10610CHEM311000-Analytical Chemistry (I)

分析化學一

First Midterm Examination

Date: 02-11-2017, 10:10 am to 12:10 pm

Answer **all 10 questions** (total 110%). You have **2** hours to finish this paper.

1. (a) To prepare a solution of NaCl, you weight out 2.634 ± 0.002 g and dissolve it in a volumetric flak whose volume is 100.00 ± 0.08 mL. Express the molarity of the solution, along with its uncertainty, with an appropriate number of digits. The molecular weight of NaCl is 58.443 ± 0.001. **[5%]**

(b) The pH of a solution is 4.44 ± 0.04. Find $[H^+]$ and its absolute uncertainty. **[5%]**

Solution:

1. (a) First, we calculate the molarity to be

mol/L = [(2.634 ± 0.002) / (58.443 ± 0.001)]/(0.10000 ± 0.00008)

= 0.4507 M

Then, we calculate the standard deviation after the propagation

$$\frac{S_y}{y} = \sqrt{\left(\frac{0.002}{2.634}\right)^2 + \left(\frac{0.001}{58.443}\right)^2 + \left(\frac{0.00008}{0.1}\right)^2}$$

Sy = 0.0011 * 0.4507

= 0.0005

So, the molarity of the solution is 0.4507 ± 0.0005 M

1. (b) Use the function $y = 10^x$ and the uncertainty is $s_y/y = 2.3026\ s$

$[H^+] = 10^{-4.44} = 3.63 \times 10^{-5}$ M

$s_y = 2.3026 * 0.04 * 3.63 \times 10^{-5} = 3.34 \times 10^{-6}$

$[H^+] = 3.6 \pm 0.3 \times 10^{-5}$ M

2. The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is found to be 12.6, 11.9, 13.0, 12.7, and 12.5 wt% in replicate analyses. Find the 80% and 90% confidence intervals for the carbohydrate content. **[4% each]**

Solution:

2. First, calculate the mean = 12.54 and standard deviation = 0.40 for the five measurements. For the 80% confidence interval, the value of t is 1.53 (degrees of freedom 5-1 = 4).

The 80% confidence interval is $\bar{x} \pm \frac{ts}{\sqrt{n}}$ = 12.54 ± $\frac{1.53\ X\ 0.4}{\sqrt{5}}$ = 12.54 ± 0.27 wt%

The 90% confidence interval is $\bar{x} \pm \frac{ts}{\sqrt{n}}$ = 12.54 ± $\frac{2.132\ X\ 0.4}{\sqrt{5}}$ = 12.54 ± 0.38 wt%

3. (a) Table 1 shows the values of bicarbonate (HCO_3^-) in the blood of racehorses obtained by two different instruments. The standard deviation from the original instrument is 0.28 (*N* = 11 measurements) and the standard deviation from the substituent instrument is 0.47 (*N* = 5 measurements). Is the substituent instrument more precise than the original? **[5%]**

(b) If there had been *N* = 13 replications in both data sets, would the substituent instrument be more precise than the original? **[5%]**

Table 1. Measurement of HCO_3^- in horse blood

	Original Instrument	**Substitute Instrument**
Mean (x̅, mM)	36.14	36.20
Standard Deviation (s, mM)	0.28	0.47
Number of Measurements, N	11	5

Solution:

3. (a) Use *F*-test to determine the precision of the two instruments. The less precise value from substitute instrument is placed in the numerator

$F_{calculate} = \frac{s_1^2}{s_2^2} = \frac{(0.47)^2}{(0.28)^2} = 2.82$

Since 2.82 ($F_{calculate}$) < 3.48 (F_{table}), we conclude that the substitute instrument does not improve the precision. We cannot reject Null hypothesis

3. (b) 2.82 ($F_{calculate}$) > 2.69 (F_{table}). Yes, there is an improvement in precision. We reject Null hypothesis and accept alternative hypothesis.

4. Sir William Ramsey, Lord Rayleigh, prepared nitrogen samples by several different methods. The density of each sample was measured as the mass of gas required to fill a particular flask at a certain temperature and pressure. Masses of nitrogen samples prepared by decomposition of various nitrogen compounds were 2.29280, 2.29940, 2.29849, and 2.30054 g. Masses of nitrogen prepared by removing oxygen from air in various ways were 2.31001, 2.31163, and 2.31028 g. Is the density of nitrogen prepared from nitrogen compounds significantly different from that prepared in air at the 95% and 99.9 confidence levels? **[10%]**

Solution:

For the first data set: $\bar{x} = 2.2978$

For the second data set: $\bar{x} = 2.3106$

s_{pooled} = 0.0027

Degrees of freedom = 4 + 3 – 2 = 5

$$t = \frac{2.2978 - 2.3106}{0.0027\sqrt{\frac{4+3}{4\times 3}}} = -6.207$$

For 5 degrees of freedom at the 95% confidence level, t = 2.57 and at the 99.9% confidence level, t = 6.87. Thus we can conclude that at 95% confidence level, the nitrogen prepared in the two ways is different. However, at the 99.9 % confidence level, the results are due to random error and the nitrogen prepared in the two ways is the same.

5. A reliable assay shows that the ATP (adenosine triphosphate) content of a certain cell type is 111 μmol/100 mL. You developed a new assay, which gave the values 117, 119, 111, 115, 120 μmol/100 mL for replicate analysis. Do your results agree with the known value at the 95% confidence level? **[10%]**

Solution:

$\bar{x}$ = 116.4, s = 3.58. the 95% confidence interval for 4 degrees of freedom is

$\bar{x} \pm \frac{ts}{\sqrt{n}} = 116.4 \pm \frac{2.78\ X\ 3.58}{\sqrt{5}} = 116.4 \pm 4.4$

= 112.0 to 120.8 μmol/100 mL.

The 95% confidence interval does not include the accepted value of 111 μmol/100 mL, so the difference is significant.

6. A single quality control (QC) sample was run in replicates of eight to produce the following mass spectral peak area signals: 2.2, 1.7, 1.9, 2.3, 2.1, 1.8, 2.7, and 2.3 peak area. The slope of the calibration curve is *m*=0.456 peak area/µM. Find the Limit of Detection (LOD) and Limit of Quantification (LOQ) values. **[4% each]**

Solution:

The standard deviation of above set of results $s=0.3_2$

LOD = $\frac{3(0.32)}{0.456}=2._1\mu M$

LOQ = $\frac{10(0.32)}{0.456}=7._0\mu M$

7. Students dissolved zinc from a galvanized nail and measured the mass lost by the nail to tell how much of the nail was zinc. Below are 12 results:

Mass loss (%): 10.2, 10.8, 11.6, 9.9, 9.4, *7.8*, 10.0, 9.2, 11.3, 9.5, 10.6, 11.6

The value *7.8* appears usually low. Should *7.8* be discarded before averaging the rest of the data or should *7.8* be retained. Use **Grubbs test** to decide. **[10%]**

Solution:

$$G_{\text{calculated}} = \frac{|x_{\text{question}} - \bar{x}|}{s}$$

$\bar{x}$ = 10.16, s = 1.11

$G_{calcualted}$ = |7.8-10.16|/1.11 = 2.13

In the Grubbs test table, G_{table} = 2.285 for 12 observations. Because $G_{calculated} < G_{table}$, the questionable point should be retained.

8. A standard method for the determination of glucose in serum is reported to have a standard deviation of 0.38 mg/L. If s = 0.38 is a good estimate of σ, how many replicates should be made in order for the mean of a sample to be within

(a) 0.3 mg/L of the true mean 99% of the time? **[4%]**

(b) 0.3 mg/L of the true mean 95% of the time? **[4%]**

(c) 0.2 mg/L of the true mean 90% of the time? **[4%]**

Solution:

(a) $0.3 = \dfrac{2.58 \times 0.38}{\sqrt{N}}$ For the 99% CI, $N = 10.7 \cong$ **11**

(b) $0.3 = \dfrac{1.96 \times 0.38}{\sqrt{N}}$ For the 95% CI, $N = 6.1 \cong$ **7**

(c) $0.2 = \dfrac{1.64 \times 0.38}{\sqrt{N}}$ For the 90% CI, $N = 9.7 \cong$ **10**

9. The phosphorous content was measured for three different soil locations. Five replicate determinations were made on each soil sample. A partial ANOVA table was shown as following:

Variation Source	**SS**	**df**	**MS**	**F**
Between Soils				
Within Soils			0.0081	
Total	0.374			

(a) Fill in the missing entries in the ANOVA table **[10%]**

(b) State the null and alternative hypotheses **[2%]**

(c) Do the three soils differ in phosphorous content at the 95% confidence level? **[5%]**

Solution:

(a)

Source	**SS**	**df**	**MS**	**F**
Between soils	0.374 – 0.0972 = 0.2768	3 – 1 = 2	0.2768/2 = 0.1384	0.1384/0.0081 = 17.09
Within soils	12 × 0.0081 = 0.0972	15 – 3 = 12	0.0081	
Total	0.374	15 – 1 = 14		

(b) H_0: $\mu_{samp1} = \mu_{samp2} = \mu_{samp3}$; H_a: at least two of the means differ.

(c) The F value for 12 degrees of freedom in the denominator and 2 degrees of freedom in the numerator at the 95% confidence level is 3.89. Since the F value calculated in the table exceeds F critical, we reject H_0 and conclude that the phosphorous contents of the soil samples taken from the 3 locations are different.

10. The homogeneity of the chloride level in a water sample from a lake was tested by analyzing portions drawn from the top and from near the bottom of the lake, with the following results in ppm Cl:

Top	**Bottom**
26.30	26.22
26.43	26.32
26.28	26.20
26.19	26.11
26.49	26.42

(a) Apply the *t* test at the 95% confidence level to determine if the chloride level from the top of the lake is different from that at the bottom. **[5%]**

(b) Now use the paired *t* test and determine whether there is a significant difference between the top and bottom values at the 95% confidence level. **[5%]**

(c) Why is a different conclusion drawn from using the paired *t* test than from just pooling the data and using the normal *t* test for differences in mean? **[5%]**

Solution:

(a)

For the Top data set, $\bar{x} = 26.338$

For the bottom data set, $\bar{x} = 26.254$

s_{pooled} = 0.1199

degrees of freedom = 5 +5 – 2 = 8

For 8 degrees of freedom at 95% confidence t_{crit} = 2.31

$t = \dfrac{26.338 - 26.254}{0.1199\sqrt{\dfrac{5+5}{5\times 5}}} = 1.11$ Since t < t_{crit}, we conclude that no significant difference exists at 95% confidence level.

(b)

From the data, $N = 5$, $\bar{d} = 0.084$ and $s_d = 0.015166$

For 4 degrees of freedom at 95% confidence $t = 2.78$

$$t = \frac{0.084 - 0}{0.015 / \sqrt{5}} = 12.52$$

Since 12.52 > 2.78, a significant difference does exist at 95% confidence level.

(c)

The large sample to sample variability causes s_{Top} and s_{Bottom} to be large and masks the differences between the samples taken from the top and the bottom.

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Appendix for Various Critical Values

TABLE 7-1

Confidence Levels for Various Values of z

Confidence Level, %	z
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

TABLE 7-3

Values of t for Various Levels of Probability

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

TABLE 7-4

Critical Values of F at the 5% Probability Level (95 % confidence level)

Degrees of Freedom (Denominator)	Degrees of Freedom (Numerator)								
	2	3	4	5	6	10	12	20	∞
2	19.00	19.16	19.25	19.30	19.33	19.40	19.41	19.45	19.50
3	9.55	9.28	9.12	9.01	8.94	8.79	8.74	8.66	8.53
4	6.94	6.59	6.39	6.26	6.16	5.96	5.91	5.80	5.63
5	5.79	5.41	5.19	5.05	4.95	4.74	4.68	4.56	4.36
6	5.14	4.76	4.53	4.39	4.28	4.06	4.00	3.87	3.67
10	4.10	3.71	3.48	3.33	3.22	2.98	2.91	2.77	2.54
12	3.89	3.49	3.26	3.11	3.00	2.75	2.69	2.54	2.30
20	3.49	3.10	2.87	2.71	2.60	2.35	2.28	2.12	1.84
∞	3.00	2.60	2.37	2.21	2.10	1.83	1.75	1.57	1.00

TABLE 4-5 Critical values of G for rejection of outlier

Number of observations	G (95% confidence)
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176
11	2.234
12	2.285
15	2.409
20	2.557

$G_{calculated}$ = |*questionable value* − *mean*|/*s*. *If* $G_{calculated} > G_{table}$, *the value in question can be rejected with 95% confidence. Values in this table are for a one-tailed test, as recommended by ASTM.*

SOURCE: *ASTM E 178-02 Standard Practice for Dealing with Outlying Observations, http://webstore.ansi.org; F. E. Grubbs and G. Beck, Technometrics* **1972,** *14, 847.*