An Infra-red Procedure For Evaluation of Wet Bath or Dry Gas Calibrating Units.

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The National Highway Traffic Safety Administration maintains Conforming Products Lists for police breath alcohol testing equipment. Equipment submitted by manufacturers for inclusion on the Lists are first evaluated at Volpe National Transportation Systems Center according to model specifications which are published in the Federal Register. The lists are offered to the states as guidance in making purchase decisions. Model specifications have been established for evidential breath testers (FR **58** 48705-48710), calibrating units (FR **49** 48865) and screening devices (FR **59** 67377-67382).

Calibrating units are devices which produce ethyl alcohol vapors at known concentration, and are used to calibrate breath alcohol testers. Wet bath calibrating units (simulators), are devices which produce alcohol vapors by bubbling air through an alcohol solution thermostated at 34°C, average breath temperature. Harger's[1] air/water partition ratio for 34°C is used to prepare the solutions. Dry gas calibrating units are compressed gas mixtures of alcohol in an inert gas, usually nitrogen.

Current Procedure

In the model specifications for calibrating units, the evaluation procedure is based on standard gas chromatography techniques. A modified procedure is being used wherein moist reference vapors prepared by use of Harger's air/water partition ratio are used to evaluate wet bath calibrating units and (dry) National Institute for Standards and Technology Reference Gas Mixtures (NIST RGMs) are used to evaluate dry gas calibrating units. Mixing of dry and moist vapors in the evaluation of a given type of calibrating unit is not feasible because of hysteresis effects which take place in the gas chomatograph separating column.

The success of the gas chromatography procedure is critically dependent on the following:

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[1] RN Harger, BB Raney, EG Bridwell, MF Kitchel, J. Biol. Chem. (1950)183197.

- Sufficient conditioning of the separation column prior to use.

- Pre-conditioning of the separation column with a number of samples of moist or dry alcoholic gas, depending on whether a wet bath or dry gas calibrating unit is being evaluated, immediately prior to evaluation of the calibrating unit.

- Precise timing of sample injections.

- Proper functioning of the heated sampling valve.

Inattention to any of the above factors can flaw the evaluation.

Proposed Infra-Red Procedure

An improved procedure, based on the Beer-Lambert Law of absorption and non-dispersive infra-red spectroscopy has been developed which overcomes the above gas chromatography difficulties and thereby offers a higher degree of reliability in calibrating unit evaluations. At the same time, the procedure is significantly easier to perform and is thus inherently less likely to go awry by human error. However, gas chromatography is still needed to screen for impurities in the calibrating unit vapors.

The infra-red procedure uses moist reference vapors for both wet bath and dry gas calibrating units. NIST RGMs are not needed. A description of the procedure, including demonstration data obtained in the evaluation of NIST RGMs is presented below. The NIST RGMs used here were prepared by Scott Specialty Gases, Inc. and then re-analyzed and certified by NIST.

A National Patent Analytical Systems, Inc. BAC Datamaster, an infra-red breath alcohol tester listed on the NHTSA Conforming Products List for evidential breath alcohol testers is used. A block diagram of the optical portion of the instrument is given in Figure 1, where treatment of detector output voltage to obtain absorbance is also indicated. The Beer-Lambert law is given where: I is the intensity of measuring radiation which passes through and emerges from the sample, I_o is the incident intensity which enters the sample, a is the absorptivity of the substance being measured, b is the length of the sample cell, and c is

the concentration of the substance being measured, in this case c = BrAC.

The optical path of the instrument is long (1.1 meter, folded twice) and the raw detector output, which is biased at +5 volts, is readily available for these measurements. The ratio I_o/I is equal to the ratio of the empty cell detector voltage to the filled cell detector voltage corrected for water vapor, if present.

The sample flowpath was modified for direct delivery of sample into the measurement chamber by bypassing the five-way air handling valve.

In addition, a water bath controlled at $34.0 \pm 0.1°C$ is used. Two reference alcohol solutions prepared to bracket the concentration of the calibrating unit at ± 0.005 BrAC are used to produce moist alcohol vapors at known concentration using Harger's air/water partition coefficient (3.93×10^{-4} at $34°C$). Bottles containing the reference solutions are placed in the water bath (see Figure 2) and helium is bubbled through the solution to carry the vapors into the sample chamber of the Datamaster instrument.

A measurement consists of two readings: First the sample chamber of the Datamaster is thoroughly flushed with the alcohol vapor and the detector reading for the sample is obtained. Then the sample chamber is thoroughly flushed with helium, which is optically clear, and the helium reading, which is the baseline reading, is obtained.

The alcohol vapors from the calibrating unit are measured as are the alcohol vapors from the two reference solutions. If a dry gas calibrating unit is to be evaluated, it is necessary to separately measure the small contribution of water vapor to the alcohol readings of the bracketing moist reference samples in order to obtain V_{corr}. This is done by simply preparing a third reference bottle using pure water and taking a series of readings before and after the reference and calibrating unit readings are taken, and subtracting the average of the water readings from the reference alcohol readings. In obtaining the readings, it will be noticed that consecutive moist samples cause a slow rise in baseline detector reading due to the temporary adsorption of water on the windows and mirrors of the sample chamber, even though the chamber is maintained at a temperature well above dew point. For this reason, it is

necessary to take a baseline reading after each sample reading.

Results of evaluation of the four NIST RGM dry gas mixtures is presented in Table 1. The concentrations obtained by NIST were stated in parts per million, units which are not influenced by atmospheric pressure. These units are converted to BrAC units, grams alcohol per 210 liters air at 34°C, used by police (which are affected by atmospheric pressure) by use of the formula:
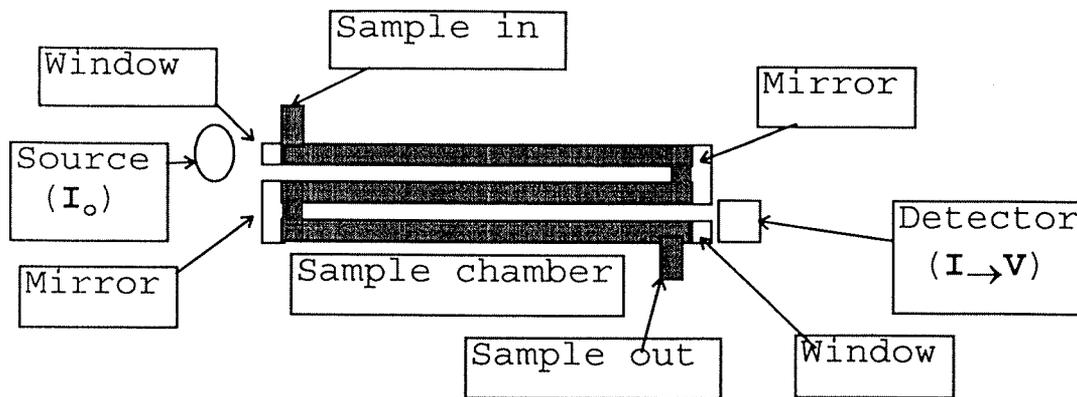
BrAC = (PPM X Barometer reading in mmHg) ÷ 1978800

A mercury barometer was used to obtain barometric pressure at the time of the measurements.

The gases were re-analyzed several times on different days and the effect of variable barometric pressure is seen. The results obtained represent the average of ten determinations at each of the barometer readings given.

The above results are also plotted in Figure 3 with relevant statistical information, and the data obtained for each of the NIST RGMs is given in Table 2.

The Model Specifications for Calibrating Units require that submitted units produce known alcohol vapors with precision defined by relative standard deviation (standard deviation ÷ average BrAC) not more than 2 per cent, and systematic error (average BrAC - stated BrAC) within ±0.002 BrAC. In all cases, the results obtained were within these tolerances.

It is noted that these gas mixtures were prepared by Scott Specialty Gases, Inc. by use of a gravimetric procedure without recourse to Harger's partition data, and re-analyzed by NIST by reference to their own gravimetrically prepared standards so that these results constitute a confirmation of the accuracy of Harger's air/water partition data to within the experimental error of this and Harger's procedure, and the procedure used by NIST.

Window

Source (I_o) →

Sample in

Mirror

Mirror

Sample chamber

Sample out

Window

Detector ($I{\rightarrow}V$)

For a given wavelength:

$I = I_o e^{-abc}$ (Beer-Lambert law)

$Ln(I_o/I) = abc = ab(BrAC) = $ **Absorbance**

+5 volt bias   **0 volts**

I   V(detector voltage)
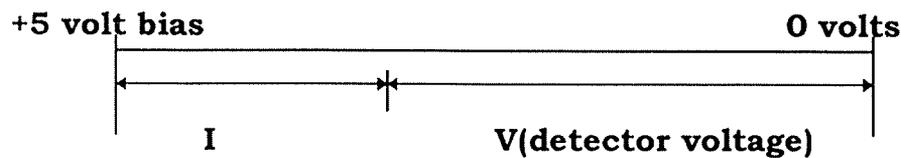
$I_o = I_{empty\ cell} \rightarrow 5 - V_{Helium}$

$I = I_{ethyl\ alcohol}\ (+\ I_{water\ vapor}) \rightarrow 5 - V_{corr}$

  For wet samples: $V_{corr} = V - V_{water\ vapor}$
  For dry samples: $V_{corr} = V$

$Ln\ (I_o/I) \rightarrow Ln\ [\ (5 - V_{Helium})/(5 - V_{corr})\ ] = $ **Absorbance**

$ab = Absorbance_{ref}\ /\ BrAC_{ref}$

$BrAC_{unk} = Absorbance_{unk}/ab$

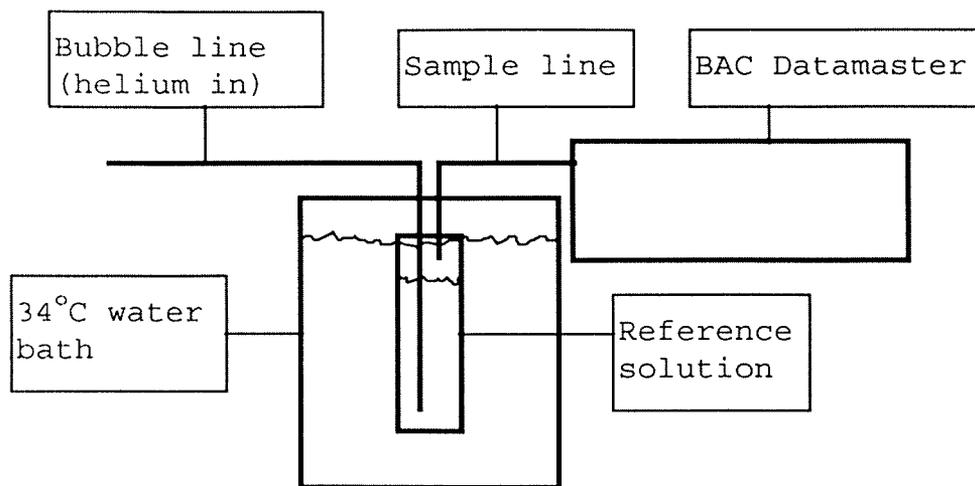Figure 1. BAC Datamaster optics and calculation of BrAC.

Figure 2. Equipment set-up. Bubble and sample lines 1/8"
teflon, minimized length. Depth of bubble line into
reference solution at least 4".

Table 1. Mean BrAC (n=10) of dry NIST RGMs by IR procedure
using moist reference vapors.

	mmHg	NIST 97.4 ppm	Gases 198 ppm	251 ppm	302 ppm
		Calculated BrAC			
1.	771	.0379	.0771	.0976	.1175
2.	754	.0371	.0754	.0956	.1151
3.	763	.0376	.0763	.0968	.1166
4.	768	.0378	.0768	.0973	.1170
		Experimental BrAC			
1.	771	.0369	.0781	.0982	.1184
2.	754	.0364	.0751	.0970	.1169
3.	763	.0381	.0774	.0981	.1184
4.	768	.0375	.0774	.0993	.1189
		Relative standard deviation, systematic error			
1.	771	.44, -.0005	.472, .00104	.354, .0006	.277, .0009
2.	754	.619, -.0002	.217, -.0003	.204, -.0014	.143, .0018
3.	763	.342, .0005	.176, .0011	.356, .0013	.235, .0018
4.	768	.828, -.0003	.374, .0006	.224, .0020	.115, .0019

Infra-Red Procedure BrAC

slope 1.0224
int -.0008
steyx .0005

302 ppm

251 ppm

198 ppm

97.4 ppm

● 771-2 mmHg
□ 754 mmHg
△ 763-4 mmHg
✕ 768 mmHg

0   0.02   0.04   0.06   0.08   0.1   0.12
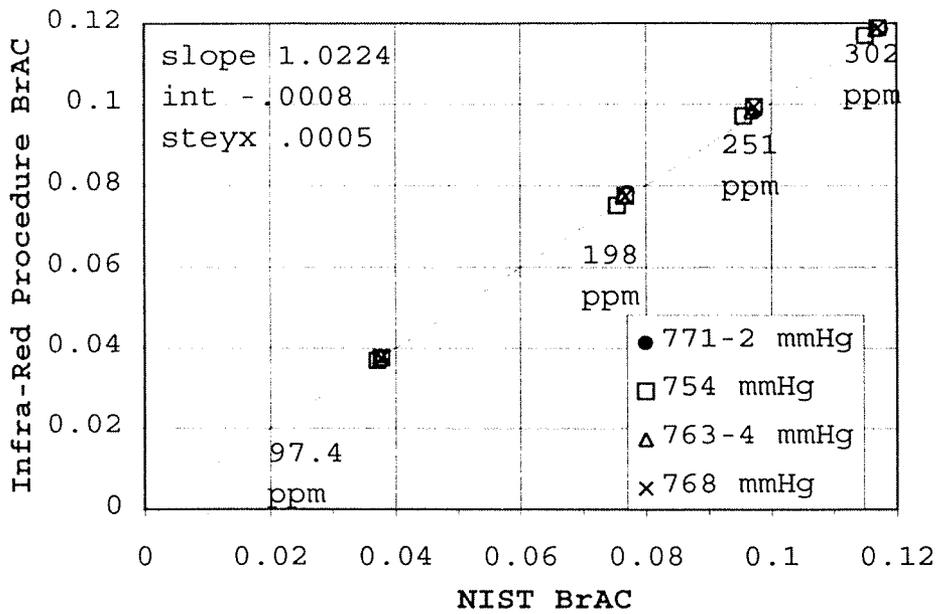
NIST BrAC

Figure 3. Calculated BrAC of NIST RGM v. experimental BrAC obtained by IR procedure.

Table 2. Experimental Data.

9/29/95		4/12/96		4/30/96		7/30/96	
cal'd	expt'l	cal'd	expt'l	cal'd	expt'l	cal'd	expt'l
0.0379	0.03743	0.03710	0.03713	0.0376	0.03800	0.03780	0.03762
0.0379	0.03757	0.03710	0.03712	0.0376	0.03824	0.03780	0.03762
0.0379	0.03758	0.03710	0.03662	0.0376	0.03822	0.03780	0.03787
0.0379	0.03733	0.03710	0.03711	0.0376	0.03797	0.03780	0.03788
0.0379	0.03708	0.03710	0.03663	0.0376	0.03822	0.03780	0.03688
0.0379	0.03733	0.03710	0.03712	0.0376	0.03797	0.03780	0.03764
0.0379	0.03733	0.03710	0.03663	0.0376	0.03797	0.03780	0.03740
0.0379	0.03733	0.03710	0.03712	0.0376	0.03823	0.03780	0.03716
0.0379	0.03757	0.03710	0.03688	0.0376	0.03822	0.03780	0.03766
0.0379	0.03757	0.03710	0.03688	0.0376	0.03822	0.03780	0.03741
0.0771	0.07748	0.07540	0.07513	0.07630	0.07725	0.07680	0.07759
0.0771	0.07823	0.07540	0.07510	0.07630	0.07750	0.07680	0.07705
0.0771	0.07874	0.07540	0.07486	0.07630	0.07724	0.07680	0.07731
0.0771	0.07848	0.07540	0.07534	0.07630	0.07724	0.07680	0.07705
0.0771	0.07769	0.07540	0.07510	0.07630	0.07724	0.07680	0.07756
0.0771	0.07797	0.07540	0.07534	0.07630	0.07750	0.07680	0.07731
0.0771	0.07826	0.07540	0.07510	0.07630	0.07724	0.07680	0.07754
0.0771	0.07830	0.07540	0.07508	0.07630	0.07750	0.07680	0.07779
0.0771	0.07802	0.07540	0.07510	0.07630	0.07750	0.07680	0.07702
0.0771	0.07826	0.07540	0.07486	0.07630	0.07750	0.07680	0.07752

Table 2 (cont.)

0.0976	0.09740	0.09560	0.09670	0.09680	0.09893	0.09730	0.09958
0.0976	0.09815	0.09560	0.09719	0.09680	0.09763	0.09730	0.09927
0.0976	0.09837	0.09560	0.09694	0.09680	0.09785	0.09730	0.09930
0.0976	0.09865	0.09560	0.09719	0.09680	0.09812	0.09730	0.09952
0.0976	0.09839	0.09560	0.09670	0.09680	0.09787	0.09730	0.09927
0.0976	0.09813	0.09560	0.09696	0.09680	0.09814	0.09730	0.09925
0.0976	0.09839	0.09560	0.09721	0.09680	0.09789	0.09730	0.09923
0.0976	0.09788	0.09560	0.09696	0.09680	0.09814	0.09730	0.09874
0.0976	0.09813	0.09560	0.09721	0.09680	0.09812	0.09730	0.09930
0.0976	0.09839	0.09560	0.09696	0.09680	0.09789	0.09730	0.09927
0.1175	0.11766	0.11500	0.11690	0.11660	0.11815	0.11700	0.11904
0.1175	0.11814	0.11500	0.11665	0.1166	0.11840	0.11700	0.11899
0.1175	0.11839	0.11500	0.11692	0.1166	0.11864	0.11700	0.11874
0.1175	0.11865	0.11500	0.11668	0.1166	0.11840	0.11700	0.11899
0.1175	0.11814	0.11500	0.11692	0.1166	0.11864	0.11700	0.11874
0.1175	0.11839	0.11500	0.11668	0.1166	0.11889	0.11700	0.11874
0.1175	0.11865	0.11500	0.11720	0.1166	0.11810	0.11700	0.11899
0.1175	0.11863	0.11500	0.11695	0.1166	0.11810	0.11700	0.11896
0.1175	0.11863	0.11500	0.11692	0.1166	0.11815	0.11700	0.11874
0.1175	0.11863	0.11500	0.11695	0.1166	0.11818	0.11700	0.11872

Summary

ppm	bp	calc'd	expt'l	rsd	se		
09/25/95							
97.4	772	0.0379	0.0374	0.438	-0.0005		
198	772	0.0771	0.0781	0.472	0.0010		
251	771	0.0976	0.0982	0.354	0.0006		
302	771	0.1175	0.1184	0.277	0.0009		
04/12/96							
97.4	754.8	0.0371	0.0369	0.619	-0.0002		
198	754.3	0.0754	0.0751	0.217	-0.0003		
251	754.7	0.0956	0.097	0.204	-0.0014		
302	754.9	0.115	0.1169	0.143	0.0018		
04/30/96							
97.4	763	0.0376	0.0381	0.342	0.0005		
198	763	0.0763	0.0774	0.176	0.0011		
251	763	0.0968	0.0981	0.356	0.0013		
302	764	0.1166	0.1184	0.235	0.0018		
07/30/96							
97.4	768.3	0.0378	0.03751	0.828	-0.0003		
198	768.2	0.0768	0.07737	0.347	0.0006		
251	767.9	0.0973	0.09928	0.224	0.0020		
302	767.8	0.117	0.1189	0.115	0.0019		

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