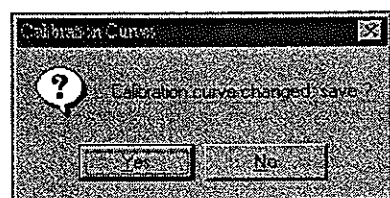*Attach the peak profile data*

4. Select View/Calibration Curve to open the Calibration Curve dialog box. This automatically opens val_test.cal.

5. Choose "Point to point without zero shift" as the Calculation Method. Select OK.

6. When prompted, save the calibration curve.



*Save the calibration curve*

7. From the Edit menu, select Recalculate. This recalculates the data based on the new calibration curve calculation parameter. In this way, the calculation function of the software can be evaluated.

8. From the File menu, choose Page Setup, and select the Default button for every tab.

9. From the File menu, select print. Confirm the printer setup and select OK.

When the report has printed, compare it to the printout given here. The reports should be identical, except for the General Information. Identical reports verify that the software is operating properly and has not been corrupted. If the reports are not the same, ensure that the procedure was followed correctly, and that the Page Setup settings are correct. Contact your Shimadzu representative for further assistance.

# Verification report for comparison

General Information

| | |
|---|---|
| Organization: | Shimadzu |
| User: | Tanaka |
| Filename: | D:\COMMON\TOCCNTRF\SOFT_VAL\VAL_TEST.TOC |

Instrument Conditions

| | |
|---|---|
| Instrument Attachments: | TOC 5000A + ASI 5000 |
| TC-Cat Type: | Normal sense TC catalyst |
| Bubble Removal: | OFF |
| Syringe Size: | 250 μl |
| Injection Speed: | STD |
| Syringe Wash: | ON |

Calibration Curves

| | |
|---|---|
| Filename: | val_test.cal |
| Title: | 0-10ppm |

| Analysis | No. of Washes | Unit | Range | Spargetime | Inj.Vol | Max SD | Max CV |
|---|---|---|---|---|---|---|---|
| TC | 4 | ppm | 1 | 0 | 53 | 200 | 2.00% |

| Sample Name | Sample ID | Conc. | No. of Inj. | Max No. of Inj. | Mean Area | SD | CV |
|---|---|---|---|---|---|---|---|
| KHP | 0 | 0.000 | 3 | 5 | 2050 | 138 | 6.73% |
| KHP | 10 | 10.00 | 3 | 5 | 34851 | 393 | 1.13% |

| | |
|---|---|
| Slope: | 3280.1 |
| Intercept: | 2049.7 |
| R^2: | 0.00000 |



Calibration curve

*Verification Report – Page 1*

Shimadzu, Tanaka          1997/12/18 09:06:17
Page 1 / 2
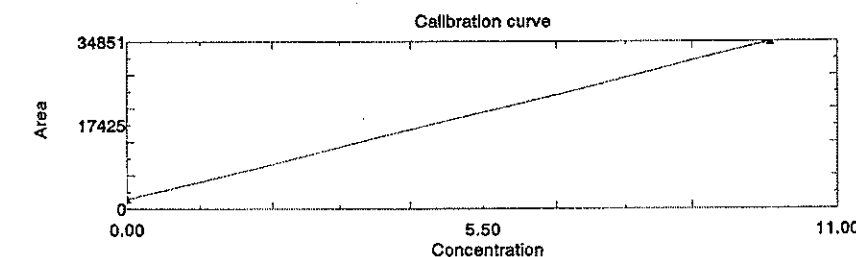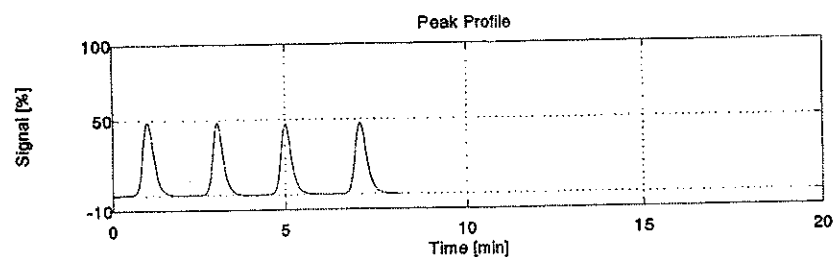
Samples

Sample Name: sample
Sample ID: 1
Method: val_test.met
Cal Curve: 1: val_test.cal

| Type | Analysis | | Sparge Time | | Date/Time |
|---|---|---|---|---|---|
| Unknown | TC | | 0 | | 1997/11/07 16:57:54 |

| Mean Area | | Conc | | Result | No. Of Washes | SD | CV |
|---|---|---|---|---|---|---|---|
| 18641 | | | | 5.058 ppm | 4 | 0.04768 | 0.943% |

| No. | Range | Inj.Vol. | Area | Conc | Excl. | Date/Time | Cal Curve |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 53 | 18479 | 5.009 | | 1997/11/07 16:51:00 | val_test.cal |
| 2 | 1 | 53 | 17974 | 4.855 | E | 1997/11/07 16:53:16 | val_test.cal |
| 3 | 1 | 53 | 18791 | 5.104 | | 1997/11/07 16:55:38 | val_test.cal |
| 4 | 1 | 53 | 18654 | 5.062 | | 1997/11/07 16:57:54 | val_test.cal |

Peak Profile



Statistics / Summary

| Sample Name | Analysis | Conc. | Result |
|---|---|---|---|
| sample | TC | | 5.058 ppm |

Shimadzu, Tanaka                    1997/12/18 09:06:18
Page 2 / 2

*Verification Report – Page 2*

# Appendix A          Error Messages

## Error Message Severity Levels

1. For information only

2. When the problem is fixed, the action can be completed; otherwise, a save alternative will occur

3. The requested action cannot be completed, but the user can continue to use the software

4. System Failure: exit the application and restart

5. Instrument Error: instrument maintenance is required

6. Fatal Instrument Error: contact your Shimadzu representative

## Error Messages

| Message | Severity | Reason | Action |
|---|---|---|---|
| Acid addition volume is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Argument Error | 4 | Communication | Check the parameters for the current action |
| ASI not initialized | 5 | Instrument | Execute [Options][Maintenance][Initialize ASI] |
| Calibration curve not found | 2 | File System | Check the path |
| Cannot create directory! | 2 | PC | Check the path |
| | | | Check the hard drive for free space |
| Cannot delete file | 2 | File System | Check the path and file name |
| Cannot open COM | 3 | Communication | Check the communication parameters |
| | | | Check the RS232 cable for correct installation |
| | | | Check the DIP switches on the instrument RS232 board |
| Cannot open method file | 4 | Methods | Check the path and file name |
| COM already opened | 3 | Communication | Use another COM port |

# Error Messages

| Message | Severity | Reason | Action |
|---|---|---|---|
| Command not sent | 5 | Communication | Retry this function later |
| Control data list is not valid, function cannot be executed. | 1 | File system | Does the file CCHART.DAT exist in the applications program directory? |
| CV is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Dilution factor is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Error in receiving data | 3 | Communication | Check the communication parameter |
| | | | Check the RS232 cable for correct installation |
| | | | Check the DIP switches on the instrument RS232 board |
| Error in sample table line: | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| ERROR!! Arm horizontal home position | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Arm horizontal pulse count | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Arm lower limit | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Arm vertical home position | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Arm vertical pause position | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Arm vertical pulse count | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Cannot find syringe zero point | 5 | Instrument error | Check the instrument |
| | | | Process "Zero Point Detection" |
| ERROR!! Illegal power off | 5 | Instrument error | Check the instrument |

| Message | Severity | Reason | Action |
|---|---|---|---|
| ERROR!! Position detection for syringe pump four-port valve abnormal | 6 | Instrument error | Shut down the instrument |
| ERROR!! RAM / ROM error | 6 | Instrument error | Shut down the instrument |
| ERROR!! SSM IC furnace not ready | 3 | Instrument error | Is the SSM connected? |
| | | | Check the settings of the temperature controller |
| ERROR!! SSM sample boat position | 5 | Instrument error | Try to move the sample rod |
| | | | Shut down the instrument |
| | | | Perform SSM maintenance |
| ERROR!! SSM sample boat position detector | 5 | Instrument error | Try to move the sample rod |
| | | | Check the SSM sample boat slider for correct position |
| ERROR!! SSM TC furnace not ready | 3 | Instrument error | Is the SSM connected? |
| | | | Check the settings of the temperature controller |
| ERROR!! Syringe pump error | 6 | Instrument error | Shut down the instrument |
| ERROR!! Syringe pump home position not detected | 3 | Communication | Perform zero point detection or change the syringe |
| ERROR!! TC furnace overheat | 6 | Instrument error | Shut down the instrument |
| ERROR!! Thermocouple disconnected | 6 | Instrument error | Shut down the instrument |
| ERROR!! Thermocouple shorted | 6 | Instrument error | Shut down the instrument |
| ERROR!! Turntable detector | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |
| ERROR!! Turntable home position | 5 | Instrument error | Shut down the instrument |
| | | | Perform ASI maintenance |

| Message | Severity | Reason | Action |
|---|---|---|---|
| ERROR!! Turntable pulse count | 5 | Instrument error | Shut down the instrument<br>Perform ASI maintenance |
| Error: COM not ready | 4 | Communication | Check the communication settings of the software<br>Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC |
| Error: Communication port not opened | 4 | Communication | Check the communication settings of the software<br>Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC |
| Error: Get EOT | 4 | Communication | Check the communication settings of the software<br>Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC |
| Error: Parity error | 4 | Communication | Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC<br>Check the communication settings of the software |
| Error: Time Out | 4 | Communication | Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC<br>Check the communication settings of the software |
| Error: Unknown Communication error | 4 | Communication | Check the communication settings of the software<br>Check the DIP switches on the instrument communication board<br>Check the RS232 cable for correct connection to the PC |

| Message | Severity | Reason | Action |
|---|---|---|---|
| File cannot be opened! The application creates a new empty control data list. | 4 | File system | Does the file CONTROL.DAT exist in the applications program directory?<br>Check the file path. |
| File not found! The application creates a new empty control data list. | 1 | File system | Does the file CCHART.DAT exist in the applications program directory?<br>Check the file path. |
| Filenames must be different! | 1 | File system | Select another file name |
| Hardware error | 5 | Communication | Check the communication parameter<br>Check the RS232 cable for correct installation<br>Check the DIP switches on the instrument RS232 board |
| Illegal Command | 2 | Communication | The instrument is not in the correct status to accept this action.<br>Check the function parameter<br>Check the instrument status<br>Execute the "ESCAPE" command<br>Retry this function later |
| Illegal Mode | 1 | Communication | The instrument is not in the correct status to accept this action.<br>Check the instrument status<br>Execute the "ESCAPE" command<br>Retry this function later |
| Illegal Parameter | 2 | Communication | The instrument is not in the correct status to accept this action.<br>Check the function parameter<br>Check the instrument status<br>Execute the "ESCAPE" command<br>Retry this function later |
| Injection volume exceeds the upper limit | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings<br>Check the syringe size |
| Injection volume is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings<br>Check the syringe size |
| Injection volume is too small | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |

| Message | Severity | Reason | Action |
|---|---|---|---|
| | | | Check the syringe size |
| Instrument Busy | 3 | Communication | Retry this function later |
| Instrument error notification | 5 | Instrument error | Check additional error messages |
| Instrument is not connected. Cannot execute this function! | 2 | Communication | Check the RS232 settings of the software<br>Connect the instrument |
| Instrument not ready | 2 | Instrument | Check the instrument conditions<br>Retry this function later |
| Max. No. of injection is not valid | 2 | Wrong Parameter | Check the Method parameters according to the current instrument settings |
| Memory allocation error! Application will be terminated! | 4 | Internal Windows error | Close other applications<br>Restart the computer<br>Increase the RAM size |
| No of washes too high | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| No. of injection not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| No. of washes is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Not Connected | 2 | Communication | Connect the instrument |
| Restart time is not OK | 1 | Instrument | Check the instrument date and time<br>The restart time has to be greater than one hour from the current instrument time |
| RS232 busy error | 5 | Communication | Retry this function later |
| SD is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Sparge time is not valid | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| Sparge time is too long | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings |
| The catalyst defined in the calibration curve is not suitable for the current instrument conditions! | 1 | Calibration curve | Does the calibration curve match the current instrument conditions?<br>Instrument conditions must be changed before creating a curve |
| The type of the calibration curve doesn't match with the method! | | Method | Does the calibration curve match the current instrument conditions?<br>Ensure that the analysis type is the same in both the calibration curve and method |

| Message | Severity | Reason | Action |
|---|---|---|---|
| This file is not in the correct format or corrupted! It can't be opened | 2 | File system | Is the file suitable for the TOC-Control application. (*.toc, *.cal,*.met,*.pkt)? |
| Timeout error | 3 | Communication | Retry this function later |
| Unknown error | 3 | Communication | Restart the application |
| Vial is not defined | 2 | Wrong Parameter | Check the Method conditions according to the current instrument settings<br>Select appropriate tray |
| Zero point of the sample syringe is not detected, cannot execute function! | 2 | Instrument error | Check the instrument conditions (Syringe Size)<br>Execute the [Options]-[Maintenance]-[Zero Point Detection] |

## Appendix B     Automatic Calibration Curve Selection

When more than one Calibration Curve has been selected in the Method dialog box, the optimum Calibration Curve is selected automatically according to the following procedure.

1. Measurement is initially conducted using the first calibration curve in the list (CAL#1).

**When the sample is lower in concentration than CAL#1:**

2. If the sample concentration (SAMP) is lower than the highest standard concentration of CAL#1, and higher than the other calibration curve standards (CALother), the first calibration curve is used.

CAL#1 > SAMP > CALother → CAL#1 used

3. If two calibration curves have been designated, the sample concentration is lower than the highest standard concentrations for both CAL#1 and CAL#2, and the concentration of CAL#2 is lower than that of CAL#1, then the second calibration curve is used.

CAL#1 > CAL#2 > SAMP → CAL#2 used

4. If three calibration curves have been designated, the selection is essentially the same; the closest concentration of standard Calibration Curve that is still higher than the sample concentration will be used.

CAL#1 > CAL#2 > SAMP > CAL#3 → CAL#2 used

CAL#1 > CAL#2 > CAL#3 > SAMP → CAL #3 used

**When the sample concentration is higher than Cal#1, and Cal#2 or Cal #3 (CALother) are higher in concentration than Cal#1:**

5. If the sample concentration is marked with an "H" (indicating that the peak height exceeded the full scale of CAL#1), the other calibration curve is used.

CALother > SAMP H > CAL#1 → CALother used

6. If SAMP is not marked with an H, the program performs a ratio calculation. The ratio of the measured sample concentration and CAL#1 is compared to the ratio of the sample concentration and CALother. In most cases, CAL#1 is selected, because the NDIR is linear for any range setting, and a concentration within full scale range will not be far greater than CAL #1. Therefore, using CAL#1 will be at least as accurate as if another calibration curve is used.

CALother > SAMP > CAL#1 ➟ CAL#1 usually used

7. If SAMP is higher than that of both CAL#1 and CALother, the other calibration curve is used.

SAMP > CALother > CAL#1 ➟ CALother used

8. If SAMP is higher than CAL#1, and the other two concentration curves have higher concentrations than CAL#1, measurement will be calculated based on the lower concentration calibration curve that is closest to the sample concentration. Then, the evaluation described in Steps 5, 6 and 7 is conducted.

CAL#2 > SAMP > CAL#3 > CAL#1 ➟ CAL#3 usually used

SAMP > CAL#2 > CAL#3 > CAL#1 ➟ CAL#2 usually used

The following points about automatic optimum calibration curve selection should also be considered:

♦ The procedures described above are valid for both single and multi-point calibration curves.

♦ For multiple injections, when the first peak is within the full scale, while succeeding peaks exceed the scale, operation will continue based on the first injection. The amount that the successive peaks exceed the range is considered too small to affect the measurement.

♦ The TC catalyst type (Normal or High sensitivity) and the syringe size must be the same for the calibration curves selected.

♦ Different units can be used for the calibration curve concentrations, provided the units are of the same grouping (i.e., a combination of ppm and ppb, or mg/L and µg/L).

♦ When analyzing samples with an expected wide range of concentrations, set the concentration ratio between two calibration curves to between 5 – 10. Since the measurement always begins with CAL#1, this should be the curve most likely to be used. The selection of CAL#2 and CAL#3 depends upon their concentrations and the expected sample concentrations.

♦ Automatic selection of the optimum calibration curve cannot be used in measurement based on the carbon equivalent.

# Index

## μ

μg C, 142

## A

Analysis
    starting, 98
    stopping, 100
    viewing current, 79
Append, 98
Arrange icons, 130
ASCII, 127
ASI
    analysis without, 98
    choosing vials, 109
    configuring for, 109
    connection, 122
    mechanical check, 118
    parameters, 109
Attach data file, 52
Auto generate, 66, 84
Auto restart, 101

## B

Background monitor, 81
Baseline, 141
Baseline fluctuation, 81
Baseline profile graph, 81
Blind value control, 169, 173
Buzzer, 106

## C

Calculation method, 73
Calculations, 165
Calibration (validation), 161
Calibration curve
    automatic selection, 205
    creating, 73
    listing, 78
    listing current, 77
    opening, 72
    specifying, 87
Cascade, 130
Catalyst
    changing, 123
    regenerating, 116
    using high sensitivity, 106
Clear data, 65
Close, 51
CNV, 142
Coefficient of determination, 74
Coefficient of variation, 76
Common status bar, 47
Configuration
    PC, 124
    saving, 125
Connect, 100
Continue, 100
Control charts
    comparison, 181
    exporting data, 188
    following, 176
    general parameters, 174, 184
    opening, 96
    overview, 169
    statistics, 179
Control tracking
    adding and editing, 95
    disabling, 96
    set-up, 94
Control-period, 175
Controls, set-up, 93
Copy, 64, 143
Cross-hair, 143
Curve fits, 73
Cut, 64

## D

Data
    excluding, 65, 76, 141, 147
    exporting, 127
    exporting control charts, 188
    exporting validation, 163
    integrity, 191
    recalculating, 71
Database, 129
Datasheet, 159
Default parameters, 4
Deleting files, 52
DIN 38402, 74, 155, 164
Display
    choosing a font, 62
    settings, 113

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