SDPD Forensic Chemistry Section

Forensic Alcohol Analysis - Uncertainty of Measurement of Ethanol in Blood and Urine By Headspace Gas Chromatography

Introduction

For this study, a Perkin Elmer Clarus 500 Gas Chromatograph (HSGC3) coupled with a flame ionization detector, a heated headspace autosampler Turbomatrix 110, and a gas chromatography data handling system was utilized. To estimate uncertainty of measurement, the process of alcohol quantitation was evaluated to include the following sources of uncertainty: HSGC3 instrument, the sample diluter, different analysts, different days, and different times of day.

Procedure

Each analyst ran at least once on HSGC3 to include ten replicates of the 0.050, 0.080, 0.200, and the 0.300 standards, two replicates of the 0.400 standard, and two replicates of the quality control reference solution (QCR). Each run was performed on different days and at different times of the day.

Defining Factors of Uncertainty of Measurement

In estimating measurement uncertainty, the following factors that affect the measurement taken will be addressed:

- **Reported Accuracy of Certified Reference Material (CRM) Ethanol Standards:**
  The standards are Certified Reference Materials (CRM) with values traceable to NIST Standardized Reference Material (SRM). Five (5) different levels of ethanol were analyzed with the following manufacturer established values (± margin of error is for a 95% confidence interval).

  1. **0.050 Standard (± 0.00018)**
  2. **0.080 Standard (± 0.00028)**
  3. **0.200 Standard (± 0.00070)**
  4. **0.300 Standard (± 0.00106)**
  5. **0.400 Standard (± 0.00140)**

- **Accuracy and Linearity:**
  The instruments' ability to measure ethanol levels accurately and throughout a range of values represents the accuracy and linearity. The overall maximum average difference encompassing the five (5) CRM standard levels tested will determine accuracy and linearity. This measurement encompasses the intra-

analyst variability, inter-analyst variability, time of day variability, and different day variability although there were no significant differences found.

- **Precision (repeatability)**

  The instruments ability to consistently deliver the same reading of a known amount. The overall maximum standard deviation of repeated measurements was calculated and is a statistical measure of precision.

- **The sample diluter and the Headspace GC/FID instrument:**
  Variability associated with these aspects of sample preparation and quantitation are incorporated into our evaluation of the whole process of alcohol quantitation and will be reflected in the measurements of accuracy and precision.

Reporting the Uncertainty of Measurement

Reporting the uncertainty will be expressed at a coverage level of k = 2 and a confidence level of approximately 95%.

- **Type A Uncertainties:** Uncertainty results from a measurement that are scattered in a random fashion due to chance. This uncertainty can be determined by a large number of repeated measurements and is considered to be a normal or Gaussian shaped distribution.
  - Precision (Repeatability)
  - Accuracy and Linearity
- **Type B Uncertainties:** Systematic inherent bias in the quantitative analytical process. This uncertainty is considered to be a uniform or rectangular distribution, with each potential value measurement bias being equally likely over an interval.
  - Accuracy of Certified Reference Material ethanol values
    The manufacturer's reported uncertainty is not a significant contributor to the overall expanded uncertainty and will not be incorporated into the calculation.

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Results:

Table 1 summarizes the uncertainty of measurement results for precision, accuracy, and linearity.

Table 1

CRM Established Value	Standard Deviation	Maximum Average Difference
0.050	0.00048	0.00104
0.080	0.00045	0.00122
0.200	0.00162	0.00184
0.300	0.00213	0.00109
0.400	0.00237	0.00100

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Uncertainty Budget Table:

Headspace GC3

Factors	Value (x)	Standard Uncertainty (u)	Distribution	*Relative contribution
Repeatability[1]	0.00237	0.00237	Normal	56%
Accuracy and Linearity[2]	0.00184	0.00184	Normal	44%

[1]Maximum standard deviation (Standards 0.050, 0.080, 0.200, 0.300, and 0.400)
[2]Maxiumum average difference over five levels (Standards 0.050, 0.080, 0.200, 0.300, and 0.400)
*Each standard uncertainty value divided by the total standard uncertainty multiplied by 100

Calculation of Combined Standard Uncertainty:

$$U_c = \sqrt{u(repeatability)^2 + u(accuracy\ and\ linearity)^2}$$

$$U_c = \sqrt{(0.00237)^2 + (0.00184)^2} = \mathbf{0.0030}$$

Calculation of Expanded Uncertainty:

$U = k \times U_c$ Where U is the expanded uncertainty and k is the coverage factor.

Approximate 95% **where k= 2** **± 0.0060**

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Reevaluating Uncertainty of Measurement

This study was performed during the following weeks: January 19th, February 1st, and February 10th. The uncertainty of measurement will be re-established annually and whenever any part of the process is altered so that it will affect the measurement quantitation. This will include repair or upgrade of GC headspace instruments with new hardware or new software that would affect quantitation, and repairing or replacing the sample diluter. The maximum standard deviation and the largest average difference will be determined using different levels of the certified reference material standards and will then be incorporated into the combined standard uncertainty measurement.

Technical Review _____ Date 2-17-16

Administrative Review _____ Date 2/17/16

Quality Assurance Manager _____ Date 2/18/16