10810CHEM311000-Analytical Chemistry (I) 分析化學 (一)

First Midterm Examination

Date: 05-11-2019, 10:10 am to 12:10 pm

Answer **all 10 questions** (total 105%). You have **2** hours to finish this paper.

1. (a) A method of analysis yields masses of gold that are low by 0.4 mg. Calculate the percent relative error caused by this result if the mass of gold in the sample is **500 mg**. **[4 %]**

(b) The method described in (a) is to be used for the analysis of ores that has about 1.2 % gold. What minimum sample mass should be taken if the relative error resulting from a 0.4 mg loss is not to exceed **-0.1 %**? **[6 %]**

Solution:

(a) (– 0.4 mg/500 mg) × 100% = – 0.08%

(b) First determine how much gold is needed to achieve the desired relative error.

(– 0.4 mg/– 0.1%) × 100% = 400 mg gold

Then determine how much ore is needed to yield the required amount of gold.

(400 mg/1.2%) × 100% = 33,000 mg ore **or** 33 g ore

2. Consider the following sets of replicate measurements (A and B):

A	B
9.5	55.35
8.5	55.32
9.1	55.20
9.3	
9.1	

For each set, calculate the (a) mean; (b) median; (c) spread, or range; (d) standard deviation; and (e) coefficient of variation. **[5 % each set]**

Solution:

Listing the data from Set A in order of increasing value:

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
$\Sigma x_i = 45.5$	$\Sigma x_i^2 = 414.61$

(a) mean: $\bar{x}$ = 45.5/5 = 9.1

(b) median = 9.1

(c) spread: w = 9.5 – 8.5 = 1.0

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

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

Results for Sets A and B, obtained in a similar way, are given in the following table.

	A	B
$\bar{x}$	9.1	55.29
median	9.1	55.32
w	1.0	0.15
s	0.37	0.08
CV, %	4.1	0.14

3. Calculate the **absolute standard deviation** and the **coefficient of variation** for the results of the following calculations. Round each result to include only significant numbers. The numbers in parentheses are absolute standard deviations.

(a) $y = 326(\pm 1) \times \frac{740(\pm 2)}{1.964(\pm 0.006)}$ **[5 %]**

(b) $y = [4.17(\pm 0.03) \times 10^{-4}]^3$ **[5 %]**

Solution:

(a) $y = 122830.9572$

$$\frac{s_y}{y} = \sqrt{\left(\frac{1}{326}\right)^2 + \left(\frac{2}{740}\right)^2 + \left(\frac{0.006}{1.964}\right)^2} = 0.00510$$

$s_y = (0.00510) \times (122830.9572) = 626$

$y = 1.228(\pm 0.006) \times 10^5$

CV = (0.00510) × 100% = 0.510%

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

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

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

$y = 7.3 (\pm 0.2) \times 10^{-11}$

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

4. Three samples of illicit heroin preparations were analyzed in replicates by a gas chromatographic method. The samples can be assumed to have been drawn randomly from the same population. Pool the following data to establish an estimate of **σ** for the procedure. **[10 %]**

Sample	**Heroin, %**
1	13, 19, 12, 17

2	42, 40, 39
3	29, 25, 26, 23, 30

Solution:

The value 7 in column 1 should be 17. You can then calculate the Spooled accordingly.

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

	A	B	C	D	E	F	G	H
1	Problem 6-21							
2								
3	Sample	1	$(x_i\text{-}x_{ave})^2$	2	$(x_i\text{-}x_{ave})^2$	3	$(x_i\text{-}x_{ave})^2$	
4								No. Sets
5		13	0.06	42	2.78	29	5.76	3
6		19	39.06	40	0.11	25	2.56	
7		12	0.56	39	1.78	26	0.36	
8		7	33.06			23	12.96	
9						30	11.56	
10								
11	mean	12.75		40.33		26.60		Total
12	*s*	4.92		1.53		2.88		
13	*N*		4		3		5	12
14	$\Sigma(x_i\text{-}x_{ave})^2$		72.75		4.67		33.20	110.62
15								
16	s_{pooled}	3.5						
17								
18	Spreadsheet Documentation							
19								
20	B11=AVERAGE(B5:B9)							
21	B12=STDEV(B5:B9)							
22	C5=(B5-B11)^2							
23	C13=COUNT(C5:C9)							
24	C14=SUM(C5:C9)							
25	H13=SUM(C13:G13)							
26	H14=SUM(C14:G14)							
27	B16=SQRT(H14/(H13-H5))							

5. Four different fluorescence flow cell designs were compared to see if they were significantly different. The following results represented relative fluorescence intensities for four replicate measurements.

Measurement No.	Design 1	Design 2	Design 3	Design 4
1	72	93	96	100
2	93	88	95	84
3	76	97	79	91
4	90	74	82	94

(a) State the appropriate hypotheses. **[2 %]**

(b) Do the follow cell designs differ at the 95% confidence level? **[13 %]**

Solution:

(a) H_0: $\mu_{Des1} = \mu_{Des2} = \mu_{Des3} = \mu_{Des4}$;

H_a: at least two of the means differ.

(b)

Measurement No.	Design 1	Design 2	Design 3	Design 4
1	72	93	96	100
2	93	88	95	84
3	76	97	79	91
4	90	74	82	94
Mean	82.75	88.00	88.00	92.25
Std. Dev	10.30	10.03	8.75	6.65
Variance	106.25	100.66	76.66	44.25

N =16, i = 4

Grand mean = $\bar{\bar{x}} = \left(\frac{N_1}{N}\right)\bar{x}_1 + \left(\frac{N_2}{N}\right)\bar{x}_2 + \cdots \left(\frac{N_i}{N}\right)\bar{x}_i$ = 87.750

SSF = $\boldsymbol{SSF} = N_1(\bar{x}_1 - \bar{\bar{x}})^2 + N_2(\bar{x}_2 - \bar{\bar{x}})^2 + \cdots + N_i(\bar{x}_i - \bar{\bar{x}})^2$ = 181.15

SSE $= (N_1 - 1)s_1^2 + (N_2 - 1)s_2^2 + \cdots + (N_i - 1)s_i^2$ = 983.5

MSF= SSF/(i-1) = 60.50

MSE= SSE/(N-i) = 81.95

F = MSF/MSE = **0.74**

From *F*-table, 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 is less than *F* critical, we accept the null hypothesis and conclude that 4 flow cell designs give the same results at the 95% confidence level.

6. 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) 41.27, 41.61, 41.84, 41.70 **[5 %]**

(b) 7.295, 7.284, 7.388, 7.292 **[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.

7. 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.

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.

(a) Use this information to estimate the relative standard deviation for the measurement. **[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? **[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 **26%**

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

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. **[3 %]**

(c) The sample taken for analysis is to weight 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? **[3 %]**

Solution:

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

(a) d = 7.3 × 0.15 + 2.6 × 0.85 = 3.3

P = 0.15 × 7.3 × 0.87 × 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 particles

(b) mass = (4/3)π(r)^3 × d × N = (4/3) π (0.175 cm)^3 × 3.3(g/cm^3) × 8.714 × 10^3

= 650 g

(c) 0.500 = (4/3)π(r)^3 × 3.3(g/cm^3) × 8.714 × 10^3

r = 0.016 cm (diameter = 0.32 mm)

10. 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 areas. The slope of the calibration curve is m = 0.456 peak area/μM. Find the minimum detectable (LOD) and quantification (LOQ) concentration. **[5 % each]**

Solution:

The standard deviation of above set of results s=0.32

$$\text{LOD}=\frac{3(0.32)}{0.456}=2.1\,\mu\text{M}$$

$$\text{LOQ}=\frac{10(0.32)}{0.456}=7.0\,\mu\text{M}$$

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Appendix for Various Critical Values

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 7-5

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