

# Improved Infra-Red Procedure for the Evaluation of Calibrating Units

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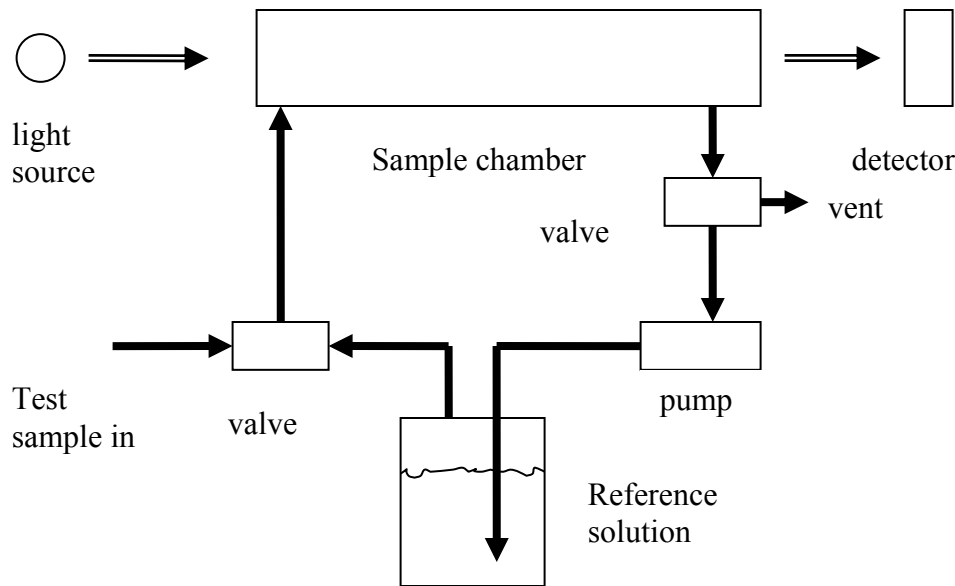
**Introduction.** The NHTSA Model Specifications for Calibrating Units for Breath Alcohol Testers (**FR** 72 34742-34748) requires that calibration units submitted for inclusion on the NHTSA Conforming Products List for such devices be evaluated using one of three alternate procedures, all of which were developed at the Volpe Center. The first uses gas chromatography and wet gas reference samples for evaluation. This procedure is no longer used because of the advent of dry gas CUs on the market. Gas chromatography is an inappropriate technique for evaluation of dry gases using wet gas reference samples. A second alternative uses gas chromatography with dry gas reference samples. The dry gas references were obtained from the National Institute for Science and Technology. A third procedure uses a non-dispersive infra-red spectrophotometry. This third procedure is the preferred one, since reference samples are prepared at the Volpe Center so that reliance on outside sources for reference samples is not necessary.

This preferred procedure uses a National Patent Analytical Systems, Inc. Datamaster breath alcohol analyzer instrument to analyze samples. This device is a non-dispersive infra-red spectrophotometer designed for breath (ethyl) alcohol analysis and is listed on the NHTSA Conforming Products List for evidential breath testers. Analysis is based on the absorption of a band of infra-red radiation centered at 3.4 microns, a wavelength area that is strongly absorbed by alcohol and which at the same time is not interfered with by other possible substances found in human breath, other than acetone.

**Improved Procedure.** The Datamaster instrument has been replaced with a Datamaster DMT instrument and the procedure has been improved by use of the simulator sample re-circulation feature that was not present in the older instrument. This re-circulation feature eliminates the gradual loss of alcohol from the reference solutions in the previous version of the procedure. An IOTech Daqview data acquisition system has been added to allow direct collection of the alcohol detector signal output through the Daqview system to a laptop computer. This addition allows averaging of the detector signal obtained in a 10 second collection window to improve data quality. Also, the data collection and number crunching process has been simplified by use of an Excel spreadsheet and Excel macro.

The previous procedure required data collection by “eyeballing” the Datamaster detector output and manually recording it on a test log.

**Optical arrangement of Datamaster DMT.** The essential features of the optical cell of the Datamaster DMT and the simulator sample re-circulation system is shown in figure 1. The test sample or reference sample is delivered into the optical cell and is irradiated with infra-red energy from the light source of the instrument. The difference in energy striking the detector when alcohol is present in the sample chamber and when not present together with the results from the known reference samples is used to calculate the amount of alcohol in the sample by use of the Beer-Lambert Law for the absorption of radiation by substances.



**Figure 1. Datamaster sample processing.**

**Alcohol reference (wet) gas.** Alcohol reference solutions are used to generate known alcohol-in-air mixtures which are compared with test samples from the wet bath or dry gas calibrator submitted for evaluation. Air bubbled through the reference solution which is thermostated at a fixed temperature, quickly equilibrates with the solution following Henry's Law so that the air emerges from the solution with a known alcohol concentration, which is calculated from the Henry's Law partition factor for the alcohol/water system<sup>1</sup>. The fact that Henry's Law is followed means that the partitioning depends on temperature, but not on atmospheric pressure. The alcohol solutions are normally thermostated at 34 °C, once supposed to be the average breath temperature of humans.

The basic law for dilution of solutions is used to calculate the concentration of reference alcohol solutions used. The law is simply:

$$C_1V_1 = C_2V_2$$

Where C is the concentration and V is the volume of the solutions. The index 1 refers to the solution before dilution and the index 2 refers to the solution after dilution. A working solution is prepared from which all reference solutions are made. The concentration of the working solution is set so that the reference solutions can be prepared using a simple dilution scheme. For instance, if a reference solution that would result in air samples corresponding to breath samples of 0.080 grams alcohol/219 liters of air (corresponding to the legal limit for alcohol impaired driving in most states) is desired, 8.0 milliliters of working solution is buretted into a 500 milliliter volumetric flask and diluted to volume. An aliquot of the resulting solution is placed in a clean, dry bubble flask; bubble and

<sup>1</sup> a)RN Harger et al J Biol Chem 183 197-213 (1950)  
 b) FR 49 48869 Dec 14, 1984

outlet tubes are attached, and the flask is placed in a thermostated water bath and allowed to reach thermal equilibrium.

**Dry gas concentrations.** The concentration of dry gas calibrators (which are compressed gases) are expressed by manufacturers of these products in terms of ppm, or parts per million, of alcohol. These units are independent of atmospheric pressure and are volume of alcohol per million volumes of inert gas, usually nitrogen. The units used for police breath alcohol testing, grams alcohol/210 liters of air, are not independent of atmospheric pressure. It is necessary to convert the stated ppm concentration of the submitted dry gas CU to a g/210L concentration at the prevailing atmospheric pressure.

**Equipment.** The equipment used is as follows:

National Patent Analytical Systems, Inc. Datamaster DMT fitted with simulator inlet and outlet ports to accommodate reference and test sample hoses.

Reference alcohol solution bottles (400ml) and stoppers fitted with inlet bubble hose and outlet sample hose.

Brand Digital Burette for preparation of reference alcohol solutions.

Volumetric flasks: 500 ml, 1 L.

Reference solution bottles: Snapple, with stopper equipped with bubble and sample tubes

Thermo Neslab Digital One temperature controlled water bath.

Iotech Daqbook 112 with Daqview software data acquisition system.

Laptop computer loaded with Excel spreadsheet and macros for data acquisition and processing. The macros used are given in Appendix 2.

The reference solutions are placed in the reference bottles, hoses are attached. The trio of low reference, high reference, and zero reference (water) bottles are placed in the water bath thermostated at 34 °C.

The flow, detector, and pressure outputs of the Datamaster are connected via bnc cables to the Daqview input, channels 0, 1, and 2, respectively.

The output channels of the Daqview are input to the laptop.

The Excel spreadsheet (new cu collect and crunch c) is opened. The Daqview tool bar is enabled.

**Step by step Procedure.** The procedure has been designed to be used by technicians with minimum training. Each step of data collection is executed by the embedded Excel Macro that controls data collection by pressing cntrl z. Data acquisition is triggered by pressing the 'go' button on the Daqview tool bar.

1. The low reference and high reference solutions are prepared to bracket the concentration of the calibrator by not more than  $\pm 0.005$  g/210L.
2. The stoppers equipped with bubble and outlet tubes are fitted to the clean, dry reference solution bottles.
3. The low reference and high reference solutions including the 0.000g/210L solution (water) are placed in the water bath and equilibrated at 34 °C for 1 hour.

4. Reference solutions are connected to the Datamaster, beginning with the 0.000 g/210L solution. Take care that the reference solution output hose is connected to the Datamaster input fitting and the reference solution input hose is connected to the Datamaster output fitting. Reversing these connections will result in the Datamaster sample chamber being flooded with solution and will require an extensive clean-up procedure.
5. Required information as indicated is entered into 'sheet 1' of the Excel Spreadsheet 'new cu collect and crunch c'.
6. Data collection is started by pressing **cntrl z**. The cell into which data must be entered will be indicated by the cell becoming highlighted. The first required data is 'start bath temp'. Enter the bath temperature.
7. Press **cntrl z** again to step through the collection of data from the Datamaster. The type of data required will be determined by the **alcohol source row** together with the **'baseline' or 'test sample' column** that corresponds to the highlighted cell.

If the alcohol source is the 0.000 bottle, connect it to the Datamaster.

If **baseline data is required**, **toggle** off the simulator button of the Datamaster and **toggle** on the pump to pass 0.800 liters of air through the sample chamber of the Datamaster (clear the volume totalyzer to observe the amount). **Toggle** off the pump. Transfer the baseline data to 'sheet 1' by pressing 'go' on the Daqview tool bar. After transfer is complete, press **cntrl z** again.

If **sample data is required**, **toggle** on the simulator of the Datamaster and **toggle** on the pump to pass 0.800 liters of sample through the sample chamber of the Datamaster (clear the volume totalyzer to observe the amount). **Toggle** off the pump. Transfer the sample data to 'sheet 1' by pressing 'go' on the Daqview tool bar. After transfer is complete, press **cntrl z** again.

If the alcohol source is a low or high reference bottle, connect it to the Datamaster and repeat the above process. If the alcohol source is a dry gas calibrator, do not toggle on the pump.

8. The final data to be entered is indicated when the data destination cell is highlighted in purple. After entry of the end bath temperature, pressing **cntrl z** again will result in moving of the collected data to the 'report' sheet and preparation of 'sheet 1' for the next data collection.
9. Re-name the 'report' sheet and save as described in the 'Instructions' sheet.

**Calculations.** The equations embedded into the data gathering and reporting Excel spreadsheets regarding solution preparation, ppm conversion to g/210L, and use of the Beer-Lambert Law for detector signal analysis are described in the Appendix 1. These embedded equations allow for the automatic preparation of the test report.

## Appendix 1. Calculations.

### Reference solution output concentrations

wet brac = concentration of solution X  $K_a/w = (77 \cdot \rho_{23} \cdot 210 \cdot V_{ref}/500) \cdot (.5828t^2 - 16.627t + 284.97) \cdot 10^{-6}$

where

The first factor is the concentration of the wet bath solution (77 milliliters of pure alcohol is diluted to 1 liter to prepare the working solution, from which the reference samples are prepared), and the second factor is Harger's air/water alcohol partition factor at temperature  $t$ .

$V_{ref}$  is ml of stock solution added to 500ml flask to prepare reference solution or simulator solution and  $t$  is temperature of the solution.

$\rho_{23}$  = density of ethanol at 23 degC = 0.78691 g/ml.

### Dry Gas ppm to BrAC conversion

For gases, ppm means volume of solute gas per million volumes of solvent gas, or in this case, liters of alcohol gas per million liters of nitrogen. The molar volume is 22.4 liters per mole at standard temperature and pressure (0 degC (273 degK) and 760 mmHg). The molecular weight of alcohol is 46.

So

$\text{ppm}/22.4 = \text{moles alcohol}/10^6 \text{ liters of air @STP}$

$(\text{ppm}/22.4) \cdot 46 = \text{gm alcohol}/10^6 \text{ liters of air @STP}$

$(\text{ppm}/22.4) \cdot 46/10^6 = \text{gm alcohol}/\text{liter of air @STP}$

$((\text{ppm}/22.4) \cdot 46/10^6) \cdot 210 = \text{gm alcohol}/210 \text{ liter of air @STP}$

From the perfect gas equation, the concentration of the gas is  $C = P/RT$ . Raising the temperature from 273 degK to the temperature of the reference gas from the reference solutions, 307 degK (34 degC) changes  $C$  by  $273/(273+34)=0.889$ . Changing the pressure from 760 to mmHg changes  $C$  by  $\text{mmHg}/760$ .

Applying the above corrections,

$\text{BrAC} = \text{ppm} \cdot \text{mmHg} \cdot /1978670$

### Beer/Lambert Law for absorption of radiation



$$I = I_0 e^{-abc}$$

$\ln(I_0/I) = abc = \text{absorbance}$

$I_0$  can be taken as  $I_{\text{baseline}}$  and  $I$  can be taken as  $I_{\text{sample}}$

I is proportional to detector voltage V

so that

$$\text{absorbance} = \ln(V_{\text{baseline}}/V_{\text{sample}})$$

but the detector of the Datamaster DMT is biased at 80.4V

so that

$$\text{absorbance} = \ln[(80.4 - V_{\text{baseline}})/(80.4 - V_{\text{sample}})]$$

The average of the absorbance/BrAC of the 5 low reference samples and the 5 high reference samples is obtained. The relative standard deviation of these 10 results must be less than 2%.

The absorbances of the 10 test samples is divided by the above average to obtain the BrACs of the test samples. The relative standard deviation of these 10 samples must be less than 2% and the systematic error must be less than 0.002.

For dry gas calibrator evaluations,  $V_{\text{sample}}$  for the reference samples must be corrected for the presence of water vapor in the reference samples, so the average of the 3 initial water samples and the 3 final water samples is subtracted from the  $V_{\text{sample}}$  for the reference samples. This correction is not necessary for wet bath calibrator evaluations since water vapor is present in both the reference sample and the test sample.

## Appendix 2. Excel Macro programs.

```
Sub EnterData()
```

```
,
```

```
' EnterData Macro
```

```
' Macro recorded 8/31/2010 by Arthur Flores
```

```
,
```

```
' Keyboard Shortcut: Ctrl+z
```

```
Dim count1 As Integer
```

```
Dim modu1 As Integer
```

```
Dim count2 As Integer
```

```
Dim modu2 As Integer
```

```
Dim count3 As Integer
```

```
count1 = Cells(1, 11)
```

```
modu1 = Cells(2, 11)
```

```
count2 = Cells(3, 11)
```

```
modu2 = Cells(4, 11)
```

```
count3 = Cells(5, 11)
```

```
If Cells(4, 6) = "dry" Then GoSub DrySub
```

```
If Cells(4, 6) = "wet" Then GoSub WetSub
```

```
Exit Sub
```

```
DrySub:
```

```
If count3 = 0 Then 'enter BrAC and start bath temp
```

```
Cells(9, 6).Select
```

```
ActiveCell.Value = Cells(4, 9).Value * Cells(5, 9).Value / 1981800
```

```
Cells(10, 6).Select
```

```
Selection.Interior.ColorIndex = 6
```

```
Cells(5, 11) = Cells(5, 11) + 1
```

```
End If
```

```
If modu1 = modu2 And count3 = 1 Then 'set for 1st daq data
```

```
Cells(10, 6).Select
```

```
Selection.Interior.ColorIndex = xlNone
```

```
Cells(count1, 6).Select
```

```
Selection.Interior.ColorIndex = 6
```

```
Cells(5, 11) = Cells(5, 11) + 1
```

```
End If
```

```
If modu1 = modu2 And count3 > 1 And count3 < 53 Then 'copy/paste baseline daq data
```

```
Cells(count1, 6).Select
```

```
Selection.Interior.ColorIndex = xlNone
```

```
ActiveCell.Value = Cells(6, 11).Value
```

```
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(count2, 8).Select
Selection.Interior.ColorIndex = 6
Cells(1, 11) = Cells(1, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If modu1 <> modu2 And count3 < 53 Then 'copy/paste sample daq data
Cells(count2, 8).Select
Selection.Interior.ColorIndex = xlNone
ActiveCell.Value = Cells(6, 11).Value
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(count1, 6).Select
Selection.Interior.ColorIndex = 6
Cells(3, 11) = Cells(3, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If modu1 <> modu2 And count3 = 53 Then 'copy/paste last sample daq data
Cells(count2, 8).Select
Selection.Interior.ColorIndex = xlNone
ActiveCell.Value = Cells(6, 11).Value
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(count1, 6).Select
Selection.Interior.ColorIndex = 8
Cells(3, 11) = Cells(3, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If count3 = 54 Then 'move data to "report", clear "sheet1" for next test
Cells(39, 6).Select
Selection.Interior.ColorIndex = xlNone
Call MoveData
End If
Return
```

WetSub:

```
If count3 = 0 Then 'enter BrAC
Cells(9, 6).Select
Selection.Interior.ColorIndex = 6
Cells(5, 11) = Cells(5, 11) + 1
GoTo line2
End If
```



```
If count3 = 1 And Cells(1, 12) = "a" Then 'enter start bath temp
Cells(9, 6).Select
Selection.Interior.ColorIndex = xlNone
Cells(10, 6).Select
Selection.Interior.ColorIndex = 6
Cells(1, 11) = Cells(1, 11) + 3
Cells(3, 11) = Cells(3, 11) + 3
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If modu1 = modu2 And count3 = 2 Then 'set for 1st daq data
Cells(10, 6).Select
Selection.Interior.ColorIndex = xlNone
Cells(count1, 6).Select
Selection.Interior.ColorIndex = 6
Cells(5, 11) = Cells(5, 11) + 1
GoTo line2
End If
```

```
If modu1 = modu2 And count3 > 2 And count3 < 42 Then 'copy/paste baseline daq
data
Cells(count1, 6).Select
Selection.Interior.ColorIndex = xlNone
ActiveCell.Value = Cells(6, 11).Value
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(count2, 8).Select
Selection.Interior.ColorIndex = 6
Cells(1, 11) = Cells(1, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If modu1 <> modu2 And count3 < 42 Then 'copy/paste sample daq data
Cells(count2, 8).Select
Selection.Interior.ColorIndex = xlNone
ActiveCell.Value = Cells(6, 11).Value
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(count1, 6).Select
Selection.Interior.ColorIndex = 6
Cells(3, 11) = Cells(3, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

```
If modu1 <> modu2 And count3 = 42 Then 'copy/paste last sample daq data
Cells(count2, 8).Select
```

```
Selection.Interior.ColorIndex = xlNone
ActiveCell.Value = Cells(6, 11).Value
ActiveCell.Offset(0, 1).Select
ActiveCell.Value = Cells(7, 11).Value
Cells(39, 6).Select
Selection.Interior.ColorIndex = 8
Cells(3, 11) = Cells(3, 11) + 1
Cells(5, 11) = Cells(5, 11) + 1
End If
```

line2:

```
Cells(1, 12) = "a"
```

```
If count3 = 43 Then 'move data to "report", clear "sheet1" for next test
Cells(39, 6).Select
Selection.Interior.ColorIndex = xlNone
Call MoveData
End If
Return
```

End Sub

Sub MoveData()

```
'
' MoveData Macro
' Macro recorded 11/1/2010 by Arthur Flores
'
' Keyboard Shortcut: Ctrl+m
'
Sheets("sheet1").Select
Cells(39, 6).Select
Selection.Interior.ColorIndex = xlNone

Columns("D:I").Select
Selection.Copy
Sheets("report").Select
Columns("A:F").Select
ActiveSheet.Paste
Sheets("sheet1").Select
range("F1:F10,I1:I10,F13:I39").Select
Application.CutCopyMode = False
Selection.ClearContents
range("L1").Select
ActiveCell.FormulaR1C1 = " "
range("k1").Select
```

```
ActiveCell.FormulaR1C1 = "13"  
range("k3").Select  
ActiveCell.FormulaR1C1 = "13"  
range("k5").Select  
ActiveCell.FormulaR1C1 = "0"  
Sheets("report").Select  
range("A1").Select  
End Sub
```