

### Problem Set 3 – Uncertainty and Statistics

Complete all problems on separate paper. Show all work for credit. Correct use of significant figures is required for full credit.

1. We can measure the concentration of an HCl solution by reaction with pure sodium carbonate:  $2\text{H}^+ + \text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$ . A volume of  $27.5 \pm 0.04$  mL of HCl solution was required for complete reaction with  $0.9674 \pm 0.0009$  g of sodium carbonate (FM  $104.988 \pm 0.001$ ). Find the formality of the HCl and its absolute uncertainty.

$$\frac{0.9674 \pm 0.0009 \text{ g Na}_2\text{CO}_3 \times 1 \text{ mol Na}_2\text{CO}_3 \times 2 \text{ mol HCl} \times 1}{104.988 \pm 0.001 \text{ g Na}_2\text{CO}_3} \times \frac{1000 \text{ mL}}{27.50 \pm 0.04 \text{ L}} = 0.670137 \pm e \text{ M}$$

$$e = 0.670137 \text{ M} \sqrt{\left(\frac{0.04 \text{ mL}}{27.50 \text{ mL}}\right)^2 + \left(\frac{0.001 \text{ g}}{104.988 \text{ g}}\right)^2 + \left(\frac{0.0009 \text{ g}}{0.9674 \text{ g}}\right)^2}$$

$e = 0.001157 \text{ M}$   
**So:  $0.670 \pm 0.001 \text{ M}$**

2. For the HCl from problem 1, determine the pH and its absolute uncertainty.

$$\text{pH} = -\log(0.670 \pm 0.001 \text{ M}) = 0.17384 \pm e$$

$$e = 0.43429 \left(\frac{0.001157}{0.670317}\right) = 0.00075$$

**So:  $\text{pH} = 0.1738 \pm 0.0008$**

3. An atomic absorption method for the determination of copper in engine oil yielded copper contents of 8.35, 8.45, 8.23, 8.55, and 8.32  $\mu\text{g Cu/mL}$ . Determine the sample mean, sample standard deviation and median for these data. Find the 95% confidence interval for these results. (You may use a calculator or computer to do the calculations but you should indicate how you found them (i.e. TI-83, Excel, etc.))

Using Excel,

mean	8.38 $\mu\text{g Cu/mL}$
stdev	0.123288 $\mu\text{g Cu/mL}$
median	8.35 $\mu\text{g Cu/mL}$

$$\text{Confidence Range} = t_{s/\text{sqrt}(n)} = (2.776 \times 0.123288 \text{ } \mu\text{g Cu/mL}) / \text{sqrt}(5) = 0.1531 \text{ } \mu\text{g Cu/mL}$$

**So, confidence limit is:  $8.4 \pm 0.2 \text{ } \mu\text{g Cu/mL}$**

4. A titrimetric method for the determination of calcium in limestone was tested by analysis of a NIST limestone sample certified to contain 30.15 % CaO. The results of four analyses of the sample gave the following data: 30.27 %, 30.00 %, 30.28 %, 30.33 %. Use a Q-test to determine if a single point may be discarded at the 90 % confidence level. Use a Grubbs test to determine if a single point may be discarded at the 95 % confidence level. Do the data indicate the presence of systematic error at the 95 % confidence level?

**Q test:**

$$Q_{\text{calc}} = \frac{(30.27-30.00)}{(30.33-30.00)} = 0.818$$

$Q_{\text{critical}}$  for 4 data points is 0.76. Since  $Q_{\text{calc}} > Q_{\text{critical}}$ , the point is suspect and may be omitted.

**Grubbs Test:**

For the original dataset. The average is 30.22 and the standard deviation is 0.149.

$$G_{\text{calc}} = \frac{(30.27-30.00)}{0.149} = 1.812$$

$G_{\text{critical}}$  for 4 data points is 1.463. Since  $G_{\text{calc}} > G_{\text{critical}}$ , the point is suspect and may be omitted.

For the new dataset 30.27 %, 30.28 %, 30.33 %, the mean is 30.293% and standard deviation is 0.03215%.

Therefore the confidence interval is  $CI = 30.293 \pm (4.303 \times 0.03215) / \sqrt{3} = 0.079896\%$

**CI = 30.29 ± 0.08%. Since the true value falls outside this confidence interval, there is an indication of systematic error.**

You could also calculate a t:

$$t_{\text{calc}} = \frac{(30.293-30.15)(3)^{1/2}}{0.03215} = 7.543$$

**$t_{\text{critical}}$  for 2 degrees of freedom is 4.303. Since  $t_{\text{calc}} > t_{\text{critical}}$ , there is indication of systematic error.**

5. A food company testing a new method for the analysis of the polyunsaturated fat content of various vegetable and animal oils obtained the results at the right for the old and new methods. Determine if the new and old analysis procedures are giving the same results at the 95% confidence level. (You may assume that the precision is approximately the same for these two methods. Feel free to use a spreadsheet to streamline calculations, just be sure you understand how do to the calculations by hand.)

Polyunsaturated Fat  
(% w/w of Total Fat)

Sample Number	Old Method	New Method
1	4.3	4.1
2	36.3	35.0
3	5.2	4.9
4	63.7	60.9
5	17.4	16.0
6	8.2	6.7
7	48.2	45.7
8	30.6	25.8

This approach requires comparing individual measurements from two methods. Therefore we look at the differences (d).

sample	method 1	method 2	d	$(d-d_{\text{average}})^2$
1	4.3	4.1	0.2	2.7225
2	36.3	35	1.3	0.3025
3	5.2	4.9	0.3	2.4025
4	63.7	60.9	2.8	0.9025
5	17.4	16	1.4	0.2025
6	8.2	6.7	1.5	0.1225
7	48.2	45.7	2.5	0.4225
8	30.6	25.8	4.8	8.7025
		mean d	1.85	
		sum of d's	15.78	
		$s_d$	1.501428	
		$t_{\text{calc}}$	3.485076	

$t_{\text{critical}}$  for 7 degrees of freedom is 2.365. Since  $t_{\text{calc}} > t_{\text{critical}}$ , there is a significant difference between the two methods.