11010CHEM311000-Analytical Chemistry (I) 分析化學一

First Midterm Examination

Date: 16-11-2021, 10:10 am to 12:10 pm

Answer **all 11 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. 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.

3. To test the quality of the work of a commercial laboratory, duplicate analyses of a purified benzoic acid (68.8% C, 4.953% H) sample were requested. It is assumed that the relative standard deviation of the method is $s_r \rightarrow \sigma = 4$ ppt for carbon and 6 ppt for hydrogen. The means of reported results are 68.5% C and 4.882% H. At the 95% confidence level, is there any indication of systematic error in either analysis? **[10 %]**

Solution

This is a two-tailed test and from Table 7-1, z_{crit} = 1.96 for the 95% confidence level, use the following equation

$$\boxed{z = \frac{(\bar{x} - \mu_0)}{\sigma/\sqrt{N}}}$$

For carbon,

$$z = \frac{68.5 - 68.8}{0.004 \times 68.8\% / \sqrt{2}} = -1.54 \geq -1.96$$

Systematic error is NOT indicated at 95% confidence level.

For hydrogen,

$$z = \frac{4.882 - 4.953}{0.006 \times 4.953\% / \sqrt{2}} = -3.38 \leq -1.96$$

Systematic error IS indicated at 95% confidence level.

4. (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* = 12 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 ($\bar{x}$, 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 ($F_{calculate}$) > 2.79 (F_{table}). Yes, there is an improvement in precision. We reject Null hypothesis and accept alternative hypothesis.

5. 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 (i) 95% and (ii) 99.9 confidence levels? **[10%]**

Solution:

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

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

$s_{\text{pooled}} = 0.0027$

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. (i) Thus we can conclude that at 95% confidence level, the nitrogen prepared in the two ways is different. (ii) 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.

6. A new automated procedure for determining glucose in serum (Method A) is to be compared to the established method (Method B). Both methods are performed on serum from the same six patients in order to eliminate patient-to-patient variability. Do the following results confirm a difference in the two methods at the **95%** and **99.9%** confidence levels? **[10 %]**

Patient	**1**	**2**	**3**	**4**	**5**	**6**
Method A glucose, mg/L	1044	720	845	800	957	650
Method B glucose, mg/L	1028	711	820	795	935	639

Solution:

Patient	**1**	**2**	**3**	**4**	**5**	**6**
Method A glucose, mg/L	1044	720	845	800	957	650
Method B glucose, mg/L	1028	711	820	795	935	639
Difference	16	9	25	5	22	11

The difference between the two sets of values was compared by using pair t-test.

$$t = \frac{\bar{d} - \Delta_0}{s_d/\sqrt{N}}$$

$\bar{d}$ = 14.67; Δ_0 = 0

s_d= 7.76

N = 6 and degrees of freedom=6-1=5

And the t statistic was calculated to be **4.628**.

At **95%** confidence level and 5 degrees of freedom, the critical value of t is 2.57. Since $t_{calculate} > t_{criti}$, we reject the null hypothesis and conclude that the two methods give different results.

At **99.9%** confidence level and 5 degrees of freedom, the critical value of t is 6.87. Since $t_{calculate} < t_{criti}$, we accept the null hypothesis and conclude that the two methods give no different results.

7. Three different analytical methods are compared for determining Ca in a biological sample. The laboratory is interested in knowing whether the methods differ. The results shown below represent Ca results in ppm determined by an ion-selective electrode (ISE) method, by EDTA titration, and by atomic absorption spectrometry:

Repetition No.	ISE	EDTA Titration	Atomic Absorption
1	39.2	29.9	44.0
2	32.8	28.7	49.2
3	41.8	21.7	35.1
4	35.3	34.0	39.7
5	33.5	39.2	45.9

(a) State the null and alternative hypotheses. **[5 %]**

(b) Determine whether there are differences in three methods at the 95% confidence levels. **[10%]**

(c) If a difference was found at the 95% confidence level, determine which methods differ from each other. **[5 %]**

Solution

(a) H_0: $\mu_{ISE} = \mu_{EDTA} = \mu_{AA}$; H_a: at least two of the means differ.

(b)

Repetition	ISE	EDTA	At. Abs.
1	39.2	29.9	44.0
2	32.8	28.7	49.2
3	41.8	21.7	35.1
4	35.3	34.0	39.7
5	33.5	39.1	45.9
Mean	36.52	30.68	42.78
Std.Dev.	3.85707	6.46313	5.49791
Variance	14.877	41.772	30.227

Grand Mean	36.660	Differences
SSF	366.172	42.78-30.68= 12.1 Sig.diff. (atomic and EDTA)
SSE	347.504	36.52-30.68= 5.94 No Sig. diff (ISE and EDTA)
SST	713.676	42.78-36.52= 6.26 No Sig.diff (Atomic and ISE)
MSF	183.086	
MSE	28.95867	
$F_{(calculated)}$	6.322321	
$LSD_{(calculated)}$	7.419519	

From Table 7-4 the *F* value for 2 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is $F_{(critical)} = 3.89$. Since *F* calculated is greater than *F* critical, we reject the null hypothesis and conclude that the 3 methods give different results at the 95% confidence level.

(c) Based on the calculated LSD value there is a significant difference between the atomic absorption method and the EDTA titration. There is no significant difference between the EDTA titration method and the ion-selective electrode method and there is no significant difference between the atomic absorption method and the ion-selective electrode method. Use the following equation to calculate the LSD

$$\mathrm{LSD} = t\sqrt{\frac{2 \times \mathrm{MSE}}{N_g}}$$

DOF for t is 12 (N-i)

t = 2.18, MSE = 28.95867, Ng = 5

LSD = 7.419519

8. Apply the Q test to the following data sets to determine whether the outlying result (underline number) should be retained or rejected at the 95% confidence level.

(a) $\underline{41.27}$, 41.61, 41.84, 41.70 **[2.5 %]**

(b) 7.295, 7.284, $\underline{7.388}$, 7.292 **[2.5 %]**

Solution:

(a) $Q = \frac{|41.27 - 41.61|}{41.84 - 41.27} = 0.596$

and Q_{crit} for 4 observations at 95% confidence = 0.829 . Since $Q < Q_{crit}$ the outlier value 41.27 cannot be rejected with 95% confidence.

(b) $Q = \frac{|7.388 - 7.295|}{7.388 - 7.284} = 0.894$

and Q_{crit} for 4 observations at 95% confidence = 0.829 . Since $Q > Q_{crit}$ the outlier value 7.388 can be rejected with 95% confidence.

9. A solution containing 3.47 mM **X** (analyte) and 1.72 mM **S** (standard) gave peak areas of 3473 and 10222, respectively, in a chromatographic analysis. Then 1.00 mL of 8.47 mM **S** was added to 5.00 mL of unknown **X**, and the mixture was diluted to 10 mL. This solution gave peak area of 5428 and 4431 for **X** and **S**, respectively.

(a) Calculate the response factor for the analyte. **[2.5 %]**

(b) Find the concentration of **S** (mM) in the 10.0 mL mixture. **[2.5 %]**

(c) Find the concentration of **X** (mM) in the 10.0 mL mixture. **[2.5 %]**

(d) Find the concentration of **X** in the original unknown. **[2.5 %]**

Solution:

(a) $\frac{Ax}{[x]} = F\left(\frac{A_S}{[s]}\right) \rightarrow \frac{3473}{[3.47mM]} = F\left(\frac{10222}{[1.72mM]}\right) \rightarrow F = 0.168_4$

(b) $[S] = (8.47mM)\left(\frac{1.00mL}{10.0mL}\right) = 0.847mM$

(c) $\frac{A_x}{[x]} = F\left(\frac{A_S}{[s]}\right) \rightarrow \frac{5428}{[x]} = 0.168_4\left(\frac{4431}{[0.847mM]}\right) \rightarrow [x] = 6.16mM$

(d) The original concentration of $[x]$ was twice as great as the diluted concentration , so $[x]$ = 12.3 mM

10. In spectrophotometry, we measure the concentration of analyte by its absorbance of light. A low-concentration sample was prepared and nine replicate measurements gave absorbances of 0.0047, 0.0054, 0.0062, 0.0060, 0.0046, 0.0056, 0.0052, 0.0044, and 0.0058. Nine reagent blanks gave values of 0.0006, 0.0012, 0.0022, 0.0005, 0.0016, 0.0008, 0.0017, 0.0010, and 0.0011.

(a) Find the absorbance detection limit. **[5 %]**

(b) The calibration curve is a graph of absorbance versus concentration. Absorbance is a dimensionless quantity. The slope of the calibration curve is $m = 2.24 \times 10^4 M^{-1}$. Find the concentration detection limit. **[2.5 %]**

(c) Find the concentration limit of quantitation. **[2.5 %]**

Solution:

(a) Standard deviation of 9 blanks $= s =$ 0.0005_{56}.

Mean blank $= y_{blank}$ $=0.0011_{89}$

$y_{dl} = y_{blank} + 3s = 0.0011_8 + (3)(0.0005_{56}) = 0.0028_5$

(b) Minimum detectable concentration $= \frac{3s}{m} = \frac{(3)(0.0005_{56})}{2.24\times10^4 M^{-1}} = 7._4\ 10^{-8} M$

(c) Limit of quantitation $= \frac{10s}{m} = \frac{(10)(0.0005_{56})}{2.24\times10^4 M^{-1}} = 2._5 \times 10^{-7} M$

11. A coating that weighs at least 3.00 mg is needed to impart adequate shelf life to a pharmaceutical tablet. A random sampling of 250 tablets revealed that 14 failed to meet this requirement.

(a) Use this information to estimate the relative standard deviation for the measurement. **[2.5 %]**

(b) Assuming that the fraction of rejects remains unchanged. How many tablets should be taken to ensure a relative standard deviation of 5% in the measurement? **[2.5 %]**

Solution:

(a) $\sigma_r = \sqrt{(1-p)/Np}$ (where p = 14/250 = 0.0560)

$\sigma_r = \sqrt{(1-0.0560)/(250 \times 0.0560)} = 0.260$ or $\underline{\mathbf{26\%}}$

(b) $N = (1 - 0.056)/[(0.05)^2 \times 0.056] = 6743 = \underline{\mathbf{6.743 \times 10^3}}$

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Appendix for Various Critical Values

Table 1. 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 2. Critical values of ***F*** at 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 3. Critical values for the rejection quotient, **Q***

Number of Observations	Q_{crit} (Reject if $Q > Q_{crit}$) 90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

Table 4. 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