

Ασκήσεις Κεφάλαια 4 και 5

Ενόργανη Χημική Ανάλυση (ΜΠ 212)

Καθ. Έλια Ψυλλάκη

Εργαστήριο Υδατικής Χημείας
Σχολή Χημικών Μηχανικών και
Μηχανικών Περιβάλλοντος
Πολυτεχνείο Κρήτης

Γραφείο διδάσκουσας: Κ1.102

Τηλ: 2821037810

email: epsillakis@tuc.gr

Κεφάλαιο 4 στατιστική

Πρόβλημα

Η επί τοις 100 περιεκτικότητα ενός προσθέτου σε βενζίνη μετρήθηκε έξι φορές και πήραμε τα παρακάτω αποτελέσματα: 0.13, 0.12, 0.16, 0.17, 0.20, 0.11 %. Βρείτε τα διαστήματα εμπιστοσύνης 90 και 99 % για την επί τοις 100 περιεκτικότητα του πρόσθετου.

Λύση

$\bar{x} = 0.148, s = 0.034$

$90\% \text{ confidence interval} = 0.148 \pm \frac{(2.015)(0.034)}{\sqrt{6}} = 0.148 \pm 0.028$

$99\% \text{ confidence interval} = 0.148 \pm \frac{(4.032)(0.034)}{\sqrt{6}} = 0.148 \pm 0.056$

Πίνακας 3.4. Θεωρητικές τιμές t (t_{theor}) σε διάφορους βαθμούς ελευθερίας εμπιστοσύνης.

Βαθμοί ελευθερίας	Στάθμη εμπιστοσύνης			
	80%	90%	95%	99%
v = n - 1				
1	3,078	6,314	12,706	63,657
2	1,886	2,920	4,303	9,925
3	1,638	2,353	3,182	5,841
4	1,533	2,132	2,776	4,604
5	1,476	2,015	2,571	4,032
6	1,440	1,943	2,447	3,707
7	1,415	1,895	2,365	3,500
8	1,397	1,860	2,306	3,355
9	1,383	1,833	2,262	3,250
10	1,372	1,812	2,228	3,169
11	1,363	1,796	2,201	3,106
12	1,356	1,782	2,179	3,055
15	1,341	1,753	2,131	2,947
20	1,325	1,725	2,086	2,845
30	1,310	1,697	2,042	2,787
∞*	1,282	1,645	1,960	2,576

[1. Select category](#)[2. Choose calculator](#)[3. Enter data](#)[4. View results](#)

Descriptive statistics and CI of mean

Enter raw data and this calculator will calculate the mean, SD, SEM and confidence interval of the mean. Enter mean, N and SD or SEM, and it will calculate the confidence interval of the mean.

1. Choose data entry format

Caution: Changing format will erase your data.

- ☒ Enter up to 50 rows
- ☐ Enter or paste up to 10000 rows
- ☐ Enter mean, SEM and N
- ☐ Enter mean, SD and N

3. View the results

[Calculate Now](#)[Clear The Form](#)

2. Enter data

- 1:
- 2:
- 3:
- 4:
- 5:
- 6:
- 7:
- 8:
- 9:
- 10:

[1. Select category](#)[2. Choose calculator](#)[3. Enter data](#)[4. View results](#)

Descriptive statistics results

Parameter	Value
Mean	0.1483
SD	0.0343
SEM	0.0140
N	6
90% CI	0.1201 to 0.1766
95% CI	0.1123 to 0.1843
99% CI	0.0919 to 0.2048
Minimum	0.11
Median	0.145
Maximum	0.2

[Learn more about descriptive statistics](#)

Πρόβλημα

Ένα πρότυπο δείγμα αναφοράς είναι πιστοποιημένο ότι περιέχει 94,6 ppm ενός οργανικού ρυπαντή σε χώμα. Η ανάλυση σας δίνει 98.6, 98.4, 97.2, 94.6 και 96.2 ppm. Τα αποτελέσματα σας διαφέρουν από το αναμενόμενο αποτέλεσμα μέσα σε ένα διάστημα εμπιστοσύνης 95 %? Εάν κάνετε άλλη μία μέτρηση και περνάτε 94,5 θα καταλήγατε σε διαφορετικό συμπέρασμα?

Λύση

$$\bar{x} = 97.0_0, \quad s = 1.6_6$$

$$95\% \text{ confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}} = 97.0_0 \pm \frac{(2.776)(1.6_6)}{\sqrt{5}} = 97.0_0 \pm 2.0_6$$

$$\text{Range} = 94.9_4 \text{ to } 99.0_6$$

The 95% confidence interval does not include the certified value of 94.6 ppm, so the difference is significant at the 95% confidence level.

If we make one more measurement, the results are $\bar{x} = 96.5_8$, $s = 1.8_0$

$$95\% \text{ confidence interval} = 96.5_8 \pm \frac{(2.571)(1.8_0)}{\sqrt{6}} = 96.5_8 \pm 1.8_9$$

$$\text{Range} = 94.6_9 \text{ to } 98.4_7$$

The 95% confidence interval still does not include the certified value of 94.6 ppm, so the difference is still significant at the 95% confidence level.

κας 3.4. Θεωρητικές τιμές t (t_{theor}) σε διάφορους βαθμούς ελευθερίας.

Βαθμοί ελευθερίας	Στάθμη εμπιστοσύνης			
	80%	90%	95%	99%
$v = n - 1$				
1	3,078	6,314	12,706	63,657
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Πρόβλημα

Τα παρακάτω δύο σετ μετρήσεων σε ένα πρότυπο δείγμα να φοράς είναι στατιστικά αντίστοιχα?

Method 1	Method 2
0.082 601	0.081 83
0.082 621	0.081 86
0.082 589	0.082 05
0.082 617	0.082 06
0.082 598	0.082 15
	0.082 08

SOURCE: S. Ahmed, N. Jabeen, and E. ur Rehman, *Anal. Chem.* **2002**, 74, 4133; L. W. Green, J. J. Leppinen, and N. L. Elliot, *Anal. Chem.* **1988**, 60, 34.

Λύση

For Method 1, we compute $\bar{x}_1 = 0.082\ 605_2$, $s_1 = 0.000\ 013_4$.

For Method 2, $\bar{x}_2 = 0.082\ 00_5$, $s_2 = 0.000\ 12_9$.

The two standard deviations differ by approximately a factor of 10. We should use the F test to compare the two standard deviations:

$$F_{\text{calculated}} = s_2^2/s_1^2 = (0.000\ 12_9)^2/(0.000\ 013_4)^2 = 92.7$$

$F_{\text{table}} = 6.26$. Since $F_{\text{calculated}} > F_{\text{table}}$, we use Equations 4-8a and 4-9a.

The following spreadsheet shows that $t_{\text{calculated}} = 11.3$ and $t_{\text{table}} = 2.57$.

$t_{\text{calculated}} > t_{\text{table}}$, so the difference is significant at the 95% confidence level.

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}}$$

$$\text{Degrees of freedom} = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\frac{(s_1^2/n_1)^2}{n_1 - 1} + \frac{(s_2^2/n_2)^2}{n_2 - 1}}$$

TABLE 4-4 Critical values of $F = s_1^2/s_2^2$ at 95% c

Degrees of freedom for s_2	2	3	4	5	6
2	19.0	19.2	19.2	19.3	19.3
3	9.55	9.28	9.12	9.01	8.94
4	6.94	6.59	6.39	6.26	6.16
5	5.79	5.41	5.19	5.05	4.95
6	5.14	4.76	4.53	4.39	4.28
7	4.74	4.35	4.12	3.97	3.87
8	4.46	4.07	3.84	3.69	3.58
9	4.26	3.86	3.63	3.48	3.37
10	4.10	3.71	3.48	3.33	3.22
11	3.98	3.59	3.36	3.20	3.10
12	3.88	3.49	3.26	3.11	3.00
13	3.81	3.41	3.18	3.02	2.92
14	3.74	3.34	3.11	2.96	2.85
15	3.68	3.29	3.06	2.90	2.79
16	3.63	3.24	3.01	2.85	2.74
17	3.59	3.20	2.96	2.81	2.70
18	3.56	3.16	2.93	2.77	2.66
19	3.52	3.13	2.90	2.74	2.63
20	3.49	3.10	2.87	2.71	2.60
30	3.32	2.92	2.69	2.53	2.42
∞	3.00	2.60	2.37	2.21	2.10

Critical values of F for a one-tailed test of the hypothesis that $s_1 > s_2$. There is a .

Πρόβλημα

Η τιμή 216 θα πρέπει να απορριφθεί από το παρακάτω σετ μετρήσεων:
192, 216, 202, 195, και 204?

Λύση

$$\bar{x} = 201.8; s = 9.34$$

$$G_{\text{calculated}} = |216 - 201.8| / 9.34 = 1.52$$

$$G_{\text{table}} = 1.672 \text{ for five measurements}$$

Because $G_{\text{calculated}} < G_{\text{table}}$, we should retain 216.

Αριθμός παρατηρήσεων	G (95% εμπιστοσύνη)
3	1.153
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110

Κεφάλαιο 5 Βαθμονόμηση

Πρόβλημα

Λύση

5-16. In a murder trial in the 1990s, the defendant's blood was found at the crime scene. The prosecutor argued that blood was left by the defendant during the crime. The defense argued that police "planted" the defendant's blood from a sample collected later. Blood is normally collected in a vial containing the metal-binding compound EDTA as an anticoagulant with a concentration of ~4.5 mM after the vial has been filled with blood. At the time of the trial, procedures to measure EDTA in blood were not well established. Even though the amount of EDTA found in the crime-scene blood was orders of magnitude below 4.5 mM, the jury acquitted the defendant. This trial motivated the development of a new method to measure EDTA in blood.

(a) *Precision and accuracy.* To measure accuracy and precision of the method, blood was fortified with EDTA to known levels.

$$\text{Accuracy} = 100 \times \frac{\text{mean value found} - \text{known value}}{\text{known value}}$$

$$\text{Precision} = 100 \times \frac{\text{standard deviation}}{\text{mean}} = \text{coefficient of variation}$$

For each of the three spike levels in the table, find the precision and accuracy of the quality control samples.

EDTA measurements (ng/mL) at three fortification levels			
Spike:	22.2 ng/mL	88.2 ng/mL	314 ng/mL
Found:	33.3	83.6	322
	19.5	69.0	305
	23.9	83.4	282
	20.8	100.0	329
	20.8	76.4	276

SOURCE: R. L. Sheppard and J. Henion, *Anal. Chem.* **1997**, *69*, 477A, 2901.

(b) *Detection and quantitation limits.* Low concentrations of EDTA near the detection limit gave the following dimensionless instrument readings: 175, 104, 164, 193, 131, 189, 155, 133, 151, and 176. Ten blanks had a mean reading of 45.0. The slope of the calibration curve is $1.75 \times 10^9 \text{ M}^{-1}$. Estimate the signal and concentration detection limits and the lower limit of quantitation for EDTA.

5-16. (a) For the fortification level of 22.2 ng/mL, the mean of the 5 values is 23.66 ng/mL and the standard deviation is 5.63 ng/mL.

$$\text{Precision} = 100 \times \frac{5.63}{23.66} = 23.8\%$$

$$\text{Accuracy} = 100 \times \frac{23.66 - 22.2}{22.2} = 6.6\%$$

For the fortification level of 88.2 ng/mL, the mean of the 5 values is 82.48 ng/mL and the standard deviation is 11.49 ng/mL.

$$\text{Precision} = 100 \times \frac{11.49}{82.48} = 13.9\%$$

$$\text{Accuracy} = 100 \times \frac{82.48 - 88.2}{88.2} = -6.5\%$$

For the fortification level of 314 ng/mL, the mean of the 5 values is 302.8 ng/mL and the standard deviation is 23.51 ng/mL.

$$\text{Precision} = 100 \times \frac{23.51}{302.8} = 7.8\%$$

$$\text{Accuracy} = 100 \times \frac{302.8 - 314}{314} = -3.6\%$$

(b) Standard deviation of 10 samples: $s = 28.2$; mean blank: $y_{\text{blank}} = 45.0$
Signal detection limit = $y_{\text{blank}} + 3s = 45.0 + (3)(28.2) = 129.6$

$$\text{Concentration detection limit} = \frac{3s}{m} = \frac{(3)(28.2)}{1.75 \times 10^9 \text{ M}^{-1}} = 4.8 \times 10^{-8} \text{ M}$$

$$\text{Lower limit of quantitation} = \frac{10s}{m} = \frac{(10)(28.2)}{1.75 \times 10^9 \text{ M}^{-1}} = 1.6 \times 10^{-7} \text{ M}$$

Πρόβλημα

Spike recovery and detection limit. Species of arsenic found in drinking water include AsO_3^{3-} (arsenite), AsO_4^{3-} (arsenate), $(\text{CH}_3)_2\text{AsO}_2^-$ (dimethylarsinate), and $(\text{CH}_3)\text{AsO}_3^{2-}$ (methylarsonate). Pure water containing no arsenic was spiked with $0.40 \mu\text{g}$ arsenate/L. Seven replicate determinations gave 0.39, 0.40, 0.38, 0.41, 0.36, 0.35, and $0.39 \mu\text{g/L}$.¹⁵ Find the mean percent recovery of the spike and the concentration detection limit ($\mu\text{g/L}$).

Λύση

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Mean = $0.383 \mu\text{g/L}$ and standard deviation = $0.0214 \mu\text{g/L}$

$$\% \text{ recovery} = \frac{0.383 \mu\text{g/L}}{0.40 \mu\text{g/L}} \times 100 = 96\%$$

The measurements are already expressed in concentration units. The concentration detection limit is 3 times the standard deviation = $3(0.0214 \mu\text{g/L}) = 0.064 \mu\text{g/L}$.

Πρόβλημα

Detection limit. Low concentrations of Ni^{2+} -EDTA near the detection limit gave the following counts in a mass spectral measurement: 175, 104, 164, 193, 131, 189, 155, 133, 151, 176. Ten measurements of a blank had a mean of 45 counts. A sample containing $1.00 \mu\text{M}$ Ni^{2+} -EDTA gave 1 797 counts. Estimate the detection limit for Ni-EDTA.

Λύση The low concentration of Ni-EDTA has a standard deviation of 28.2 counts for 10 measurements. The detection limit is estimated to be

$$y_{\text{dl}} = y_{\text{blank}} + 3s = 45 + 3(28.2) = 129.6 \text{ counts}$$

To convert counts to molarity, we note that a $1.00 \mu\text{M}$ solution gave a net signal of $1797 - 45 = 1752$ counts. The slope of the calibration curve is therefore estimated to be

$$m = \frac{y_{\text{sample}} - y_{\text{blank}}}{\text{sample concentration}} = \frac{1797 - 45}{1.00 \mu\text{M}} = 1.752 \times 10^9 \frac{\text{counts}}{\text{M}}$$

The minimum detectable concentration is

$$\frac{3s}{m} = \frac{(3)(28.2) \text{ counts}}{1.752 \times 10^9 \text{ counts/M}} = 4.8 \times 10^{-8} \text{ M}$$