Experiment 4: Troubleshooting the Breathalyzer Test by UV-Vis Spectroscopy
CH3400: Instrumental Analysis, Plymouth State University


Introduction:
The “Breathalyzer test” used by law enforcement officials to determine a suspect's Blood Alcohol Level (BAC) is a calorimetric technique that depends on the oxidation of ethanol by chromate according to the reaction:

\[ 3\text{C}_2\text{H}_5\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16 \text{H}^+ \rightarrow 3\text{CH}_3\text{CO}_2\text{H} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O} \]

Dichromate (Cr₂O₇²⁻) is an intensely orange colored compound, and as it reacts with the ethanol, the color fades. Thus, the concentration of ethanol can be deduced by using UV-Vis spectrophotometry to measure the amount of dichromate.

“An Experiment in Forensic Chemistry: the Breathalyzer” is an article published in the Journal of Chemical Education by WC Timmer (Vol 63, page 897, 1986), however, there is an error in the procedure as published, which yields erroneous results. Your job in this lab is to work together in a group to troubleshoot the procedure and find a way to run the analysis to get a reasonable analysis.

Equipment: Read through the procedures and make a list of the equipment you will need.

Safety Considerations:
1. Chromium (Cr) is a toxic heavy metal! DO NOT THROW ANY SOLUTIONS DOWN THE SINK. All solutions and first washes must be disposed of in a properly labeled waste container.
2. Many of the solutions you will be using contain 50% sulfuric acid!
3. In consideration of points 1 and 2, wear your safety glasses and wash your hands frequently. Be careful in your handling of all reagents and solutions in this experiment. KEEP YOUR WORKING AREA CLEAN!

Procedure:
Pre-Lab You MUST do these steps and calculations (included in your Notebook) before lab.
1. Obtain a copy of the article WC Timmer, “An Experiment in Forensic Chemistry: the Breathalyzer,” J Chem Ed, 63(10):897 (1986). You can get this through the University's subscription to the journal either online or in the library.
2. Given that the density of Ethanol is 0.785 g/mL at 25°C, calculate the molarity of a solution containing 31 µL of Ethanol in 1.0 L of aqueous solution.
3. Using the following information, calculate the concentration of ethanol in the Ethanol Sample. The details for making up these solutions will be the same as in your lab procedure; the only new information here are the absorbances:
   • Chromate solution: 0.0125 g K₂Cr₂O₇ in 50.0 mL of 50% sulfuric acid
   • Standard solution: 10.0 mL of Chromate solution + 1.0 mL water. Absorbance: 0.270
   • Sample reaction: 10.0 mL of Chromate solution + 1.0 mL Ethanol Solution. Abs: 0.215
You should calculate a concentration of 2.62 mM (which is NOT the same as in Q2, due to the "error" in this lab!). Hints: did you correctly account for dilution in the Standard and Sample? Did you correctly calculate molecular weight and consider stoichiometry?
In Lab

1. Prepare the solutions outlined in this paper with some modifications:
   a) You will be given a 50% solution of H$_2$SO$_4$. Accurately weigh ~ 12.5 mg of AgNO$_3$ and K$_2$Cr$_2$O$_7$. (Note: you do NOT have to have exactly 12.5 mg! Get close and record exactly what you did weigh to all the decimal places on the balance.) Add these to a 50 mL flask and dilute to the mark with the 50% H$_2$SO$_4$. Calculate the actual molarity of this solution to the proper number of sig figs. Transfer to a plastic bottle.
   b) You will be given a stock solution of 3,100 μL/L of ethanol in water. Dilute this 1:100 by adding 0.500 mL to a 50.0 mL volumetric flask and diluting to the mark with distilled water. This is your Sample

2. Prepare a blank and a sample solution according to the published procedure, except use 0.5 mL and 5.0 mL dispensed by an auto-pipette.

3. Run the blank and the sample solution on the UV-Vis spectrophotometer. Record the absorbance at 440 nm

4. Calculate the concentration of Ethanol in the Sample.

5. The amount you found in '4' should be 31 μL/L. (Hint: you may do calculations in mM using numbers in Pre-Lab Question 2), but it is almost certainly not. Calculate your percent error.

6. Discuss with your group some things you might try to fix the problem. Make a list of at least 3.

7. Consult your instructor with your list. Once you have his approval, try your potential solutions. Repeat until you solve the problem!

Analysis (Lab Notebook)
The following must be completed in your lab notebook before you can turn in your Notebook Report:

1. Provide the equations you used and a sample calculation for calculating the concentration of ethanol in your solutions.

2. Provide a table of concentrations of solutions, parameters, etc. used in each of your analyses, along with the calculated concentration of ethanol and the percent error.

Lab Report including Conclusions and Discussion

Your lab report is due by lecture on Wednesday,. Your report must be handed in BOTH electronically (via Moodle) and in hard copy form. See the document "LabReportGuide.pdf" on the course website (http://oz.plymouth.edu/~jsduncan/courses/2011_Fall/InstrumentalAnalysis) for guidelines on writing your report.

In addition to the Analysis performed in your notebook, include the following in your report (place them in the most relevant sections):

1. Briefly discuss your troubleshoot methodology. What aspects of the analysis did you consider in trying to solve the problem? Which of these did you try, and which did you rule out before trying?

2. What was your final solution to the problem? Include in your discussion any and all relevant figures of merit of the instrument (e.g., accuracy, precision, bias, sensitivity, detection limit, dynamic range and/or selectivity).