

11310CHEM311000-Analytical Chemistry (I) 分析化學一

First Midterm Examination

Date: 24-10-2024, 10:10 am to 12:30 pm

Answer **all 10 questions** (total 100%). You have **2 hours** and 20 minutes to finish this paper.

1. Calculate the mean and median for the following data: [5%]

19.4, 19.5, 19.6, 19.8, 20.1, 20.3

Solution:

$$\text{mean} = \bar{x} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6} = 19.78 \approx 19.8 \text{ ppm Fe}$$

Because of the set contains an even number of measurements, the median is the average of the central pair:

$$\text{median} = \frac{19.6 + 19.8}{2} = 19.7 \text{ ppm Fe}$$

2. Suppose that 0.50 mg of a precipitate is lost as a result of being washed with 200 mL of wash liquid. [10%]

(a) If the precipitate weighs 500 mg, what is the relative error due to solubility loss?

(b) If 0.50 mg is lost from 50 mg of precipitate, what is the relative error?

Solution:

(a)

$$\% \text{Relative error} = \frac{0.50 \text{ mg}}{500 \text{ mg}} \times 100\% = 0.1\%$$

(b)

$$\% \text{Relative error} = \frac{0.50 \text{ mg}}{50 \text{ mg}} \times 100\% = 1\%$$

3. The following results were obtained in the replicate determination of the lead content of a blood sample: 0.752, 0.756, 0.752, 0.751, and 0.760 ppm Pb. [5%]

(a) Find the mean and the standard deviation of this set of data.

(b) Calculate the variance.

(c) Calculate the RSD in parts per thousand.

(d) Calculate the coefficient of variation in percent.

(e) Calculate the spread.

Solution:

(a)

$$\bar{x} = \frac{0.752 + 0.756 + 0.752 + 0.751 + 0.760}{5} = 0.7542 \approx 0.754 \text{ ppm Pb}$$

$$s = \sqrt{\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{N}}{N - 1}} = \sqrt{\frac{2.844145 - \frac{(3.771)^2}{5}}{5 - 1}} = 0.00377 \approx 0.004 \text{ ppm Pb}$$

(b)

$$s^2 = (0.004)^2 = 1.6 \times 10^{-5}$$

(c)

$$\text{RSD} = \frac{0.004}{0.754} \times 1000 \text{ ppt} = 5.3 \text{ ppt}$$

(d)

$$\text{CV} = \frac{0.004}{0.754} \times 100\% = 0.53\%$$

(e)

$$w = 0.760 - 0.751 = 0.009 \text{ ppm Pb}$$

4. The inside diameter of an open cylindrical tank was measured. The results of four replicate measurements were 5.2, 5.7, 5.3, and 5.5 m. Measurements of the height of the tank yielded 7.9, 7.8, and 7.6m. Calculate the volume in liters of the tank ($\pi = 3.14159$) and the standard deviation of the result. [10%]

Solution:

The mean diameter of the tank is $\bar{d} = \frac{5.2 + 5.7 + 5.3 + 5.5}{4} = 5.425 \text{ m}$

The standard deviation of the diameter is $s_d = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}} = 0.222 \text{ m}$

The mean height of the tank is $\bar{h} = \frac{7.9 + 7.8 + 7.6}{3} = 7.767 \text{ m}$ and $s_h = 0.153 \text{ m}$

The Volume of the tank is given by

$$V = h \times \pi \left(\frac{d}{2}\right)^2 = 7.767(\pm 0.153) \times \pi \times \left(\frac{5.425(\pm 0.222)}{2}\right)^2$$

The error in the 3rd factor is given by

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.222}{5.425}\right)^2} = 0.0409 \quad y = \frac{5.425}{2} = 2.7125 \quad s_y = 0.0409 \times 2.7125 = 0.111$$

$$V = 7.767(\pm 0.153) \times 3.14159 \times (2.7125(\pm 0.111))^2$$

$$\frac{s_y}{y} = 2 \left(\frac{0.111}{2.7125}\right) = 0.0818 \quad y = (2.7125)^2 = 7.358 \quad s_y = 0.0818 \times 7.358 = 0.602$$

$$V = 7.767(\pm 0.153) \times 3.14159 \times 7.358(\pm 0.602)$$

Next, we propagate the error in volume by assuming the error in pi is negligible.

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.153}{7.767}\right)^2 + \left(\frac{0.602}{7.358}\right)^2} = 0.0841 \quad y = 7.767 \times 3.14159 \times 7.358 = 179.5$$

$$s_y = 0.0841 \times 179.5 = 15.09$$

$$V = 180(\pm 15) \text{ m}^3$$

Converting to liters, we have

$$V = 180(\pm 15) \text{ m}^3 \times \frac{1000 \text{ L}}{\text{m}^3} = 1.8(\pm 0.15) \times 10^5 \text{ L}$$

5. The U.S. Food and Drug Administration requires that calcium content of food be reported. The mean content (mg/g) and standard deviation (\pm s) for triplicate ($n=3$) determinations with a new and conventional method were shown below: [15%]

Method	Ca concentration (mg/g) found	
	New method	Conventional method
Cheese	4.70 ± 0.32	4.84 ± 0.13
Infant formula	3.81 ± 0.17	3.82 ± 0.06

- (a) For cheese, is the standard deviation for the new method significantly different from that of the conventional method at the 95% confidence level?
- (b) Are the mean Ca concentrations for cheese significantly different from each other at the 95% confidence level?
- (c) Using the new method, is the mean concentration in infant formula significantly different from that in cheese at the 95% confidence level?

Solution:

- (a) F-test can be used to compare whether the two standard deviations are significantly different. For triplicate determinations, degrees of freedom are both $n-1 = 2$.

According to the data: $F = \frac{0.32^2}{0.13^2} = 6.06 \leq 19.00$

No significant difference exists at the 95% confidence level.

- (b) t-test can be used to determine if the two means are significantly different.
Degree of freedom = $N_1 + N_2 - 2 = 4$.

According to the data: $t = \frac{|4.70 - 4.84|}{\sqrt{\frac{0.32^2}{3} + \frac{0.13^2}{3}}} \approx 0.70 \leq 2.78$

No significant difference exists at the 95% confidence level.

(c) t-test can be used to determine if the two means are significantly different.

Degree of freedom = $N_1 + N_2 - 2 = 4$.

According to the data: $t = \frac{|3.81 - 4.70|}{\sqrt{\frac{0.17^2}{3} + \frac{0.32^2}{3}}} \approx 4.26 \geq 2.78$

The mean concentration in infant formula is significantly different from that in cheese at the 95% confidence level.

6. A student used two different methods to measure the sulfite content (wt%) in several solid samples. The results are shown in the table. [10%]

Sample	Method A	Method B
1	48.17	47.68
2	43.26	43.86
3	49.38	50.12
4	51.82	50.85
5	44.95	44.01
6	51.27	50.38

Determine if the two methods give significantly different results at the 95% confidence level.

Solution:

Use the paired t-test to determine if the two methods give significantly different results.

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

$$\bar{d} = \frac{0.49 + (-0.60) + (-0.74) + 0.97 + 0.94 + 0.89}{6} = 0.325$$

$$\Sigma d_i = 1.95$$

$$\Sigma d_i^2 = 0.49^2 + (-0.60)^2 + (-0.74)^2 + 0.97^2 + 0.94^2 + 0.89^2 = 3.7643$$

$$s_d = \sqrt{\frac{3.7643 - \frac{1.95^2}{6}}{6 - 1}} \approx 0.791$$

$$t = \frac{0.325}{0.791/\sqrt{6}} = 1.006 \leq 2.57$$

The two methods do not give significantly different results at the 95% confidence level.

7. 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: [15%]

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.
- (b) Do the flow cell designs differ at the 95% confidence level?
- (c) If a difference was detected in part (b), which designs differ from each other at the 95% confidence level?

Solution:

- (a) The null hypothesis $H_0: \mu_{Des1} = \mu_{Des2} = \mu_{Des3} = \mu_{Des4}$

The alternative H_a : at least two of means differ.

- (b) Design 1: $N = 4$, $\bar{x} = 82.75$, $s = 10.30776$, variance = 106.2500

Design 2: $N = 4$, $\bar{x} = 88.00$, $s = 10.03328$, variance = 100.6667

Design 3: $N = 4$, $\bar{x} = 88.00$, $s = 8.75595$, variance = 76.6667

Design 4: $N = 4$, $\bar{x} = 92.25$, $s = 6.65207$ variance = 44.2500

$$\text{Grand Mean} = \frac{\sum x_i}{N} = 10.16$$

$$\text{SSF} = N_1(\bar{x}_1 - \bar{\bar{x}})^2 + \dots + N_4(\bar{x}_4 - \bar{\bar{x}})^2 = 181.5$$

$$SSE = (N_1 - 1)S_1^2 + \dots + (N_4 - 1)S_4^2 = 983.5$$

$$SST = SSE + SSF = 1165$$

$$MSF = \frac{SSF}{I - 1} = 60.500, MSE = \frac{SSE}{N - I} = 81.95833$$

$$F = \frac{MSF}{MSE} = 0.73818$$

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.

(c) No differences were detected

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. [10%]

(a) 51.27, 51.61, 51.84, 51.70

(b) 7.295, 7.284, 7.388, 7.292

Solution:

(a)

$$Q = \frac{|51.27 - 51.61|}{51.84 - 51.27} = 0.596$$

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

Since $Q < Q_{\text{crit}}$ the outlier value 51.27 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 $Q > Q_{\text{crit}}$ the outlier value 7.388 can be rejected with 95% confidence.

9. Perform a least-squares analysis of the calibration of isooctane in a hydrocarbon mixture provided in the two columns of the table below to determine the following parameters. [10%]

- (a) The equation for the least-squares line
- (b) The standard deviation about regression
- (c) The standard deviation of the slope
- (d) The standard deviation of the intercept

Mole Percent Isooctane, x_i	Peak Area, y_i
0.352	1.09
0.803	1.78
1.08	2.60
1.38	3.03
1.75	4.01

Solution:

- (a)

$$\Sigma x_i = 5.365, \Sigma y_i = 12.51, \Sigma x_i^2 = 6.9021, \Sigma y_i^2 = 36.3775, \Sigma x_i y_i = 15.81992$$

$$S_{xx} = \Sigma x_i^2 - \frac{(\Sigma x_i)^2}{N} = 6.90201 - \frac{(5.365)^2}{5} = 1.14537$$

$$S_{yy} = \Sigma y_i^2 - \frac{(\Sigma y_i)^2}{N} = 36.3775 - \frac{(12.51)^2}{5} = 5.07748$$

$$S_{xy} = \Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{N} = 15.81992 - \frac{5.365 \times 12.51}{5} = 2.39669$$

$$m = \frac{2.39669}{1.14537} = 2.0925 \approx 2.09$$

$$b = \frac{12.51}{5} - 2.0925 \times \frac{5.365}{5} = 0.2567 \approx 0.26$$

Thus, the equation for the least-squares line is $y = 2.09x + 0.26$.

(b) The standard deviation about regression

$$s_r = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{N - 2}} = \sqrt{\frac{5.07748 - (2.0925)^2 \times 1.14537}{5 - 2}} \approx 0.1442$$

(c) The standard deviation of the slope

$$s_m = \sqrt{\frac{s_r^2}{S_{xx}}} = \sqrt{\frac{(0.1442)^2}{1.14537}} \approx 0.13$$

(d) The standard deviation of the intercept

$$s_b = 0.1442 \times \sqrt{\frac{1}{5 - (5.365)^2/6.9021}} \approx 0.16$$

10. The calibration curve found in Q.9 was used for the chromatographic determination of isooctane in a hydrocarbon mixture. A peak area of 2.65 was obtained. Calculate the mole percent of isooctane in the mixture and the standard deviation if the area was (a) the result of a single measurement (b) the mean of four measurements. **[10%]**

Solution:

In either case, the unknown concentration is found from rearranging the least-squares equation for the line, which gives

$$x = \frac{y - b}{m} = \frac{y - 0.2567}{2.0925} = \frac{2.65 - 0.2567}{2.0925} = 1.144 \text{ mole\%}$$

(a)

$$s_c = \frac{0.1442}{2.0925} \times \sqrt{\frac{1}{1} + \frac{1}{5} + \frac{\left(2.65 - \frac{12.51}{5}\right)^2}{(2.0925)^2 \times 1.145}} = 0.076 \text{ mole\%}$$

The results may be expressed as 1.144±0.076 mole% or 1.14±0.08 mole%.

(b)

$$s_c = \frac{0.1442}{2.0925} \times \sqrt{\frac{1}{4} + \frac{1}{5} + \frac{\left(2.65 - \frac{12.51}{5}\right)^2}{(2.0925)^2 \times 1.145}} = 0.046 \text{ mole\%}$$

The results may be expressed as 1.144±0.046 mole% or 1.14±0.05 mole%.

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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 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