

### Problem Set 3 –Figures of Merit, Calibration and Least Squares Analysis

Complete all problems on separate paper. Show all work for credit. Correct use of significant figures is required for full credit. You can use a spreadsheet or other software package for this problem set but make sure that you also understand how to find all of the values and their associated uncertainties by hand.

1. Here are the mass spectrometric signals for known concentrations of methane in H<sub>2</sub>:

CH <sub>4</sub> (vol %)	0	0.062	0.122	0.245	0.486	0.971	1.921
Signal (mV)	9.1	47.5	95.6	193.8	387.5	812.5	1671.9

- Subtract the blank value (9.1 mV) from all other values. Then use the method of least squares to find the slope and intercept and their uncertainties. Construct a calibration curve.
  - Replicate measurements of an unknown gave 144.1, 144.9, 143.9, and 145.1 mV. Determine the concentration of the unknown and its uncertainty. Determine the 95% confidence interval for the unknown.
  - A blank gave 8.4, 9.3, 10.8, 8.8, 9.6, 7.4 and 7.3 mV when measured multiple times. Determine the limit of detection at the 99% confidence level for the procedure.
- Pure water containing no mercury was spiked with 0.40 µg mercury /L. Seven replicate determinations gave 0.39, 0.40, 0.38, 0.41, 0.36, 0.35, and 0.39 µg/L mercury. Find the mean percent recovery of the spike and the detection limit for the method.
  - An unknown sample of Cu<sup>2+</sup> gave an absorbance of 0.262 in an atomic absorption analysis. Then 1.00 mL of a solution containing 100.0 ppm (i.e. µg/mL) Cu<sup>2+</sup> was mixed with 95.0 mL of the unknown and the mixture was diluted to 100.0 mL in a volumetric flask with DI water. The absorbance of the new solution was 0.500.
    - Denoting the initial, unknown concentration as [Cu<sup>2+</sup>]<sub>i</sub>, write an expression for the final concentration, [Cu<sup>2+</sup>]<sub>f</sub>, after dilution. Units of concentration are ppm.
    - In a similar manner, write the final concentration of added standard Cu<sup>2+</sup>, designated as [S]<sub>f</sub>
    - Find [Cu<sup>2+</sup>]<sub>i</sub> in the unknown.
  - A constant volume standard addition experiment is performed. Five flasks containing 25.00 mL of a serum with unknown concentration of Na<sup>+</sup> are labeled 1-5. Into each, varying volumes (see below) of 1.940 M NaCl standard is added. Each flask is then diluted to 50.00 mL.

Flask	1	2	3	4	5
Volume of standard added (mL)	0	1.000	2.000	3.000	4.000
Na <sup>+</sup> atomic emission signal (mV)	3.13	5.40	7.89	10.30	12.48

- Use Excel or Minitab to prepare a standard addition graph and find the concentration of Na<sup>+</sup> in the serum.
- Determine the uncertainty in the result.