

10710CHEM311000-Analytical Chemistry (I)

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First Midterm Examination

Date: 13-11-2018, 10:10 am to 12:10 pm

Answer **all 10 questions** (total 115%). You have **2** hours to finish this paper.

1. In inductively coupled plasma atomic emission spectrometry, the number of atoms excited to a particular energy level is a strong function of temperature. For an element of excitation energy E in joules (J), the measured ICP emission signal S can be written

$$S = k'e^{-E/kt}$$

where k' is a constant independent of temperature, T is the absolute temperature in kelvin (K), and k is Boltzmann's constant ($1.3807 \times 10^{-23} J K^{-1}$). For an ICP of average temperature $6,500 K$ and for Cu with an excitation energy of $6.12 \times 10^{-19} J$, how precisely does the ICP temperature need to be controlled for the coefficient of variation (CV) in the emission signal to be 1% or less? **[10%]**

Solution

To obtain a CV in S of 1% or less,

$$\frac{S_S}{S} \leq 0.01 = \sqrt{\left(\frac{S_{k'}}{k'}\right)^2 + \left(\frac{S_{e^{-E/kT}}}{e^{-E/kT}}\right)^2}$$

Since k' is a constant, the first term is zero resulting in:

$$0.01 = \frac{S_{e^{-E/kT}}}{e^{-E/kT}} \quad \text{From Table 6-4} \quad \frac{S_{e^{-E/kT}}}{e^{-E/kT}} = S_{-E/kT}$$

$S_{-E/kT}$ can be determined by evaluation of the errors in each of the numbers.

$$\frac{S_{-E/kT}}{-E/kT} = \sqrt{\left(\frac{S_E}{E}\right)^2 + \left(\frac{S_k}{k}\right)^2 + \left(\frac{S_T}{T}\right)^2}$$

Since both E and k have no uncertainty, this equation reduces to:

$$S_{-E/kT} = \left(\frac{S_T}{T}\right) \times \frac{-E}{kT} = \left(\frac{S_T}{6500}\right) \left(\frac{-6.12 \times 10^{-19}}{(1.3807 \times 10^{-23})(6500)}\right) = 0.01$$

Solving for s_T gives:

$$s_T \leq 9.5 \text{ K}$$

2. Calculate a pooled estimate of σ from the following spectrophotometric analysis for NTA (nitrilotriacetic acid) in water from the Ohio River: **[5 %]**

Sample	NTA, ppb
1	13, 19, 12, 7
2	42, 40, 39
3	29, 25, 26, 23, 30

Solution

Equation for calculating the pooled standard deviation:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1} (x_i - \bar{x}_1)^2 + \sum_{j=1}^{N_2} (x_j - \bar{x}_2)^2 + \sum_{k=1}^{N_3} (x_k - \bar{x}_3)^2 + \dots}{N_1 + N_2 + N_3 + \dots - N_t}}$$

The calculation:

Sample	1	$(x_i - x_{ave})^2$	2	$(x_i - x_{ave})^2$	3	$(x_i - x_{ave})^2$	
	13	0.06	42	2.78	29	5.76	
	19	39.06	40	0.11	25	2.56	
	12	0.56	39	1.78	26	0.36	
	7	33.06			23	12.96	
					30	11.56	
Mean	12.7		40.3		26.60		
	5		3				
s	4.92		1.53		2.88		Total
N		4		3		5	12
$\Sigma(x_i - x_{ave})^2$		72.75		4.67		32.20	110.6
							2

$$s_{pooled} = 3.5$$

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

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

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. Sewage and industrial pollutants dumped into a body of water can reduce the dissolved oxygen concentration and adversely affect aquatic species. In one study, weekly readings are taken from the same location in a river over a two-month period. Some scientists think that 5.0 ppm is a dissolved O₂ level that is marginal for fish to live. Conduct a statistical test to determine whether the mean dissolved O₂ concentration is less than 5.0 ppm at the 95% confidence level. State clearly the null and alternative hypotheses. **[10 %]**

Week Number	Dissolved O ₂ , ppm
1	4.9
2	5.1
3	5.6
4	4.3
5	4.7
6	4.9
7	4.5
8	5.1

Solution

The null hypothesis is that $\mu = 5.0$ ppm dissolved O₂ and the alternative hypothesis is

that $\mu < 5.0$ ppm dissolved O₂.

This is a one-tailed test and from Table 7-1, $z_{\text{crit}} = -1.96$ for the 95% confidence level.

For the data set, $\bar{x} = 4.888$ and $s = 0.40$

$$z = \frac{4.888 - 5.0}{0.4/\sqrt{8}} = -0.79 \leq -1.96$$

Thus, we must accept the null hypothesis that the mean dissolved O₂ is 5.0 ppm at the 95% confidence level.

5. The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is found to be 12.6, 11.9, 13.0, 12.7, and 12.5 wt% (g carbohydrate/100g glycoprotein) in replicate analyses. Find the 90% confidence intervals for the carbohydrate content. [5 %]

Solution:

1. First calculate \bar{x} ($= 12.5_4$) and S ($= (0.4_0)$) for the five measurements. For the 90 % confidence interval, look up t -Table under 90 and across from *four* degrees of freedom (degrees of freedom = $n - 1$).

The value of t is 2.132 for the 90% confidence interval, DOF = 4

90% confidence interval

$$= \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(2.132)(0.4_0)}{\sqrt{5}} = 12.5_4 \pm 0.3_8 wt\%$$

6. 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	28.9586
	7
F _(calculated)	6.32232
	1
LSD	7.41951
(calculated)	9

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

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

DOF for t is 12 (N-i)

$t = 2.18$, $MSE = 28.95867$, $N_g = 5$

$LSD = 7.419519$

7. 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:

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

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.

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

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.

8. 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. [5 %]
- (b) Find the concentration of **S** (mM) in the 10.0 mL mixture. [5 %]
- (c) Find the concentration of **X** (mM) in the 10.0 mL mixture. [5 %]
- (d) Find the concentration of **X** in the original unknown. [5 %]

Solution:

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

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

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

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

9. 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. [5 %]

(c) Find the concentration limit of quantitation. [5 %]

Solution:

(a) Standard deviation of 9 samples $= s = 0.0006_{44}$.

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

$$y_{dl} = y_{blank} + 3s = 0.0011_8 + (3)(0.0006_{44}) = 0.0031_{12}$$

(b) Minimum detectable concentration =

$$\frac{3s}{m} = \frac{(3)(0.0006_{44})}{2.24 \times 10^4 M^{-1}} = 8.6 \times 10^{-8} M$$

$$(c) \text{ Lower limit of quantitation} = \frac{10s}{m} = \frac{(10)(0.0006_{44})}{2.24 \times 10^4 M^{-1}} = 2.9 \times 10^{-7} M$$

10. The following results were obtained for the determination of calcium in a NIST limestone sample: %CaO = 50.33, 50.2, 50.36, 50.21, and 50.44. Five gross samples were then obtained for a carload of limestone. The average percent CaO values for the gross samples were found to be 49.53, 50.12, 49.60, 49.87, and 50.4. Calculate the relative standard deviation association with the sampling step. **[10 %]**

Solution:

$$s_o^2 = s_s^2 + s_m^2$$

From the NIST sample: $s_m^2 = 0.00947$ From the gross sample: $s_o^2 = 0.15547$

$$s_s = \sqrt{0.15547 - 0.00947} = 0.38$$

$$\text{The relative standard deviation} = \left(\frac{s_s}{\bar{x}} \right) \times 100\% = \left(\frac{0.38}{49.92} \right) \times 100\% = 0.76\%$$

Appendix for Various Critical Values

z-table

TABLE 7-1

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

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t-table (values of t for various level of probability)

Degrees of freedom	Confidence level (%)				Degrees of freedom	Confidence level (%)			
	90	95	99	99.9		90	95	99	99.9
1	6,31	12,7	63,7	637	21	1,72	2,08	2,83	3,82
2	2,92	4,30	9,92	31,6	22	1,72	2,07	2,82	3,79
3	2,35	3,18	5,84	12,9	23	1,71	2,07	2,81	3,77
4	2,13	2,78	4,60	8,61	24	1,71	2,06	2,80	3,75
5	2,01	2,57	4,03	6,86	25	1,71	2,06	2,79	3,73
6	1,94	2,45	3,71	5,96	26	1,71	2,06	2,78	3,71
7	1,89	2,36	3,50	5,41	27	1,70	2,05	2,77	3,69
8	1,86	2,31	3,36	5,04	28	1,70	2,05	2,76	3,67
9	1,83	2,26	3,25	4,78	29	1,70	2,05	2,76	3,66
10	1,81	2,23	3,17	4,59	30	1,70	2,04	2,75	3,65
11	1,80	2,20	3,11	4,44	35	1,69	2,03	2,72	3,59
12	1,78	2,18	3,05	4,32	40	1,68	2,02	2,70	3,55
13	1,77	2,16	3,01	4,22	45	1,68	2,01	2,69	3,52
14	1,76	2,14	2,98	4,14	50	1,68	2,01	2,68	3,50
15	1,75	2,13	2,95	4,07	55	1,67	2,00	2,67	3,48
16	1,75	2,12	2,92	4,02	60	1,67	2,00	2,66	3,46
17	1,74	2,11	2,90	3,97	80	1,67	1,99	2,64	3,42
18	1,73	2,10	2,88	3,92	100	1,66	1,98	2,63	3,39
19	1,73	2,09	2,86	3,88	120	1,66	1,98	2,62	3,37
20	1,72	2,09	2,85	3,85	∞	1,64	1,96	2,58	3,29

F-table

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

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Q-table

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

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