Concentration Verification of Ethanol/Nitrogen Compressed Gas Cylinders Prior to use for Periodic Determinations of Accuracy in California

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Abstract

A method that uses compressed gas ethanol breath standard (EBS) cylinders to perform periodic determinations of accuracy on evidential breath alcohol instruments in California was developed. To use EBS cylinders, the California State Department of Health Services required verification of the ethanol content of the EBS cylinders using an infrared method. The infrared method developed employs a modified Alcotest 7110 MK III-C manufactured by National Draeger, Inc. that functions at the 9.5-mm wavelength of the infrared spectrum. Criteria and methodology for verifying EBS cylinder ethanol concentrations are described.

Introduction

California State Department of Health Services (DOHS) regulates forensic alcohol analysis of blood, breath, urine, and tissue specimens performed by laboratories in the state of California (California Health and Safety Code, Chapter 5, Sections 436.51 and 436.52). Although certain compressed gas ethanol breath standards (EBS) are on the Conforming Products List of Calibrating Units for Breath Alcohol Testers published by the U.S. Department of Transportation National Highway Traffic Safety Administration (1), DOHS has traditionally not allowed laboratories to calibrate evidential breath alcohol instruments using compressed gas EBS. Further, DOHS has traditionally required forensic alcohol laboratories to use reference alcohol water solutions to perform periodic determinations of accuracy (PDAO) on evidentiary breath alcohol instruments. In order to use compressed gas EBS to perform PDAOs, DOHS required the Kern County Regional Criminalistics Laboratory (KCRCL) to perform a concentration verification of commercially produced compressed gas ethanol/nitrogen mixtures using infrared spectroscopy. The alternate testing procedure using infrared spectroscopy proposed by the Department of Transportation National Highway Traffic Safety Administration for evaluating the accuracy and precision of dry gas ethanol calibrating units (2) was used by the KCRCL as a guideline in developing the method. The method was approved by DOHS December 17, 1999, and implemented shortly thereafter.

The primary reason for implementation of compressed gas PDAOs was the size of coverage area for KCRCL. The County of Kern is located at the southern end of the San Joaquin Valley in California and encompasses large areas of valley farm land, the southern Sierra mountains, and vast portions of the Mojave desert. KCRCL maintains a total of 16 breath alcohol evidentiary instrument stations located throughout this region, which covers a total of 8073 square miles. Travel time to the most remote station is 2 h one way.

Because of this remote access, the use of reference alcohol water solutions to perform periodic determinations of accuracy has been problematic throughout the years. These problems have included proper storage and handling of solution, proper set up of solution in the simulator, proper hook up of the simulator to the evidentiary instrument, transportation of solution, and training of key law enforcement personnel to perform accuracy checks. These problems have frequently led to erratic results, necessitating an unscheduled visit to the site by laboratory personnel.

Apparatus

A modified Alcotest 7110 MK III-C designed and manufactured by National Draeger, Inc. (Durango, CO) is used by the laboratory to perform EBS concentration verifications. The modified Alcotest 7110 MK III-C, hence referred to as the Alcotest EBS Verifier (AEV), is a stand-alone instrument that uses an infrared sensor to
detect ethanol in the 9.5-μm region of the infrared spectrum. It is compact (40 cm W × 13 cm H × 26 cm D), has a lid, weighs only 7.3 kg, and can be stored in a cabinet between uses. The breath hose of the modified Alcotest 7110 MK III-C was removed, eliminating subject breath alcohol analysis functionality. Additionally, the AEV contains an absolute pressure transducer to compensate for changes in barometric pressure. An Alcotest® CU34 wet-bath Simulator at 34.0 ± 0.1°C, supplied by National Draeger, Inc., is used to deliver reference alcohol vapors to calibrate the AEV. The compressed gas used in the method is the SCOTTY® V model EBS™ Gaseous Ethanol Breath Standard (National Draeger, Inc.) ([EtOH] = 0.100% ± 2% ethanol in nitrogen), which is directly traceable to NIST Research-Gas Mixture (RGM) gas standards (3). Each cylinder is labeled with a lot number by the manufacturer, with a lot being 24 cylinders filled at the same time from the same source of ethanol/nitrogen gas.

Methods and Calculations

Preparation of reference alcohol solutions

Alcohol reference solutions are generated using 200 proof EtOH (Sigma Chemical Co., St. Louis, MO) and Type I deionized water at 20°C. All glassware and equipment were certified Class A. The concentration of each reference solution is determined by a modified potassium dichromate/ferrous ammonium sulfate direct oxidimetric (D.O.) titration method. Briefly, an aliquot of each reference alcohol solution is removed and analyzed. Parameters of the assay require six replicate determinations for each reference alcohol solution that do not differ by more than ±0.002% relative to their mean. This calculated mean value then becomes the assigned D.O. value for that reference alcohol solution. D.O. values are reported to three decimal places as grams percent (g/dL).

Using the method of Harger et al. (4), the D.O. value is converted to a breath alcohol equivalent value (BrAE) corresponding to liquid/vapor equilibrium values for aqueous EtOH solutions at 34.0°C. Alcohol reference solutions which produce 0.090% and 0.002% relative to their mean. This calculated mean value then becomes the assigned D.O. value for that reference alcohol solution. D.O. values are reported to three decimal places as grams percent (g/dL).

Calibration of AEV

An Alcotest CU34 simulator at 34.0 ± 0.1°C was used to deliver the BrAE reference alcohol vapors to the AEV. The AEV contains an air pump that uses room air to carry the vapor samples into the sample chamber. The sample chamber of the AEV was thoroughly flushed with room air, and a raw IR signal numerical value (NV) was obtained for the room air sample vapor (see Calculations section). Then, the sample chamber of the AEV was thoroughly flushed with reference alcohol sample vapor, and a raw IR signal NV was obtained for the reference alcohol sample vapor. After that, the sample chamber of the AEV was thoroughly flushed with room air, and a raw IR signal NV was obtained for this room air sample vapor. In all, 12 room air sample vapors and 6 reference alcohol sample vapors per reference alcohol solution were analyzed in this manner. The average NV for the room air sample vapor before and after each reference alcohol sample vapor was calculated and recorded along with the readings for the six reference alcohol sample vapors. The AEV is calibrated each day a lot of cylinders is tested.

Testing of cylinders

A concentration verification was performed on at least 25% of cylinders from each specific lot received by the laboratory. The process is analogous to that for AEV calibration with the substitution of EBS gas from a cylinder for the reference alcohol sample vapor from the wet bath simulator. Because of the possibility that cylinders may have been exposed to low temperatures during shipping, which may cause condensation of EtOH vapor, all cylinders received into the laboratory must sit overnight to reach room temperature and be periodically rolled back and forth during a 30-min period prior to use in order to assure homogeneity.

A minimum of 20 room air sample vapors and 10 compressed gas EBS samples per cylinder lot were analyzed in this manner. The average reading for the room air sample vapor before and after each EBS sample vapor was calculated and recorded. The identification number of each cylinder tested and the resultant sample vapor readings were recorded. The absorbance for each sample vapor was calculated and recorded (see Calculations section).

Calculations

The infrared procedure using the AEV is based on the Beer-Lambert Law of absorption and non-dispersive spectroscopy. The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorbing species expressed by

$$I = I_0e^{-abc}$$

where I is the intensity of measuring radiation which passes through and emerges from the sample chamber; I₀ is the incident intensity which enters the sample chamber; a is the absorbivity 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 = Breath Alcohol Equivalent Vapor Value).

The ratio I₀/I is equal to the ratio of the raw IR signal from the empty cell to the raw IR signal from the filled cell (corrected for water vapor, if present). This raw IR signal is the integrated value directly from the instrument IR circuitry's AC signal. This integral is displayed by the instrument as a 5-digit, unitless numeric value (NV).

Contribution of water vapor

Although the reference alcohol solutions are water saturated, the EBS samples are not, so the contribution of water vapor to the raw IR signal reading of a reference alcohol sample vapor reading must be accounted for. An Alcotest CU34 Simulator at 34.0 ± 0.1°C was used to deliver a series of six pure water sample vapors to the AEV in a process analogous to that for AEV calibration and gas cylinder testing. In all, 12 room air sample vapors and 6 water sample vapors were analyzed in this manner. The average NV for the room air sample vapor before and after each water sample vapor was calculated and recorded along with the readings for the six water sample vapors. The water vapor correction for each of the six water sample vapor readings was calculated using the equation
and each result is subsequently recorded. Using the average water vapor correction result, the corrected reference alcohol vapor value is calculated for each reference alcohol sample using the equation

\[
NV_{\text{corrected}} = NV_{\text{water vapor}} + NV_{\text{room air}}
\]

There is also a small correction necessary to account for the water vapor in room air versus totally dry nitrogen/ethanol gas. Room air blanks were run against pure, dry nitrogen, and the water vapor contribution by room air water was calculated and used to adjust all subsequent room air blank values.

**Compensation for ambient pressure differences**

As stated earlier, the Alcotest 7110 MK III-C is equipped with an absolute pressure transducer that automatically accounts for differences in ambient pressure versus sea level, which can produce changes in ethanol/nitrogen gas concentrations. DOHS currently requires that these corrections be checked manually during every cylinder lot analysis. Consequently, the day the AEV is used to verify a lot of cylinders, the barometric pressure is obtained from the official local National Weather Service (NWS) station and calculated BrAE values are adjusted according to the equation

\[
\text{Actual BrAE}_{\text{EBS vapor}} = \frac{\text{BrAE}_{\text{EBS vapor}} \times \text{Barometric pressure at sea level}}{\text{Local barometric pressure (per NWS)}}
\]

The AEV barometric pressure reading must be within ±1% of the local value.

**Calculation of ab factor for reference alcohol solutions**

Recall, according to Beer-Lambert: \( \ln \left( \frac{I_o}{I} \right) = abc = ab(\text{BrAE}) \)

where \( I_o \) is \( NV_{\text{empty cell avg.}} \); \( I \) is \( NV_{\text{ref alc vapor}} \) - Average \( NV_{\text{water vapor}} \); \( a \) 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, \( c = \text{BrAE} \)).

Therefore:

\[
\ln \left( \frac{NV_{\text{empty cell avg.}}}{\text{Average } NV_{\text{water vapor}}} \right) = ab(\text{BrAE})
\]

\[
\text{Absorbance}_{\text{ref alc vapor}}/\text{Average ab} = \text{BrAE}_{\text{EBS vapor}}
\]

**Discussion**

In order for a lot of compressed gas EBS cylinders to be used for PDOAs, DOHS requires each EBS test sample result from the lot be within the manufacturer's accuracy and precision specification (0.100% ± 2%). The KCRCL has used this method to test several lots of compressed gas EBS cylinders, and all results have been 0.100% ± 2%. The method is a simple and effective means for verifying the concentration of compressed gas EBS cylinders. Since the approval of the KCRCL concentration verification method by DOHS, the California Department of Justice, Bureau of Forensic Services (BFS) has adopted the procedure for use with their evidentiary breath alcohol instruments. Application of new technology being an iterative process, DOHS has allowed BFS some minor modifications in the method that streamline the procedure and make compliance easier. These include (1) allowing BFS to calculate an average value for all cylinders tested in any one lot which must then fall within the ±2% target range and (2) allowing the use of different BrAE values (0.080 ± 0.002% and 0.120 ± 0.002%) for alcohol reference solutions that are used to calibrate the AEV.

Use of compressed gas EBS cylinders represents a marked improvement in evidentiary breath instrument accuracy verification procedures in terms of both the scientific confidence in the results obtained and ease of operation and maintenance. Not only are the logistical problems normally attendant with wet bath simulators avoided, but the need for Harger-type calculations converting directly measured liquid-phase concentrations of ethanol/water solutions into gas-phase ethanol concentrations is eliminated.

Dry gas cylinder verification procedures used by other agencies range from no independent verification to the purchase of NIST-traceable primary ethanol/nitrogen gas cylinders from the vendor and subsequent filling of the smaller individual tanks by the agency itself. Previously, gas chromatographic analysis has been used to verify cylinder gas concentrations, but several technical issues made the method difficult to use. To our knowledge, this is the first method that uses a modified IR breath alcohol testing instrument for EBS cylinder verification. The method does not require special set-up or instrumentation, eliminating the need to purchase a dedicated bench-top unit. Expanded use of compressed gas EBS cylinders for PDOAs by additional agencies along with the continued high percentage of concentration verification test results that fall within specification might eventually lead to the acceptance of compressed gas EBS cylinders for calibration of evidentiary breath alcohol instruments by DOHS in California.

**Acknowledgments**

The authors thank Hansueli Ryser of National Draeger, Inc., Lance Silverman of Scott Specialty Gases, Inc., and Clay Larson.
of the California Department of Health Services for their support and technical assistance.

References


Manuscript received May 2, 2000; revision received October 3, 2000.