10910CHEM311000-Analytical Chemistry (I) 分析化學一

First Midterm Examination

Date: 10-11-2020, 10:10 am to 12:30 pm

Answer **all 11 questions** (total 110%). You have **2** hours and 20 minutes to finish this paper.

1. Consider replicate measurements of the two sample sets (**A** and **B**):

A	B
9.5	0.972
8.5	0.943
9.1	0.986
9.3	0.937
9.1	0.954

For each set, calculate the (i) mean; (b) median; (iii) spread, or range; (iv) standard deviation; and (v) coefficient of variation. **[0.5 % each]**

ANS: (a) For Set **A**

x_i`	x_i^2
9.5	90.25
8.5	72.25
9.1	82.81
9.3	86.49
9.1	82.81
$\Sigma x_i = 45.5$	$\Sigma x_i^2 = 414.61$

(i) mean $\bar{x}$ = 45.5/5 = 9.1, (ii) median = 9.1, (iii) spread: w = 9.5 – 8.5 = 1.0

(iv) standard deviation: $s = \sqrt{\dfrac{414.61-(45.5)^2/5}{5-1}} = 0.37$

(v) coefficient of variation: CV = (0.37/9.1) × 100% = 4.1%

(b) For Set **B**

x_i`	x_i^2
0.972	90.25
0.943	72.25
0.986	82.81
0.937	86.49

0.954	82.81
$\Sigma x_i = 4.792$	$\Sigma x_i^2 = 4.594$

(i) mean $\bar{x}$ = 4.792/5 =0.958

(ii) median = 0.954

(iii) spread: w = 0.986 – 0.937 = 0.049

(iv) standard deviation: s = $\sqrt{\frac{4.594 - {(4.792)^2}/{5}}{5-1}}$ = 0.02

(v) coefficient of variation: CV = (0.02/0.958) $\times$ 100% = 2.1%

2. Determine the absolute deviation and the coefficient of variation for the following calculations. The numbers in parentheses are absolute standard deviation.

(i) y = 3.95 (±0.03) + 0.993 (±0.001) – 7.025 (±0.001) **[5 %]**

(ii) y = [4.17 (±0.03) X $10^{-4}]^3$ **[5 %]**

ANS:

(i)

$$s_y = \sqrt{(0.03)^2 + (0.001)^2 + (0.001)^2} = 0.030$$

CV = (0.03/–2.08) × 100% = –1.4%

y = –2.08 (±0.03)

(ii)

$y = (4.17 \times 10^{-4})^3 = 7.251 \times 10^{-11}$

$$\frac{s_y}{y} = 3\left(\frac{0.03 \times 10^{-4}}{4.17 \times 10^{-4}}\right) = 0.0216$$

$s_y = (0.0216)(7.251 \times 10^{-11}) = 1.565 \times 10^{-12}$

$CV = (1.565 \times 10^{-12}/7.251 \times 10^{-11}) \times 100\% = 2.2\%$

$y = 7.25\ (\pm 0.16) \times 10^{-11}$

3. A new procedure for the rapid determination of sulfur in kerosene was tested on a sample known from its method of preparation to contain 0.123% S (μ_o = 0.123% S). The results for % S were 0.112, 0.118, 0.115 and 0.119. Do the data indicate that there is a bias in the method at the (i) 95% and (ii) 99% confidence level? **[5 % each]**

ANS:

$$\Sigma x_i = 0.112 + 0.118 + 0.115 + 0.119 = 0.464$$
$$\bar{x} = 0.464/4 = 0.116\%\ \mathrm{S}$$
$$\Sigma x_i^2 = 0.012544 + 0.013924 + 0.013225 + 0.014161 = 0.53854$$
$$s = \sqrt{\frac{0.053854 - (0.464)^2/4}{4 - 1}} = \sqrt{\frac{0.000030}{3}} = 0.0032\%\ \mathrm{S}$$

The test statistic can now be calculated as

$$t = \frac{\bar{x} - \mu_0}{s/\sqrt{N}} = \frac{0.116 - 0.123}{0.032/\sqrt{4}} = -4.375$$

From Table 7-3, we find that the critical value of t for 3 degrees of freedom and the 95% confidence level is 3.18. Since $t \leq -3.18$, we conclude that there is a significant difference at the 95% confidence level and thus bias in the method. Note that if we do this test at the 99% confidence level, $t_{crit} = 5.84$ (see Table 7-3). Since $-5.84 < -4.375$, we would accept the null hypothesis at the 99% confidence level and conclude that there is no difference between the experimental and the accepted values. Note in this case that the outcome depends on the confidence level that is used. As we will see, choice of the confidence level depends on our willingness to accept an error in the outcome. The significance level (0.05 or 0.01) is the probability of making an error by rejecting the null hypothesis (see Section 7B-3).

You can also refer to Chapter 7, example 7-5

4. Glucose levels are routinely monitored in patients suffering from diabetes. The glucose concentrations in a patient with mildly elevated glucose levels were determined in different months by a spectrophotometric analytical method. The patient was placed on a low-sugar diet to reduce the glucose levels. The following results were obtained during a study to determine the effectiveness of the diet. Calculate a pooled estimate of the standard deviation for the method. **[10 %]**

Month	Glucose Conc. (mg/L)
1	1108, 1122, 1075, 1099, 1115, 1083, 1100
2	992, 975, 1022, 1001, 991
3	788, 805, 779, 822, 800
4	788, 805, 779, 822, 800
5	799, 745, 750, 774, 777, 800, 758

ANS:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i - \bar{x}_i)^2 + \sum_{j=1}^{N_2}(x_j - \bar{x}_2)^2 + \sum_{k=1}(x_k - \bar{x}_3)^2 + \ldots}{N_1 + N_2 + N_3 + \ldots - N_t}}$$

For the first month, the sum of the squares in the next to last column was calculated as follows:

$$\text{Sum of squares} = (1108 - 1100.3)^2 + (1122 - 1100.3)^2 + (1075 - 1100.3)^2 + (1099 - 1100.3)^2 + (1115 - 1100.3)^2 + (1083 - 1100.3)^2 + (1100 - 1100.3)^2 = 1687.43$$

The other sums of squares were obtained similarly. The pooled standard deviation is then

$$s_{\text{pooled}} = \sqrt{\frac{6907.89}{24 - 4}} = 18.58 \approx 19 \text{ mg/L}$$

You can also refer to Chapter 6, example 6-2

5. 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), EDTA titration and atomic absorption spectrometry methods.

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

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

(ii) Determine whether there are differences in the three methods at the 95% confidence levels. **[7 %]**

(iii) If a difference was found at the 95% confidence level, determine which methods differ from each other. **[6 %]**

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

(ii)

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
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
*S*um of *s*quares due to the *Factor* (SSF): 366.172
Sum of squares due to the Error (SSE): 347.504
Total Sum of squares (SST): 713.676
MSF: 183.086

MSE: 28.95867

F: 6.322321

From the *F* Table, the value for 2 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 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.

(iii) To determine which results differ, we first calculate the least significant difference (LSD) by using equation 7-6 (Skoog text book, page 146)

LSD: 7.453554

Difference of mean between

(a) ISE and EDTA = 36.52 – 30.68 = 5.94 (No significant difference)

(b) ISE and A.A. = 42.78 – 36.52 = 6.26 (No significant difference)

(c) EDTA and A.A. = 42.78 – 30.68 = 12.1 (Significant difference)

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.

6. Determination of phosphorous (P) in blood serum gave results of 4.40, 4.42, 4.60, 4.48, and 4.50 ppm P. Determine whether the 4.60 ppm result is an outlier or should be retained at the 95% confidence level by using Q-test. **[5 %]**

ANS:

$Q = \frac{|4.60 - 4.50|}{4.60 - 4.40} = 0.5$ and Q_{crit} for 5 observations at 95% confidence = 0.710.

Since $Q < Q_{crit}$ the outlier value 4.60 ppm cannot be rejected with 95% confidence.

7. A column-packing material for chromatography consists of a mixture of two types of particles. Assume that the average particle in the batch being sampled is approximately spherical with a radius of about 0.5 mm. Roughly 20% of the particles appear to be pink in color and are known to have about 30% by mass of a polymeric stationary phase attached (analyte). The pink particles have a density of 0.48 g/cm^3. The remaining particles have a density of about 0.24 g/cm^3 and contain little or none polymeric stationary phase. What mass of the material should the gross sample contain if the sampling uncertainty is to be kept below 0.5% relative? **[10 %]**

ANS:

We first compute values for the average density and percent polymer:

$$d = 0.20 \times 0.48 + 0.80 \times 0.24 = 0.288 \text{ g/cm}^3$$

$$P = \frac{(0.20 \times 0.48 \times 0.30) \text{ g polymer/cm}^3}{0.288 \text{ g sample/cm}^3} \times 100\% = 0.10\%$$

Then, substituting into Equation 8-5 gives

$$N = 0.20(1 - 0.20)\left[\frac{0.48 \times 0.24}{(0.288)^2}\right]^2\left(\frac{30 - 0}{0.005 \times 10.0}\right)^2$$

$$= 1.11 \times 10^5 \text{ particles required}$$

$$\text{mass of sample} = 1.11 \times 10^5 \cancel{\text{particles}} \times \frac{4}{3}\pi(0.05)^3 \frac{\cancel{\text{cm}^3}}{\cancel{\text{particle}}} \times \frac{0.288 \text{ g}}{\cancel{\text{cm}^3}}$$

$$= 16.7 \text{ g}$$

You can also refer to Chapter 8, example 8-1

8. 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.

(i) Use this information to estimate the relative standard deviation for the measurement. **[5 %]**

(ii) What is the 95% confidence interval for the number of unsatisfactory tablets? **[5 %]**

(iii) 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? **[5 %]**

ANS:

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

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

(ii) σ= 14 × 0.26 = 3.6 = 4 tablets

95% CI = 14 $\pm\ z\sigma\sqrt{N} = 14 \pm 1.96 \times 3.6/\sqrt{1}$ = 14 ± 7

(where z = 1.96 was obtained from Table 7-1)

(iii) N = (1 – 0.056)/[(0.05)^2 × 0.056] = 6743 = 6.743 × 10^3

9. A trainee in a medical lab will be released to work on her own when her results agree with those of an experienced worker at the 95% confidence level. Results for a blood urea nitrogen analysis are shown below.

	Mean ($\bar{x}$) mg/dL	Stand. deviation (s) mg/dL	No. samples
Trainee	14.57	0.53	6
Exp. worker	13.95	0.42	5

(i) Is the variance obtained from the trained more precise than the experience worker? **[5 %]**

(ii) Compare the difference in two means and decide whether the trainee should be released to work alone. **[5 %]**

ANS:

(i) Apply the F-test

$F_{calculated} = (0.53)^2/(0.42)^2 = 1.59 < F_{table}$ ($F_{table} = 6.26$, tor 5 degrees of freedom in the numerator and 4 degrees of freedom in the denominator).

Since $F_{calculated} < F_{table}$, we can conclude that the data from the trainee gave better precision at the 95% confidence level.

(ii) Apply the t-test

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}\sqrt{\frac{N_1 + N_2}{N_1 N_2}}} \qquad \mathbf{s_{pooled}} = \sqrt{\frac{s_1^2(N_1 - 1) + s_2^2(N_2 - 1) + s_3^2(N_3 - 1) + \cdots}{N_1 + N_2 + N_3 - N_t}}$$

$$S_{pooled} = \sqrt{\frac{(0.53)^2(5)+(0.42)^2(4)}{6+5-2}} = 0.484$$

$$t = \frac{|\ 14.57-13.95\ |}{0.484\sqrt{\frac{6+5}{6\times 5}}} = 2.12 < 2.26 \text{ (for 9 degrees of freedom at 95 \% confidence level)}$$

Since $t_{calculated} < t_{table}$, we conclude that the trainee should be released.

10. A manufacturer tested the lifetimes of 4768 electric light bulbs. He found that the lifetimes of those light bulbs approximate a Gaussian distribution. The mean value (μ) is 842 hours and the standard deviation (σ) is 94.2 hours.

(i) Calculate the fraction of bulbs expected to have a lifetime greater than 1005.3 hours. **[5 %]**

(ii) What fraction of bulbs is expected to have a lifetime between 798.1 and 901.7 hours. **[5 %]**

ANS:

(i) 1005.3 hours corresponds to z = (1005.3 – 845.2)/94.2 = 1.7

From the Z-table, the area from the mean to z = 1.7 is 0.4554.

The area above z = 1.7 is 0.500 – 0.4554 = 0.0446.

Therefore, the fraction of bulbs greater than 1005.3 is **<u>4.46%.</u>**

(ii) 798.1 corresponds to z = (798.1 – 845.2)/94.2 = – 0.500

The area from the mean to z = – 0.50 is the same as the area from the mean to z = 0.50,0 which is 0.1915 in the z-table.

901.7 corresponds to z = (901.7-845.2)/94.2 = 0.600.

The area from the mean to z = 0.600 is 0.2258.

The area between 798.1 and 901.7 is the sum of the two areas: 0.1915 + 02258 = 0.4173.

Therefore, the fraction of bulbs having lifetime between 798.1 and 901.7 is **<u>41.73 %.</u>**

11. To detect a low concentration analyte, the signal detection limit was estimated to be in the low nanoampere (nA) range. Signals from seven replicate samples with a concentration about three times the detection limit were 5.0, 5.0, 5.2, 4.2, 4.6, 6.0, and 4.9 nA. Reagents blanks gave values of 1.4, 2.2, 1.7, 0.9, 0.4, 1.5, and 0.7 nA. The slope of the calibration curve is m = 0.299 nA/μM.

(i) Find the signal detection limit and the minimum detectable concentration (LOD). **[5 %]**

(ii) What is the concentration of analyte in a sample that gave a signal of 7.0 nA? **[5 %]**

ANS:

(i) First compute the mean for the blanks and the standard deviation for the samples.

Blank: Mean = y_{blank} = 1.26 nA

Blank: Standard deviation = s = 0.62 nA

The signal detection limit is y = y_{blank} + 3s = **3.12 nA**

The minimum detectable concentration (LOD) is

Detection limit = 3s/m = (3)(0.62)/0.299 = **6.2 μM**

(ii) To find the concentration of a sample whose signal is 7.0 nA, we have

$Y_{sample} - y_{blank}$ = m x concentration

Concentration = $(y_{sample}-y_{blank})/m$ = (7.0 nA – 1.26)/0.299 = **19.2 μM**

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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

Table 5. Ordinate and area for various values of ***z***.

$\lvert z\rvert^a$	y	Area[b]	$\lvert z\rvert$	y	Area	$\lvert z\rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5