-d8	217	18.00	94.4	107.3	1.6	90.5	2.5	97.2	3.0	97.1	3.0
Group Averages										107.6	7.8

$$9.9 = \sqrt{\left(\frac{.066}{.965}\right)^2 + \left(\frac{.055}{.734}\right)^2} \times 0.978 \times 100$$

error = .0655

- The relative volatility predicted recovery and error (R.V. Predict/err) are found using relative volatility group five (because groups 4 and 5 share endpoints, the low endpoint of group 5 is 477.5 - see Appendix 3):

$$90.8 = \left(\ln 510 \times (0.1618) + -0.1011\right) \times 100$$

error = .309

- The total predicted recovery (Total Predict) is the product of the boiling point and relative volatility predicted recoveries:

$$87.6 = \left(0.965 \times 0.90.8\right) \times 100$$

- The total predicted error (in percent) is given by Equation 11, Appendix 5:

$$30.4 = \sqrt{\left(\frac{.0655}{.965}\right)^2 + \left(\frac{.309}{.908}\right)^2} \times .876 \times 100$$

- The corrected recovery (Recovery) is the measured recovery divided by the predicted recovery:

$$127.5 = \frac{111.7}{87.6}$$

- The corrected recovery error (in percent) is given by:

$$44.2 = \sqrt{\left(\frac{.0655}{.965}\right)^2 + \left(\frac{.309}{.908}\right)^2} \times 1.275 \times 100$$

- The group averages are arithmetic means.

APPENDIX 9
QUANTITATION REPORT

The quantitation report shows correction results for analytes only. There are two version of this report – a printout and a semicolon delimited text file – that are printed from the Process Files dialog box (Figure 16). The printout includes the following information:

- Report header
  - 'File Identification' is the sample file being reported. This is a directory path. The file which contains the sample area counts is the path + '\results.ini'.
  - The date and time the report was printed.
  - The sample size (ml or g).
  - The sample type.
  - Comments.
  - The calibration file used for calculations.
  - The 8261 library file used.
  - The surrogate file used to define surrogate groups.

- For each analyte:
  - The compound name.
  - The concentration (ng/volume) of the analyte in the sample.
  - The concentration deviation (ng/volume).
  - The predicted total recovery.
  - The total recovery deviation.

Calculations used in this report are explained in Appendix 5, section 2. The specific surrogate report for the quantitation must be used to duplicate the values in the report. See Appendix 8 for an explanation of the surrogate report.

The second example listing is the semicolon delimited text file. This report is automatically saved in each data directory in the Process Files dialog list box (see section 3.1.2.15 – "Process" button). It can also be displayed in a NotePad window (section 2.1.2.15 – "Review" button). This report can be imported into a spreadsheet for any desired further processing. The listing includes column headings (PM refers to the ± sign).

Quantitation Report

Page: 1

File Identification: C:\HPCHEM\1\DATA\aJANUARY\01280205.D
Process Date: 7/24/2002 4:06:57 PM
Sample Size: 2
Sample Type:
Comment 1:
Comment 2:

Calibration File: C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\CALIBRATION\MTBE-5PT.CAL
Compound Library File: C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini
Surrogate Groups: C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\SURROGATES\ANTEON_SURR0102.

Compound	ng/mL	Error	Pred.Recovery	±Deviation
31: dichlorodifluoromethane	9.6	± 0.469	66.50	± 3.23
32: chloromethane	8.40	± 0.384	70.76	± 3.23
33: vinylchloride	8.62	± 0.419	66.50	± 3.23
34: bromomethane	11.4	± 0.502	73.35	± 3.23
35: chloroethane	8.39	± 0.399	67.97	± 3.23
36: trichlorofluoromethane	10.8	± 0.527	66.50	± 3.23
37: ether	26.9	± 0.408	93.47	± 1.42
38: acetone	11.3	± 3.74	93.41	± 30.89
39: 1,1-dichloroethene	9.6	± 0.467	66.50	± 3.23
40: iodomethane	21.8	± 0.934	75.45	± 3.23
41: allylchloride	9.5	± 0.436	70.55	± 3.23
42: acetonitrile	61.5	± 20.68	91.86	± 30.89
43: methylenechloride	7.78	± 0.222	86.14	± 2.46
44: MTBE	5.67	± 0.086	93.48	± 1.42
45: acrylonitrile	33.3	± 0.506	93.42	± 1.42
46: trans-1,2-dichloroethene	11.1	± 0.475	75.49	± 3.23
47: 1,1-dichloroethane	9.5	± 0.345	80.51	± 2.91
48: methacrylonitrile	37.6	± 2.64	89.51	± 6.27
49: 2-butanone	53.2	± 16.87	97.45	± 30.89
50: propionitrile	27.8	± 8.21	103.34	± 30.56
51: 2,2-dichloropropane	11.2	± 0.511	70.76	± 3.23
52: cis-1,2-dichloroethene	15.8	± 0.564	81.58	± 2.91
53: chloroform	16.6	± 0.494	82.67	± 2.46
54: bromochloromethane	16.8	± 0.464	89.33	± 2.46
55: 1,1,1-trichloroethane	9.6	± 0.443	70.35	± 3.23
56: 1,1-dichloropropene	17.6	± 1.47	64.53	± 5.38
57: carbontetrachloride	8.19	± 0.398	66.50	± 3.23
58: 1,2-dichloroethane	15.8	± 0.429	90.80	± 2.46
59: benzene	14.6	± 0.596	79.46	± 3.23
60: trichloroethene	16.7	± 1.35	72.32	± 5.84
61: 1,2-dichloropropane	16.9	± 1.25	83.41	± 6.16
62: methylmethacrylate	37.3	± 2.60	90.20	± 6.28
63: bromodichloromethane	18.6	± 1.37	83.95	± 6.21
64: 1,4-dioxane	127	± 31.48	125.47	± 31.01
65: dibromomethane	16.7	± 1.22	89.20	± 6.52
66: 4-methyl-2-pentanone	76.3	± 5.25	91.18	± 6.28
67: trans-1,3-dichloropropene	83.8	± 6.11	86.23	± 6.28
68: toluene	13.9	± 1.06	78.01	± 5.97
69: pyridine	89.6	± 20.97	134.40	± 31.45
70: cis-1,3-dichloropropene	83.0	± 6.05	88.17	± 6.43
71: ethylmethacrylate	32.0	± 2.21	91.21	± 6.28
72: n-nitrosodimethylamine	171	± 11.52	93.47	± 6.29
73: 2-hexanone	35.7	± 2.44	91.86	± 6.28
74: 1,1,2-trichloroethane	16.0	± 1.16	90.92	± 6.57
75: tetrachloroethene	14.8	± 1.20	69.62	± 5.63

Compound	ng/mL	Error	Pred.Recovery	±Deviation
76: 1,3-dichloropropane	16.8	± 1.21	90.91	± 6.55
77: dibromochloromethane	16.1	± 1.16	88.99	± 6.43
78: 2-picoline	38.2	± 9.24	130.56	± 31.61
79: 1,2-dibromoethane	17.3	± 1.18	92.15	± 6.28
80: chlorobenzene	16.4	± 1.24	80.95	± 6.10
81: 1,1,1,2-tetrachloroethane	16.6	± 1.20	85.86	± 6.21
82: ethylbenzene	15.0	± 1.17	78.67	± 6.12
83: n-nitroso-methyl-ethylamine	83.1	± 22.91	114.78	± 31.64
84: m,p-xylenes	7.50	± 0.566	79.48	± 6.00
85: styrene	16.0	± 1.16	82.75	± 5.98
86: o-xylene	16.4	± 1.23	81.23	± 6.09
87: isopropylbenzene	15.9	± 1.24	77.05	± 6.00
88: bromoform	16.4	± 1.16	92.29	± 6.54
89: cis-1,4-dichloro-2-butene	71.2	± 4.80	93.39	± 6.29
90: n-nitrosodiethylamine	315	± 76.48	131.10	± 31.79
91: 1,1,2,2-tetrachloroethane	17.5	± 1.18	93.02	± 6.29
92: 1,2,3-trichloropropane	18.6	± 0.283	95.43	± 1.45
93: propylbenzene	15.2	± 0.648	77.65	± 3.30
94: trans-1,4-dichloro-2-butene	66.7	± 1.02	95.40	± 1.45
95: 1,3,5-trimethylbenzene	15.0	± 0.605	81.90	± 3.31
96: bromobenzene	16.3	± 0.477	86.00	± 2.51
97: 2-chlorotoluene	15.1	± 0.547	82.19	± 2.98
98: 4-chlorotoluene	15.8	± 0.567	82.99	± 2.98
99: pentachloroethane	16.3	± 0.455	90.19	± 2.52
100: tert-butylbenzene	15.4	± 0.648	79.01	± 3.32
101: 1,2,4-trimethylbenzene	15.9	± 0.571	82.97	± 2.99
102: sec-butylbenzene	15.1	± 0.662	75.82	± 3.32
103: aniline	146	± 32.73	142.21	± 31.88
104: p-isopropyltoluene	15.4	± 0.651	78.66	± 3.34
105: 1,3-dichlorobenzene	16.5	± 0.586	84.12	± 2.99
106: 1,4-dichlorobenzene	16.8	± 0.596	84.45	± 2.99
107: n-butylbenzene	15.4	± 0.675	75.97	± 3.34
108: 1,2-dichlorobenzene	16.6	± 0.485	86.79	± 2.54
109: n-nitrosodi-n-propylamine	10.1	± 2.69	120.58	± 32.15
110: acetophenone	28.9	± 0.441	97.12	± 1.48
111: o-toluidine	161	± 36.11	143.11	± 32.08
112: 1,2-dibromo-3-chloropropane	17.1	± 0.261	96.91	± 1.48
113: hexachlorobutadiene	16.3	± 0.750	79.35	± 3.65
114: nitrobenzene	28.9	± 0.441	97.45	± 1.48
115: 1,2,4-trichlorobenzene	17.1	± 0.566	89.11	± 2.95
116: naphthalene	16.5	± 0.515	96.97	± 3.03
117: 1,2,3-trichlorobenzene	16.9	± 0.541	93.78	± 3.01
118: 2-methylnaphthalene	34.2	± 0.713	106.41	± 2.22
119: 1-methylnaphthalene	35.2	± 0.735	106.41	± 2.22

```
                                        sample.prn
Quantitation Report

File Identification: C:\HPCHEM\1\DATA\aJANUARY\01280205.D;Calibration
File:C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\CALIBRATION\MTBE-5PT.CAL
Process Date: 7/27/2002 3:29:48 PM;Compound
Library:C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini
Sample Size: 2.00;Surrogate Groups:
C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\SURROGATES\ANTEON_SURR0102.INI
Sample Type:
Comment 1:
Comment 2:

Compound#;Compound;ng/mL;PM;Error;Pred.Recovery;PM;Deviation
31;dichlorodifluoromethane;9.64;±;0.469;66.50;±;3.23;
32;chloromethane;8.40;±;0.384;70.76;±;3.23;
33;vinylchloride;8.62;±;0.419;66.50;±;3.23;
34;bromomethane;11.38;±;0.502;73.35;±;3.23;
35;chloroethane;8.39;±;0.399;67.97;±;3.23;
36;trichlorofluoromethane;10.84;±;0.527;66.50;±;3.23;
37;EthylEther;26.86;±;0.408;93.47;±;1.42;
38;acetone;11.30;±;3.735;93.41;±;30.89;
39;1,1-dichloroethene;9.61;±;0.467;66.50;±;3.23;
40;iodomethane;21.79;±;0.934;75.45;±;3.23;
41;allylchloride;9.51;±;0.436;70.55;±;3.23;
42;acetonitrile;61.50;±;20.682;91.86;±;30.89;
43;methylenechloride;7.78;±;0.222;86.14;±;2.46;
44;MTBE;5.67;±;0.086;93.48;±;1.42;
45;acrylonitrile;33.28;±;0.506;93.42;±;1.42;
46;trans-1,2-dichloroethene;11.10;±;0.475;75.49;±;3.23;
47;1,1-dichloroethane;9.53;±;0.345;80.51;±;2.91;
48;methacrylonitrile;37.63;±;2.637;89.51;±;6.27;
49;2-butanone;53.21;±;16.866;97.45;±;30.89;
50;propionitrile;27.77;±;8.211;103.34;±;30.56;
51;2,2-dichloropropane;11.20;±;0.511;70.76;±;3.23;
52;cis-1,2-dichloroethene;15.81;±;0.564;81.58;±;2.91;
53;chloroform;16.60;±;0.494;82.67;±;2.46;
54;bromochloromethane;16.82;±;0.464;89.33;±;2.46;
55;1,1,1-trichloroethane;9.63;±;0.443;70.35;±;3.23;
56;1,1-dichloropropene;17.62;±;1.468;64.53;±;5.38;
57;carbontetrachloride;8.19;±;0.398;66.50;±;3.23;
58;1,2-dichloroethane;15.81;±;0.429;90.80;±;2.46;
59;benzene;14.65;±;0.596;79.46;±;3.23;
60;trichloroethene;16.65;±;1.345;72.32;±;5.84;
61;1,2-dichloropropane;16.92;±;1.249;83.41;±;6.16;
62;methylmethacrylate;37.33;±;2.597;90.20;±;6.28;
63;bromodichloromethane;18.56;±;1.373;83.95;±;6.21;
64;1,4-dioxane;127.36;±;31.477;125.47;±;31.01;
65;dibromomethane;16.73;±;1.223;89.20;±;6.52;
66;4-methyl-2-pentanone;76.27;±;5.252;91.18;±;6.28;
67;trans-1,3-dichloropropene;83.82;±;6.109;86.23;±;6.28;
68;toluene;13.90;±;1.064;78.01;±;5.97;
69;pyridine;89.60;±;20.967;134.40;±;31.45;
70;cis-1,3-dichloropropene;82.96;±;6.051;88.17;±;6.43;
71;ethylmethacrylate;32.04;±;2.206;91.21;±;6.28;
72;n-nitrosodimethylamine;171.34;±;11.523;93.47;±;6.29;
73;2-hexanone;35.67;±;2.439;91.86;±;6.28;
74;1,1,2-trichloroethane;16.03;±;1.159;90.92;±;6.57;
75;tetrachloroethene;14.81;±;1.199;69.62;±;5.63;
76;1,3-dichloropropane;16.77;±;1.209;90.91;±;6.55;
77;dibromochloromethane;16.11;±;1.164;88.99;±;6.43;
78;2-picoline;38.17;±;9.242;130.56;±;31.61;
79;1,2-dibromoethane;17.34;±;1.182;92.15;±;6.28;
80;chlorobenzene;16.41;±;1.236;80.95;±;6.10;
                                        Page 1
```

APPENDIX 10
CHECK CALIBRATION REPORT

This report compares analyte recoveries from a sample run with the analyte recoveries in the calibration. It includes the following information:

- Report header
  - The calibration file used for calculations.
  - The date and time the report was printed.
  - The surrogate file containing the surrogate groups used.
  - The check standard file being reported. This is a directory path. The file which contains the sample area counts is the path + '\results.ini'.
- For each analyte:
  - The response factor shown in the calibration file shown in the header.
  - The response factor deviation listed the calibration file.
  - The concentration (ng) of the analyte in the check standard.
  - The predicted recovery for the check standard.
  - The recovery deviation for the check standard.
  - The response factor for the check standard.
  - The percent difference between the calibration response factor and the check standard response factor.

Calculations in this report are shown in Appendix 5, section 3. The specific surrogate report for the check calibration must be used to duplicate the values in the report. See Appendix 8 for an explanation of the surrogate report.

Check Calibration Report Page: 1

Calibration File: A:\MTBE-5PTEDITED.CAL
Process Date: 5/30/2002 10:22:29 AM
Surrogate Groupings File: C:\HPCHEM\1\METHODS\MTBE_1.M\8261DIR\SURROGATES\SURR0102.INI
Check Standard File: C:\HPCHEM\1\DATA\TestMeth\01280205.D

	Compound	Calibration response	Calibration deviation	Check Standard (concentrations)	Check Standard Pred_Rec	Check Standard R_Dev	Check Standard response	Difference %
31	dichlorodifluoromethane	1998.82	1000.61	(25.00)	66.50	3.23	2798.89	40.0%
32	chloromethane	1776.91	657.98	(25.00)	70.76	3.23	2269.19	27.7%
33	vinylchloride	1495.74	701.09	(25.00)	66.50	3.23	2121.85	41.9%
34	bromomethane	1408.32	724.61	(25.00)	73.35	3.23	2260.27	60.5%
35	chloroethane	1968.80	947.94	(25.00)	67.97	3.23	2125.23	7.9%
36	trichlorofluoromethane	3792.57	1645.28	(25.00)	66.50	3.23	5476.46	44.4%
37	ether	1364.27	611.17	(50.00)	93.47	1.42	1918.57	40.6%
38	acetone	11807.80	19640.52	(50.00)	93.41	30.89	4381.21	-62.9%
39	1,1-dichloroethene	2377.03	987.76	(25.00)	66.50	3.23	3320.87	39.7%
40	iodomethane	1744.34	792.61	(50.00)	75.45	3.23	2632.43	50.9%
41	allylchloride	1118.82	490.26	(25.00)	70.55	3.23	1633.87	46.0%
42	acetonitrile	577.73	270.56	(100.00)	91.86	30.89	799.88	38.5%
43	methylenechloride	13268.63	16424.08	(25.00)	86.14	2.46	6252.89	-52.9%
44	MTBE	1329.63	0.00	(20.00)	93.48	1.42	198.22	-85.1%
45	acrylonitrile	1560.80	825.74	(50.00)	93.42	1.42	2077.87	33.1%
46	trans-1,2-dichloroethene	2303.47	1217.42	(25.00)	75.49	3.23	3554.61	54.3%
47	1,1-dichloroethane	7251.29	7898.19	(25.00)	80.51	2.91	5528.23	-23.8%
48	methacrylonitrile	1928.91	815.96	(50.00)	89.51	6.27	2903.63	50.5%
49	2-butanone	1017.01	631.68	(100.00)	97.45	30.89	1147.84	12.9%
50	propionitrile	379.61	389.11	(50.00)	103.34	30.56	644.48	69.8%
51	2,2-dichloropropane	4032.82	3210.20	(25.00)	70.76	3.23	3611.94	-10.4%
52	cis-1,2-dichloroethene	2627.87	1236.13	(25.00)	81.58	2.91	3778.17	43.8%
53	chloroform	5732.93	2254.23	(25.00)	82.67	2.46	7614.17	32.8%
54	bromochloromethane	1736.51	772.87	(25.00)	89.33	2.46	2336.65	34.6%
55	1,1,1-trichloroethane	4881.39	2403.40	(25.00)	70.35	3.23	7394.76	51.5%
56	1,1-dichloropropene	3110.87	1417.89	(25.00)	64.53	5.38	4779.24	53.6%
57	carbontetrachloride	8512.17	10698.15	(25.00)	66.50	3.23	5578.72	-34.5%
58	1,2-dichloroethane	5207.66	2598.08	(25.00)	90.80	2.46	6586.87	26.5%
59	benzene	8713.15	4564.22	(25.00)	79.46	3.23	13597.54	56.1%
60	trichloroethene	3737.70	1700.06	(25.00)	72.32	5.84	4979.25	33.2%
61	1,2-dichloropropane	1953.71	836.80	(25.00)	83.41	6.16	2645.01	35.4%
62	methylmethacrylate	3740.91	1771.67	(50.00)	90.20	6.28	5585.74	49.3%
63	bromodichloromethane	3883.17	2868.38	(25.00)	83.95	6.21	5766.84	48.5%
64	1,4-dioxane	41.93	13.69	(250.00)	125.47	31.01	47.86	14.1%
65	dibromomethane	2223.32	1022.24	(25.00)	89.20	6.52	2975.83	33.8%
66	4-methyl-2-pentanone	702.38	301.05	(100.00)	91.18	6.28	1071.45	52.5%
67	trans-1,3-dichloropropene	3520.40	1867.18	(125.00)	86.23	6.28	4721.33	34.1%
68	toluene	13173.73	7915.91	(25.00)	78.01	5.97	14644.82	11.2%
69	pyridine	106.21	89.51	(125.60)	134.40	31.45	191.30	80.1%
70	cis-1,3-dichloropropene	3962.86	1979.76	(125.00)	88.17	6.43	5259.86	32.7%
71	ethylmethacrylate	13.94	10.32	(50.00)	91.21	6.28	17.87	28.2%
72	n-nitrosodimethylamine	905.08	0.00	(500.10)	93.47	6.29	157.72	-82.6%
73	2-hexanone	1269.00	501.78	(50.10)	91.86	6.28	1807.04	42.4%
74	1,1,2-trichloroethane	2447.65	1072.51	(25.00)	90.92	6.57	3527.04	44.1%
75	tetrachloroethene	3961.38	2542.11	(25.00)	69.62	5.63	4693.80	18.5%
76	1,3-dichloropropane	4491.75	2048.89	(25.00)	90.91	6.55	6027.14	34.2%
77	dibromochloromethane	3502.46	1691.37	(25.00)	88.99	6.43	4513.48	28.9%
78	2-picoline	45.83	55.05	(125.10)	130.56	31.61	27.26	-40.5%
79	1,2-dibromoethane	3118.50	1406.35	(25.00)	92.15	6.28	4325.71	38.7%
80	chlorobenzene	9065.28	4206.34	(25.00)	80.95	6.10	11900.60	31.3%
81	1,1,1,2-tetrachloroethane	3158.19	1597.21	(25.00)	85.86	6.21	4198.99	33.0%
82	ethylbenzene	4392.98	2798.27	(25.00)	78.67	6.12	5277.39	20.1%
83	n-nitroso-methyl-ethylamine	871.37	0.00	(500.10)	114.78	31.64	63.17	-92.8%
84	m,p-xylenes	11080.09	6606.84	(12.50)	79.48	6.00	13293.17	20.0%
85	styrene	5398.31	2722.44	(25.00)	82.75	5.98	6914.36	28.1%
86	o-xylene	4912.45	2471.95	(25.00)	81.23	6.09	6434.36	31.0%
87	isopropylbenzene	3726.05	2537.31	(25.00)	77.05	6.00	4747.32	27.4%
88	bromoform	2104.23	1157.33	(25.00)	92.29	6.54	2758.81	31.1%
89	cis-1,4-dichloro-2-butene	530.38	324.07	(100.00)	93.39	6.29	892.36	68.2%
90	n-nitrosodiethylamine	10.23	4.37	(500.00)	131.10	31.79	12.91	26.2%
91	1,1,2,2-tetrachloroethane	3814.76	1663.06	(25.00)	93.02	6.29	5336.68	39.9%
92	1,2,3-trichloropropane	3711.38	1883.24	(25.00)	95.43	1.45	5518.65	48.7%
93	propylbenzene	4295.09	2848.61	(25.00)	77.65	3.30	5231.06	21.8%
94	trans-1,4-dichloro-2-butene	925.91	544.45	(100.00)	95.40	1.45	1235.82	33.5%
95	1,3,5-trimethylbenzene	6235.34	4232.75	(25.00)	81.90	3.31	7466.63	19.7%
96	bromobenzene	4055.73	1830.29	(25.00)	86.00	2.51	5297.56	30.6%
97	2-chlorotoluene	3995.41	2587.53	(25.00)	82.19	2.98	4825.27	20.8%

APPENDIX 11
MDL REPORT

This is about as simple as it gets. Zeros for MDLs indicate that there is no MDL calculated.

MDL Report: C:\HPCHEM\1\METHODS\MTBE_1.m\8261dir\Mdl\mdl2.mdl

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Creation Date: 7/23/2002 12:12:52 PM
Compound Library File: C:\HPCHEM\1\METHODS\MTBE_1.M\8261dir\lib8261.ini
Surrogate Groups: C:\HPCHEM\1\METHODS\MTBE_1.m\8261dir\Surrogates\anteon_surr0102_MDL.ini
Sample Size: 2
Matrix: no matrix given
Other:
Unit: ng/mL

Compound		MDL
31:	dichlorodifluoromethane	7.00
32:	chloromethane	10.00
33:	vinylchloride	13.00
34:	bromomethane	0.00
35:	chloroethane	0.00
36:	trichlorofluoromethane	0.00
37:	ether	0.00
38:	acetone	0.00
39:	1,1-dichloroethene	0.00
40:	iodomethane	0.00
41:	allylchloride	0.00
42:	acetonitrile	35.00
43:	methylenechloride	0.00
44:	MTBE	2.00
45:	acrylonitrile	0.00
46:	trans-1,2-dichloroethene	0.00
47:	1,1-dichloroethane	0.00
48:	methacrylonitrile	0.00
49:	2-butanone	0.00
50:	propionitrile	0.00
51:	2,2-dichloropropane	0.00
52:	cis-1,2-dichloroethene	0.00
53:	chloroform	0.00
54:	bromochloromethane	0.00
55:	1,1,1-trichloroethane	0.00
56:	1,1-dichloropropene	0.00
57:	carbontetrachloride	0.00
58:	1,2-dichloroethane	0.00
59:	benzene	0.00
60:	trichloroethene	0.00
61:	1,2-dichloropropane	0.00
62:	methylmethacrylate	0.00
63:	bromodichloromethane	0.00
64:	1,4-dioxane	0.00
65:	dibromomethane	0.00
66:	4-methyl-2-pentanone	0.00
67:	trans-1,3-dichloropropene	0.00
68:	toluene	0.00
69:	pyridine	0.00
70:	cis-1,3-dichloropropene	0.00
71:	ethylmethacrylate	0.00
72:	n-nitrosodimethylamine	0.00
73:	2-hexanone	0.00
74:	1,1,2-trichloroethane	0.00
75:	tetrachloroethene	0.00
76:	1,3-dichloropropane	0.00
77:	dibromochloromethane	0.00
78:	2-picoline	0.00
79:	1,2-dibromoethane	0.00
80:	chlorobenzene	0.00
81:	1,1,1,2-tetrachloroethane	0.00
82:	ethylbenzene	0.00
83:	n-nitroso-methyl-ethylamine	0.00
84:	m,p-xylenes	0.00
85:	styrene	0.00
86:	o-xylene	0.00
87:	isopropylbenzene	0.00
88:	bromoform	0.00
89:	cis-1,4-dichloro-2-butene	0.00
90:	n-nitrosodiethylamine	0.00
91:	1,1,2,2-tetrachloroethane	0.00
92:	1,2,3-trichloropropane	0.00
93:	propylbenzene	0.00
94:	trans-1,4-dichloro-2-butene	0.00
95:	1,3,5-trimethylbenzene	0.00
96:	bromobenzene	0.00
97:	2-chlorotoluene	0.00
98:	4-chlorotoluene	0.00
99:	pentachloroethane	0.00
100:	tert-butylbenzene	0.00
101:	1,2,4-trimethylbenzene	0.00
102:	sec-butylbenzene	0.00
103:	aniline	0.00
104:	p-isopropyltoluene	0.00
105:	1,3-dichlorobenzene	0.00
106:	1,4-dichlorobenzene	0.00
107:	n-butylbenzene	0.00
108:	1,2-dichlorobenzene	0.00
109:	n-nitrosodi-n-propylamine	0.00
110:	acetophenone	0.00
111:	o-toluidine	0.00
112:	1,2-dibromo-3-chloropropane	0.00
113:	hexachlorobutadiene	0.00
114:	nitrobenzene	0.00
115:	1,2,4-trichlorobenzene	0.00
116:	naphthalene	0.00
117:	1,2,3-trichlorobenzene	0.00
118:	2-methylnaphthalene	0.00
119:	1-methylnaphthalene	30.00

APPENDIX 12
LIBRARY SYNCHRONIZATION PRINTOUT

This report is produced when the Method 8261 library and the surrogate file are not synchronized – that is, the surrogate file does not include same surrogate compounds as the Method 8261 library and in the same order. On the left side, the surrogate compounds are listed, along with surrogate groupings. 'CS' and 'FP' following a compound mean that the compound is a check surrogate or first pass surrogate. Relative volatility and boiling point groups are indicated by rvwg# and bpg#, where # is replaced by the appropriate group number. On the right side the corresponding Method 8261 library compounds are listed.

For example, in the following report:

- Surrogate compound 1 – diethylether-d10 – is a member of relative volatility groups 3 and 4. Library compound 1 is diethylether-d10 – the '=' sign shows that the compounds are the same in both libraries.
- Surrogate compound 4 – nitromethane-C13 – is a check surrogate. Library compound 4 is also nitromethane-C13.
- Surrogate compound 24 – 1,2-dichlorobenzene-d5 – is a member of boiling point group 2. The Method 8261 library shows compound 24 as 1,2-dichlorobenzene-d4. If the spelling of this compound was changed from 1,2-dichlorobenzene-d5, the surrogate compound can safely be renamed to match. However, if the libraries have distinctly different compounds, the surrogate file must be recreated to match the Method 8261 library. Because all surrogate settings are listed, the surrogate file can largely be recreated.
- All analytes are listed, but have no corresponding entries in the surrogate file.

Process Date: 9/23/2003 2:58:06 PM
Compound Library C:\HPCHEM\1\METHODS\MVDX7.M\8261dir\lib8261.inl
Surrogate File C:\HPCHEM\1\METHODS\MVDX7.M\8261DIR\SURROGATES\SURRVDX7B.INI
FP: First Pass - CS: Check Surrogate

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N	Surrogate Compound		Library Compound
1:	diethylether-d10	rvwa3 rvwa4	=
2:	acetone-C13	rvwg4 rvwg5	=
3:	methylenechloride-d2	CS	=
4:	nitromethane-C13	CS	=
5:	hexafluorobenzene	rvwa1 FP	=
6:	teterahydrofuran-d8	rvwg4 rvwg5 FP	=
7:	ethylacetate-c13	CS	=
8:	pentafluorobenzene	bpg1	=
9:	benzene-d6	CS	=
10:	1,2-dichloroethane-d4	FP	=
11:	Fluorobenzene	rvwa1 rvwa2 FP	=
12:	1,4-difluorobenzene	rvwg1 rvwg2	=
13:	1,2-dichloropropane-d6	CS	=
14:	1,4-dioxane-d8	rvwa5	=
15:	toluene-d8	bpa1	=
16:	pyridine-d5	rvwg5 CS	=
17:	1,1,2-trichloroethane-d3	CS	=
18:	1,2-dibromoethane-d4	rvwa3 rvwa4	=
19:	chlorobenzene-d5	rvwa2 rvwa3	=
20:	o-xylene-d10	rvwg2 rvwg3	=
21:	4-bromofluorobenzene	CS	=
22:	bromobenzene-d5	bpg1 bpg2	=
23:	aniline-13C6	CS	=
24:	1,2-dichlorobenzene-d5	bpg2	1,2-dichlorobenzene-d4
25:	decafluorobiphenyl	CS	=
26:	nitrobenzene-d5	CS	=
27:	acetophenone-d5	CS	=
28:	1,2,4-trichlorobenzene-d3	bpa2 bpg3	=
29:	naphthalene-d8	bpg3 CS	=
30:			1-methylnaphthalene-d10
31:			dichlorodifluoromethane
32:			chloromethane
33:			vinylchloride
34:			bromomethane
35:			chloroethane
36:			trichlorofluoromethane
37:			EthylEther
38:			acetone
39:			1,1-dichloroethene
40:			iodomethane
41:			allylchloride
42:			acetonitrile
43:			methylenechloride
44:			acrylonitrile
45:			trans-1,2-dichloroethene
46:			1,1-dichloroethane
47:			methacrylonitrile
48:			2-butanone
49:			propionitrile
50:			2,2-dichloropropane
51:			cis-1,2-dichloroethene
52:			chloroform
53:			bromochloromethane
54:			1,1,1-trichloroethane
55:			1,1-dichloropropene