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Technical Note: The Stability of Aqueous Alcohol Standard Used in Breath Alcohol Testing after Twenty-Six Years Storage

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TECHNICAL NOTE: THE STABILITY OF AQUEOUS ALCOHOL STANDARD USED IN BREATH ALCOHOL TESTING AFTER TWENTY-SIX YEARS STORAGE

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ABSTRACT

The long-term stability of dilute alcohol aqueous solutions used in breath alcohol testing was determined after approximately twenty-six years storage at room temperature. At each alcohol concentration, aliquots from four single-sealed polyethylene bottles containing 500 mL of solution at manufactured alcohol concentrations of 0.484, 2.420, 3.025, and 3.630 mg/mL, were analysed in triplicate by headspace gas chromatography. After twenty-six years storage, the mean percent changes (and ranges) were +4.4 (–6.5 to +8.3), +0.6 (–13.9 to +5.5), –2.0 (–15.6 to +3.5) and –26.3 (–39.1 to +3.9) for each concentration, respectively. The greatest percent loss in alcohol occurred in the alcohol standard at the highest concentration and decreased at the lower alcohol concentrations tested. Dilute aqueous alcohol solutions (of 3.035 mg/mL or less) show remarkable stability after long term storage at ambient temperatures.

RÉSUMÉ

La stabilité à long terme des solutions d'alcool type utilisées dans le cadre des analyses d'alcool dans l'haleine a été déterminée à la suite d'un entreposage de vingt-six ans à la température de la pièce. Des échantillons provenant de quatre bouteilles de polypropylène scellées contenant 500 mL de solution d'alcool produite à des concentrations de 0,484, 2,420, 3,025 et 3,630 mg/mL ont été analysés en triplicata en chromatographie en phase gazeuse à pression de tête dynamique. Après un entreposage de vingt-six ans, le pourcentage moyen des changements (et l'écart) étaient =4,4 (–6,5 à +8,3), +0,6 (–13,9 à +5,5), –2,0 (–15,6 à +3,5) et –26,3 (–39,1 à +3,9), respectivement, à chaque concentration; la plus grande perte en alcool se produisant dans les solutions d'alcool type à plus haute concentration et diminuant avec la teneur en alcool. Les solutions d'alcool type les plus faibles (de 3,035 mg/100 mL ou moins) ont démontré une stabilité remarquable après une longue période d'entreposage à la température de la pièce.

INTRODUCTION

The stability of the dilute aqueous alcohol solutions used to check the calibration of breath alcohol testing instruments and devices is occasionally questioned in court. Different manufacturers of alcohol standards have different expiry dates. Currently, Alcohol Countermeasure Systems (Mississauga, Ontario) has a two-year expiry date from the day of manufacture, CALWave Inc (Laval, Quebec) has an expiry date of two years and up to one month (i.e. expires after two years at the end of the month it was manufactured), and Laboratoire Atlas Inc (Montreal, Quebec) has an expiry date of three years and up to one month. There are few published scientific studies on the long-term stability of dilute aqueous alcohol standard solutions, especially solutions stored under ambient con-

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ditions (1–3). Most of these studies determined the stability of the alcohol standard for between one and 2.25 years (1, 3). The longest published stability study currently is thirteen years (2). In the present study, the stability of alcohol standard was determined after storage of approximately twenty-six years.

METHODS AND MATERIALS

Aliquots of solution from four bottles of each of four different labeled alcohol concentrations were analysed in triplicate by headspace gas chromatography using dual columns (4). The accuracy of this method is 0.05 milligrams of alcohol in each millilitre of sample (mg/mL) at concentrations of less than 1.0 mg/mL or 5% at concentrations exceeding 1.0 mg/mL.

The alcohol standard concentrations were labeled as containing 0.484, 2.420, 3.025, and 3.630 milligrams of ethyl alcohol in each millilitre of solution. The concentrations correspond to a result of 40, 200, 250, and 300 milligrams of alcohol in 100 millilitres of blood when used in a simulator at 34°C for a breath alcohol-testing instrument calibrated using a blood/breath ratio of 2100/1 (5). The solutions were manufactured by BDH Chemicals (Toronto) on March 1978, August 1978, December 1978, and December 1978, respectively, and used for the evaluation of an approved screening device according to the Alcohol Test Committee Standards (6). The initial concentrations of the alcohol standards were verified in 1978 using the modified Widmark method (7), however, the exact analytical results are no longer available at this laboratory. The unopened bottles of the alcohol solutions not used in the evaluation were stored in a cupboard at room temperature at the Centre of Forensic Sciences and were analysed in May 2004.

The expiry dates on these bottles were listed as one year from the date of manufacture. The volume of alcohol standard solutions in each polyethylene bottle was approximately 500 mL. The bottles were sealed with a single seal. Currently the alcohol standards used in Ontario are double sealed. All seals were intact at the time of the analysis. The solutions did not contain any preservatives.

RESULTS AND DISCUSSION

The results of the analyses (in triplicate) for each bottle are shown in Table 1. The mean percent changes (and ranges) were +4.4 (-6.5 to +8.3), +0.6 (–13.9 to +5.5), –2.0 (–15.6 to +3.5) and –26.3 (–39.1 to +3.9) for initial alcohol concentrations of 0.484, 2.420, 3.025, and 3.630 mg/mL, respectively. Figure 1 shows the mean results at the four concentrations. Only ethanol was detected by headspace gas chromatography. No other volatiles such as acetaldehyde, acetone, or n-propanol, which may indicate bacterial or other microorganism metabolism, were detected (4,8).

Two previous studies have found no significant changes in the alcohol concentration of dilute aqueous solutions for storage up to 2.25 years at room temperature (1,3). The other study found that after 13.5 years storage at room temperature, there was a decrease of between 13 and 22% from an initial alcohol concentration of 0.847 mg/mL (2). This was an apparent annual decrease of between 1 and 1.6% a year. In our study, a similar apparent decrease in alcohol concentration was observed only in one bottle containing a much higher alcohol concentration (3.630 mg/mL). The largest percent loss in alcohol concentration in this instance was 39.1%, which is equivalent to an annual loss, if uniform, of approximately 1.5% per year. At alcohol concentrations less than 3.630 mg/mL, the greatest decrease was 15.6% which, when annualized, is 0.6% a year. The long-term stability of the alcohol standard with concentrations less than 3.630 mg/mL is even more impres-

TABLE 1

The detected alcohol concentration (the result for each bottle is the mean of triplicate analyses), the percent change and the mean at each concentration.

Labeled initial Concentration (mg/mL)	Detected Concentration (mg/mL)	Per Cent Change
0.484	0.520	+7.5
	0.524	+8.2
	0.524	+8.3
	0.452	-6.5
Mean	**0.505**	**+4.4**
2.420	2.543	+5.1
	2.554	+5.5
	2.084	-13.9
	2.553	+5.5
Mean	**2.434**	**-0.6**
3.025	3.072	+1.5
	2.552	-15.6
	3.130	+3.5
	3.102	+2.6
Mean	**2.964**	**-2.0**
3.630	2.357	-35.1
	2.364	-34.9
	2.212	-39.1
	3.772	+3.9
Mean	**2.676**	**-26.3**

sive as the solutions were not refrigerated and no preservatives such as sodium fluoride were added to the solutions.

As alcohol is more volatile than water, it would be expected that only losses in alcohol would occur upon storage. The apparent increases in detected alcohol concentrations, especially in the solutions at the lower alcohol concentration, are probably due to the analytical variability of the headspace GC method and do not reflect an actual increase.

In our study, four different alcohol concentrations were measured. Generally, there was a greater mean percent decrease in alcohol concentration after 26 years storage at higher initial alcohol concentrations. This has not been observed in other studies as usually only one concentration of alcohol standard has been measured. The greater percentage of alcohol lost at the higher alcohol standard concentration may be due in part to Fick's First Law of Diffusion (9), in which there is a greater concentration gradient at higher alcohol concentrations. The concentration of the alcohol standard used in simulators in Ontario for the Intoxilyzer® 5000C and the Alcotest 7410 GLC is 1.21 mg/mL (5). Although no bottles containing this concentration of alcohol standard had been stored, this concentration is between the lower two measured concentrations (i.e. 0.484 mg/mL and 2.420 mg/mL) and would be expected to have similar changes over twenty-six years. In addition, bottles of the alcohol standard currently in use in Ontario have double seals around the cap, and it would be expected that any losses due to storage would be reduced. Based on the findings in this study, the manufacturers' expiry date for alcohol solutions at a concentration of 1.21 mg/mL are very conservative.

CONCLUSION

Dilute aqueous alcohol standards at concentrations of 3.025 mg/mL and less are remarkably stable when stored at room temperature for approximately 26 years. The greatest

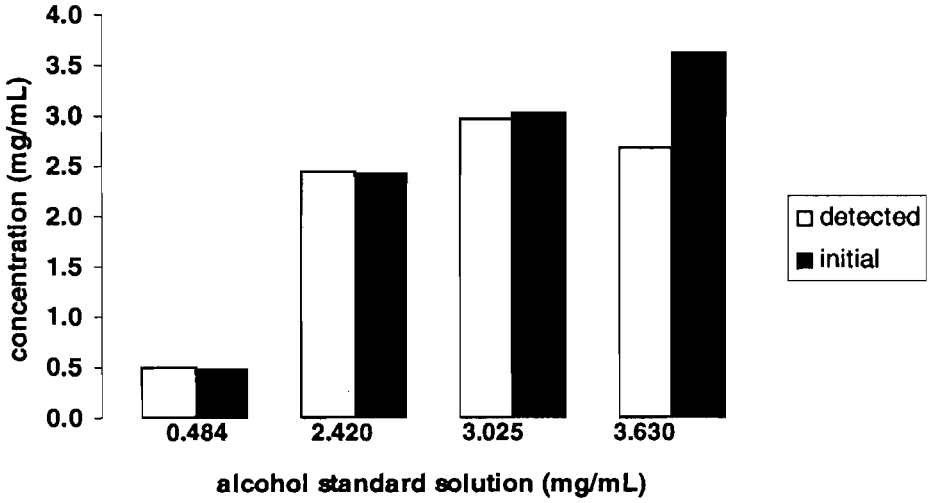

Figure 1. A bar graph of the initial and mean alcohol concentrations detected after twenty-six years storage.

decrease in alcohol concentration was 15.6%, which if uniform, indicates an annual loss of approximately 0.6% per year. Much higher losses of alcohol concentration occurred at the highest alcohol standard tested (3.630 mg/mL) in which the greatest annual loss, if uniform, was 1.5% per year.

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