11210CHEM311000-Analytical Chemistry (I) 分析化學一

First Midterm Examination

Date: 16-11-2023, 10:10 am to 12:10 pm

Answer **all 10 questions** (total 100%). You have **2** hours to finish this paper.

1. The standard deviation in measuring the diameter d of a sphere is $\pm$ 0.02 cm. What is the standard deviation in the calculated volume V of the sphere if d = 2.35 cm? **[5 %]**

Solution:

From the equation for the volume of a sphere, we have

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi\left(\frac{2.35}{2}\right)^3 = 6.80 \ cm^3$$

Hence, we may write

$$\frac{s_v}{V} = 3 \times \frac{s_d}{d} = 3 \times \frac{0.02}{2.35} = 0.0255$$

$$S_V = 6.80 \times 0.0255 = 0.173$$

$$V = 6.8(\pm 0.2) \ cm^3$$

2. Analysis of several plant-food preparations for potassium ion yielded the following data:

Sample	Percent K⁺
1	6.02, 6.04, 5.88, 6.06, 5.82
2	7.48, 7.47, 7.29
3	3.90, 3.96, 4.16, 3.96
4	4.48, 4.65, 4.68, 4.42
5	5.29, 5.13, 5.14, 5.28, 5.20

The preparations were randomly drawn from the same population.

(a) Find the mean and standard deviation s for each sample. **[5 %]**

(b) Obtain the pooled value s_{pooled}. **[5 %]**

Solution:

$$\text{mean} = \frac{\sum_{i=1}^{N} X_i}{N}$$

$$\text{sample } 1 = \frac{(6.02 + 6.04 + 5.88 + 6.06 + 5.82)}{5} = 5.964$$

$$\text{sample } 2 = \frac{(7.48 + 7.47 + 7.29)}{3} = 7.413$$

$$\text{sample } 3 = \frac{(3.90 + 3.96 + 4.16 + 3.96)}{4} = 3.995$$

$$\text{sample } 4 = \frac{(4.48 + 4.65 + 4.68 + 4.42)}{4} = 4.558$$

$$\text{sample } 5 = \frac{(5.29 + 5.13 + 5.14 + 5.28 + 5.20)}{5} = 5.208$$

$$\text{standard deviation} = \sqrt{\frac{\sum(x_i - x_{av})^2}{n-1}}$$

$$\text{sample 1} = \sqrt{\frac{0.0031 + 0.0058 + 0.0071 + 0.0092 + 0.0207}{4}} = 0.107$$

$$\text{sample 2} = \sqrt{\frac{0.0044 + 0.0032 + 0.0152}{2}} = 0.107$$

$$\text{sample 3} = \sqrt{\frac{0.0090 + 0.0012 + 0.0272 + 0.0012}{3}} = 0.114$$

$$\text{sample 4} = \sqrt{\frac{0.0060 + 0.0086 + 0.0150 + 0.0189}{3}} = 0.127$$

$$\text{sample 5} = \sqrt{\frac{0.0067 + 0.0061 + 0.0046 + 0.0052 + 0.0001}{4}} = 0.075$$

(b)

$$S_{pooled} = \sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2 + (n_3 - 1)S_3^2 + (n_4 - 1)S_4^2 + (n_5 - 1)S_5^2}{n_1 + n_2 + n_3 + n_4 + n_5 - 5}}$$

$$= \sqrt{\frac{4 \times 0.107^2 + 2 \times 0.107^2 + 3 \times 0.114^2 + 3 \times 0.127^2 + 4 \times 0.075^2}{21 - 5}} = 0.11$$

3. An atomic absorption method for the determination of the amount of iron present in used jet engine oil was found from pooling 30 triplicate analyses to have a standard deviation $s = 2.9$ µg Fe/mL. If s is a good estimate of σ, calculate the 95% and 99% confidence intervals for the result 17.2 µg Fe/mL if it was based on

(a) a single analysis **[3 %]**

(b) the mean of two analyses **[3 %]**

(c) the mean of four analyses **[3 %]**

Solution:

(a)

$$99\% \ \text{Cl} = 17.2 \pm 2.58 \times 2.9 = 17.2 \pm 7.5 \ \text{µg Fe/mL}$$

$$95\% \ \text{Cl} = 17.2 \pm 1.96 \times 2.9 = 17.2 \pm 5.7 \ \text{µg Fe/mL}$$

(b)

$$99\% \ \text{Cl} = 17.2 \pm \frac{2.58 \times 2.9}{\sqrt{2}} = 17.2 \pm 5.3 \ \text{µg Fe/mL}$$

$$95\% \ \text{Cl} = 17.2 \pm \frac{1.96 \times 2.9}{\sqrt{2}} = 17.2 \pm 4.0 \ \text{µg Fe/mL}$$

(c)

$$99\% \ \text{Cl} = 17.2 \pm \frac{2.58 \times 2.9}{\sqrt{4}} = 17.2 \pm 3.7 \ \text{µg Fe/mL}$$

$$95\% \ \text{Cl} = 17.2 \pm \frac{2.58 \times 2.9}{\sqrt{4}} = 17.2 \pm 2.8 \ \text{µg Fe/mL}$$

4. A volumetric calcium analysis on triplicate samples of the blood serum of a patient believed to be suffering from a hyperparathyroid condition produced the following data: mmol Ca/L = 3.15, 3.25, 3.26. What is the 95% confidence interval for the mean of the data, assuming

(a) no prior information about the precision of the analysis? **[3 %]**

(b) $s \rightarrow \sigma$ = 0.056 mmol Ca/L? **[3 %]**

Solution:

(a)

For the data set, $\bar{x} = 3.22$ and $s = 0.06$

$$95\% \ \text{Cl} = 3.22 \pm \frac{4.30 \times 0.06}{\sqrt{3}} = 3.22 \pm 0.15 \ \text{meq Ca/mL}$$

(b)

$$95\% \ \text{Cl} = 3.22 \pm \frac{1.96 \times 0.056}{\sqrt{3}} = 3.22 \pm 0.06 \ \text{meq Ca/mL}$$

5. A prosecuting attorney in criminal case presented as principal evidence small fragments of glass found imbedded in the coat of the accused. The attorney claimed that the fragments were identical in composition to a rare Belgian stained glass window broken during the crime. The average of triplicate analyses for five elements in the glass are in the table. On the basis of these data, does the defendant have grounds for claiming reasonable doubt as to guilt? Use the 99% confidence level as a criterion for doubt. **[10 %]**

	Concentration, ppm		Standard deviation
Element	**From Cloths**	**From window**	**s→σ**
As	129	119	9.5
Co	0.53	0.60	0.025
La	3.92	3.52	0.20
Sb	2.75	2.71	0.25
Th	0.61	0.73	0.043

Solution:

This is a two-tailed test where s → σ and from Table 4, Z_{crit} = 2.58 for the 99% confidence level.

For As: $z = \dfrac{129-119}{9.5\sqrt{\frac{3+3}{3\times3}}} = 1.28 \leq 2.58$

No significant difference exists at the 99% confidence level.

Proceeding in a similar fashion for the other elements

Element	z	Significant Difference?
As	1.28	No
Co	-3.43	Yes
La	2.45	No
Sb	0.20	No
Th	-3.42	Yes

For two of the elements there is a significant difference, but for three there are not. Thus, the defendant might have grounds for claiming reasonable doubt. It would be prudent, however, to analyze other windows and show that these elements are good diagnostics for the rare window.

6. Two different analytical methods were used to determine residual chlorine in sewage effluents. Both methods were used on the same samples, but each sample came from various locations with differing amounts of contact time with the effluent. Two methods were used to determine the concentration of Cl in mg/L, and the results are shown in the following table:

Sample	Method A	Method B
1	0.39	0.36
2	0.84	1.35
3	1.76	2.56
4	3.35	3.92
5	4.69	5.35
6	7.70	8.33
7	10.52	10.70
8	10.92	10.91

(a) What type of t test should be used to compare the two methods and why? **[5 %]**

(b) Do the two methods give different results? State and test the appropriate hypotheses. **[5 %]**

(c) Does the conclusion depend on whether the 90%, 95%, or 99% confidence levels are used? **[5 %]**

Solution:

(a) A paired t test should definitely be used in this case due to the large variation in the Cl concentrations resulting from the various contact times and various locations from which the samples were obtained.

(b) H_0: $\mu_d = 0$; H_a: $\mu_A \neq 0$, where μ_d is the mean difference between the methods

From the data N = 8, $\bar{d} = -0.414$ and $s_d = 0.32$

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For 7 degrees of freedom at 90% confidence level, t_{crit} = 1.90

$$t = \frac{0.414 - 0}{0.32/\sqrt{8}} = 3.65$$

Since t > t_{crit}, a significant difference is indicated at the 90% confidence level

(c) For 7 degrees of freedom at 95% confidence level, t_{crit} = 2.36

Therefore, a significant difference in the 2 methods exists at the 95% confidence level.

For 7 degrees of freedom at the 99% confidence level, t_{crit} = 3.50

Thus, a significant difference is indicated even at the 99% confidence level. The conclusion does not depend on which of the three confidence levels is used.

7. Four analysts perform replicate sets of Hg determinations on the same analytical

sample. The results in ppb Hg are shown in the following table:

Determination	Analyst 1	Analyst 2	Analyst 3	Analyst 4
1	10.19	10.19	10.14	10.24
2	10.15	10.11	10.12	10.26
3	10.16	10.15	10.04	10.29
4	10.10	10.12	10.07	10.23

(a) State the appropriate hypotheses.   **[4 %]**

(b) Do the analysts differ at the 95% confidence level? At the 99% confidence level

(F$_{crit}$ = 5.95)? At the 99.9% confidence level (F$_{crit}$ = 10.80)?   **[8 %]**

(c) Which analysts differ from each other at the 95 % confidence level?   **[8 %]**

Solution:

(a) The null hypothesis $H_0: \mu_{Analyst1} = \mu_{Analyst2} = \mu_{Analyst3} = \mu_{Analyst4}$

The alternative H_a: at least two of means differ

(b)

Analyst 1: $N = 4$, $\bar{x} = 10.15, S = 0.03742$, variance $= 0.00140$

Analyst 2: $N = 4$, $\bar{x} = 10.14, S = 0.03594$, variance $= 0.00129$

Analyst 3: $N = 4$, $\bar{x} = 10.09, S = 0.04573$, variance $= 0.00209$

Analyst 4: $N = 4$, $\bar{x} = 10.26, S = 0.02646$, variance $= 0.00070$

Grand Mean $= \dfrac{\sum x_i}{N} = 10.16$

$SSF = N_1(\bar{x}_1 - \bar{\bar{x}})^2 + \cdots + N_4(\bar{x}_4 - \bar{\bar{x}})^2 = 0.05595$

$SSE = (N_1 - 1)S_1{}^2 + \cdots + (N_4 - 1)S_4{}^2 = 0.01645$

$$\text{SST} = \text{SSE} + \text{SSF} = 0.07240$$

$$\text{MSF} = \frac{\text{SSF}}{\text{I} - 1} = 0.01865, \text{MSE} = \frac{\text{SSE}}{\text{N} - \text{I}} = 0.001371$$

$$\text{F} = \frac{\text{MSF}}{\text{MSE}} = 13.60486$$

The F value for 3 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 3.49. Since F calculated exceeds F critical, we reject the null hypothesis and conclude that the analysts differ at 95% confidence. The F value calculated of 13.60 also exceeds the critical values at the 99% and 99.9% confidence levels so that we can be certain that the analysts differ at these confidence levels.

(c) $\text{LSD} = \text{t} \times \sqrt{\frac{2 \times \text{MSE}}{\text{N}}} = 0.057335$

Based on the calculated LSD value of 0.0573, there are significant differences between analysts 1 and 4, analysts 1 and 3, analysts 2 and 4, and analysts 3 and 4. There is no significant difference between analysts 1 and 2 and 2 and 3.

analysts 1 and 4

$10.15 - 10.26 = -0.11$ significant different

analysts 1 and 3

$10.15 - 10.09 = 0.06$ significant different

analysts 2 and 4

$10.14 - 10.26 = -0.12$ significant different

analysts 3 and 4

$10.09 - 10.26 = -0.17$ significant different

analysts 1 and 2

$10.15 - 10.14 = 0.01$ no significant different

analysts 2 and 3

$10.14 - 10.09 = 0.05$ no significant different

8. Apply the Q test to the following data sets to determine whether the outlying

result should be retained or rejected at the 95 % confidence level.

(a) <u>95.10</u>, 94.62, 94.70   **[2.5 %]**

(b) <u>95.10</u>, 94.62, 94.65, 94.70   **[2.5 %]**

Solution:

(a)

$$Q = \frac{|\,95.10 - 94.70\,|}{95.10 - 94.62} = 0.833$$

and Q_{crit} for 3 observations at 95% confidence = 0.970.

Since $Q < Q_{crit}$ the outlier value 95.10 cannot be rejected with 95% confidence.

(b)

$$Q = \frac{|\,95.10 - 94.70\,|}{95.10 - 94.62} = 0.833$$

and Q_{crit} for 4 observations at 95% confidence = 0.829.

Since $Q > Q_{crit}$ the outlier value 95.10 can be rejected with 95% confidence.

9. Approximately 15% of the particles in a shipment of silver-bearing ore are judged to be argentite, Ag_2S (d= 7.3 g cm^{-3}, 87% Ag); the remainder are siliceous (d= 2.6 g cm^{-3}) and contain essentially no silver.

(a) Calculate the number of particles that should be taken for the gross sample if the relative standard deviation due to sampling is to be 2% or less. **[4 %]**

(b) Estimate the mass of the gross sample, assuming that the particles are spherical and have an average diameter of 3.5 mm. **[4 %]**

(c) The sample taken for analysis is to weigh 0.500 g and contain the same number of particles as the gross sample. To what diameter must the particles be ground to satisfy these criteria? **[2 %]**

Solution:

(a) $N = p(1 - p)\left(\frac{d_A\, d_B}{d^2}\right)^2 \left(\frac{P_A - P_B}{\sigma_r P}\right)^2$

$d = 7.3 \times 0.15 + 2.6 \times 0.85 = 3.3$

$P = 0.15 \times 7.3 \times 0.87 \times 100/3.3 = 29\%$

$N = 0.15(1 - 0.15)\left(\frac{7.3 \times 2.6}{(3.3)^2}\right)^2 \left(\frac{87 - 0}{0.020 \times 29}\right)^2 = 8714$ particle

(b) $\text{mass} = \frac{4}{3}\pi r^3 \times d \times N = \frac{4}{3}\pi(0.175 \text{ cm})^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

$\qquad = 650$ g

(c) $0.500 = \frac{4}{3}\pi r^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

$\qquad r = 0.016$ cm (diameter $= 0.32$ mm)

10. Copper was determined in a river water sample by atomic absorption spectrometry and the method of standard additions. For the addition, 100.0 μL of a 1000.0-μg/mL Cu standard was added to 100.0 mL of solution. The following data were obtained:

Absorbance of reagent blank 0.020

Absorbance of sample = 0.520

Absorbance of sample plus addition - blank = 1.020

(a) Calculate the copper concentration in the sample.   **[5 %]**

(b) Later studies showed that the reagent blank used to obtain the preceding data was inadequate and that the actual blank absorbance was 0.100. Find the copper concentration with the appropriate blank, and determine the error caused by using an improper blank.   **[5 %]**

Solution:

(a)

$$\frac{C_{Unk}}{(V_{Std}C_{Std}+V_{Unk}C_{Unk})/V_{Tot}} = \frac{A(\text{sample} - \text{blank})}{A(\text{sample} + \text{addition} - \text{blank})}$$

$$\frac{C_{Unk}}{\dfrac{(0.1000\ \text{mL} \times 1000\ \mu\text{g/mL} + 100.0\ \text{mL} \times C_{Unk}}{100.1\ \text{mL}}} = \frac{(0.520 - 0.020)}{1.020}$$

$$\frac{C_{Unk}}{0.99900 + 0.99900C_{Unk}} = 0.490196$$

$$C_{Unk} = 0.490196(0.99900 + 0.99900C_{Unk})$$

$$0.510294C_{Unk} = 0.489706, \ C_{Unk} = 0.96\ \mu\text{g/mL}$$

(b)

$$\frac{C_{Unk}}{\frac{(0.1000 \ mL \times 1000 \frac{\mu g}{mL} + 100.0 \ mL \times C_{Unk})}{100.1 \ mL}} = \frac{(0.520 - 0.100)}{(1.020 - 0.080)}$$

Proceeding as in (a) we obtain $C_{Unk} = 0.81 \frac{\mu g}{mL}$

%error = (0.96 – 0.81)/0.81 x 100% = 19%

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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 $Q > Q_{\text{crit}}$)		
	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 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