

7.6: Exercises

1. Use this [link](#) to access a case study on data analysis and complete the last investigation in Part V: Ways to Draw Conclusions from Data.

2. Ketkar and co-workers developed an analytical method to determine trace levels of atmospheric gases. An analysis of a sample that is 40.0 parts per thousand (ppt) 2-chloroethylsulfide gave the following results from Ketkar, S. N.; Dulak, J. G.; Dheandhanou, S.; Fite, W. L. *Anal. Chim. Acta* **1991**, 245, 267–270.

43.3	34.8	31.9
37.8	34.4	31.9
42.1	33.6	35.3

Determine whether there is a significant difference between the experimental mean and the expected value at $\alpha = 0.05$.

3. To test a spectrophotometer's accuracy a solution of 60.06 ppm $\text{K}_2\text{Cr}_2\text{O}_7$ in 5.0 mM H_2SO_4 is prepared and analyzed. This solution has an expected absorbance of 0.640 at 350.0 nm in a 1.0-cm cell when using 5.0 mM H_2SO_4 as a reagent blank. Several aliquots of the solution produce the following absorbance values.

0.639	0.638	0.640	0.639	0.640	0.639	0.638
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Determine whether there is a significant difference between the experimental mean and the expected value at $\alpha = 0.01$.

4. Monna and co-workers used radioactive isotopes to date sediments from lakes and estuaries. To verify this method they analyzed a ^{208}Po standard known to have an activity of 77.5 decays/min, obtaining the following results.

77.09	75.37	72.42	76.84	77.84	76.69
78.03	74.96	77.54	76.09	81.12	75.75

Determine whether there is a significant difference between the mean and the expected value at $\alpha = 0.05$. The data in this problem are from Monna, F.; Mathieu, D.; Marques, A. N.; Lancelot, J.; Bernat, M. *Anal. Chim. Acta* **1996**, 330, 107–116.

5. A 2.6540-g sample of an iron ore, which is 53.51% w/w Fe, is dissolved in a small portion of concentrated HCl and diluted to volume in a 250-mL volumetric flask. A spectrophotometric determination of the concentration of Fe in this solution yields results of 5840, 5770, 5650, and 5660 ppm. Determine whether there is a significant difference between the experimental mean and the expected value at $\alpha = 0.05$.

6. Horvat and co-workers used atomic absorption spectroscopy to determine the concentration of Hg in coal fly ash. Of particular interest to the authors was developing an appropriate procedure for digesting samples and releasing the Hg for analysis. As part of their study they tested several reagents for digesting samples. Their results using HNO_3 and using a 1 + 3 mixture of HNO_3 and HCl are shown here. All concentrations are given as ppb Hg sample.

HNO_3 :	161	165	160	167	166	
1 + 3 HNO_3 – HCl:	159	145	140	147	143	156

Determine whether there is a significant difference between these methods at $\alpha = 0.05$. The data in this problem are from Horvat, M.; Lupsina, V.; Pihlar, B. *Anal. Chim. Acta* **1991**, 243, 71–79.

7. Lord Rayleigh, John William Strutt (1842-1919), was one of the most well known scientists of the late nineteenth and early twentieth centuries, publishing over 440 papers and receiving the Nobel Prize in 1904 for the discovery of argon. An important turning point in Rayleigh's discovery of Ar was his experimental measurements of the density of N_2 . Rayleigh approached this experiment in two ways: first by taking atmospheric air and removing O_2 and H_2 ; and second, by chemically producing N_2 by decomposing nitrogen containing compounds (NO , N_2O , and NH_4NO_3) and again removing O_2 and H_2 . The following table shows

his results for the density of N_2 , as published in *Proc. Roy. Soc.* **1894**, LV, 340 (publication 210); all values are the grams of gas at an equivalent volume, pressure, and temperature.

atmospheric origin	chemical origin
2.31017	2.30143
2.30986	2.29890
2.31010	2.29816
2.31001	2.30182
2.31024	2.29869
2.31010	2.29940
2.31028	2.29849
	2.29889

Explain why this data led Rayleigh to look for and to discover Ar. You can read more about this discovery here: Larsen, R. D. J. *Chem. Educ.* **1990**, 67, 925–928.

8. Gács and Ferraroli reported a method for monitoring the concentration of SO_2 in air. They compared their method to the standard method by analyzing urban air samples collected from a single location. Samples were collected by drawing air through a collection solution for 6 min. Shown here is a summary of their results with SO_2 concentrations reported in $\mu L/m^3$.

standard method	new method
21.62	21.54
22.20	20.51
24.27	22.31
23.54	21.30
24.25	24.62
23.09	25.72
21.02	21.54

Using an appropriate statistical test, determine whether there is any significant difference between the standard method and the new method at $\alpha = 0.05$. The data in this problem are from Gács, I.; Ferraroli, R. *Anal. Chim. Acta* **1992**, 269, 177–185.

9. One way to check the accuracy of a spectrophotometer is to measure absorbances for a series of standard dichromate solutions obtained from the National Institute of Standards and Technology. Absorbances are measured at 257 nm and compared to the accepted values. The results obtained when testing a newly purchased spectrophotometer are shown here. Determine if the tested spectrophotometer is accurate at $\alpha = 0.05$.

standard	measured absorbance	expected absorbance
1	0.2872	0.2871
2	0.5773	0.5760
3	0.8674	0.8677
4	1.1623	1.1608
5	1.4559	1.4565

10. Maskarinec and co-workers investigated the stability of volatile organics in environmental water samples. Of particular interest was establishing the proper conditions to maintain the sample's integrity between its collection and its analysis. Two preservatives were investigated—ascorbic acid and sodium bisulfate—and maximum holding times were determined for a number of volatile organics and water matrices. The following table shows results for the holding time (in days) of nine organic compounds in surface water.

compound	Ascorbic Acid	Sodium Bisulfate
methylene chloride	77	62
carbon disulfide	23	54
trichloroethane	52	51
benzene	62	42
1,1,2-trichloroethane	57	53
1,1,2,2-tetrachloroethane	33	85
tetrachloroethene	32	94
chlorobenzene	36	86

Determine whether there is a significant difference in the effectiveness of the two preservatives at $\alpha = 0.10$. The data in this problem are from Maxkarinec, M. P.; Johnson, L. H.; Holladay, S. K.; Moody, R. L.; Bayne, C. K.; Jenkins, R. A. *Environ. Sci. Technol.* **1990**, 24, 1665–1670.

11. Using X-ray diffraction, Karstang and Kvalheim reported a new method to determine the weight percent of kaolinite in complex clay minerals using X-ray diffraction. To test the method, nine samples containing known amounts of kaolinite were prepared and analyzed. The results (as % w/w kaolinite) are shown here.

actual	5.0	10.0	20.0	40.0	50.0	60.0	80.0	90.0	95.0
found	6.8	11.7	19.8	40.5	53.6	61.7	78.9	91.7	94.7

Evaluate the accuracy of the method at $\alpha = 0.05$. The data in this problem are from Karstang, T. V.; Kvalheim, O. M. *Anal. Chem.* **1991**, 63, 767–772.

12. Mizutani, Yabuki and Asai developed an electrochemical method for analyzing *l*-malate. As part of their study they analyzed a series of beverages using both their method and a standard spectrophotometric procedure based on a clinical kit purchased from Boehringer Scientific. The following table summarizes their results. All values are in ppm. The data in this problem are from Mizutani, F.; Yabuki, S.; Asai, M. *Anal. Chim. Acta* **1991**, 245, 145–150.

Sample	Electrode	Spectrophotometric
Apple Juice 1	34.0	33.4
Apple Juice 2	22.6	28.4
Apple Juice 3	29.7	29.5
Apple Juice 4	24.9	24.8
Grape Juice 1	17.8	18.3
Grape Juice 2	14.8	15.4
Mixed Fruit Juice 1	8.6	8.5
Mixed Fruit Juice 2	31.4	31.9
White Wine 1	10.8	11.5

White Wine 2	17.3	17.6
White Wine 3	15.7	15.4
White Wine 4	18.4	18.3

13. Alexiev and colleagues describe an improved photometric method for determining Fe^{3+} based on its ability to catalyze the oxidation of sulphanilic acid by KIO_4 . As part of their study, the concentration of Fe^{3+} in human serum samples was determined by the improved method and the standard method. The results, with concentrations in $\mu\text{mol/L}$, are shown in the following table.

Sample	Improved Method	Standard Method
1	8.25	8.06
2	9.75	8.84
3	9.75	8.36
4	9.75	8.73
5	10.75	13.13
6	11.25	13.65
7	13.88	13.85
8	14.25	13.43

Determine whether there is a significant difference between the two methods at $\alpha = 0.05$. The data in this problem are from Alexiev, A.; Rubino, S.; Deyanova, M.; Stoyanova, A.; Sicilia, D.; Perez Bendito, D. *Anal. Chim. Acta*, **1994**, 295, 211–219.

14. Ten laboratories were asked to determine an analyte's concentration of in three standard test samples. Following are the results, in $\mu\text{g/mL}$.

Laboratory	Sample 1	Sample 2	Sample 3
1	22.6	13.6	16.0
2	23.0	14.2	15.9
3	21.5	13.9	16.9
4	21.9	13.9	16.9
5	21.3	13.5	16.7
6	22.1	13.5	17.4
7	23.1	13.5	17.5
8	21.7	13.5	16.8
9	22.2	12.9	17.2
10	21.7	13.8	16.7

Determine if there are any potential outliers in Sample 1, Sample 2 or Sample 3. Use all three methods—Dixon's Q -test, Grubb's test, and Chauvenet's criterion—and compare the results to each other. For Dixon's Q -test and for the Grubb's test, use a significance level of $\alpha = 0.05$. The data in this problem are adapted from Steiner, E. H. "Planning and Analysis of Results of Collaborative Tests," in *Statistical Manual of the Association of Official Analytical Chemists*, Association of Official Analytical Chemists: Washington, D. C., 1975.

15. Use an appropriate non-parametric test to reanalyze the data in some or all of Exercises 7.6.2 to 7.6.14.

16. The importance of between-laboratory variability on the results of an analytical method are determined by having several laboratories analyze the same sample. In one such study, seven laboratories analyzed a sample of homogenized milk for a selected aflatoxin [data from Massart, D. L.; Vandeginste, B. G. M; Deming, S. N.; Michotte, Y.; Kaufman, L. *Chemometrics: A Textbook*, Elsevier: Amsterdam, 1988]. The results, in ppb, are summarized below.

lab A	lab B	lab C	lab D	lab E	lab F	lab G
1.6	4.6	1.2	1.5	6.0	6.2	3.3
2.9	2.8	1.9	2.7	3.9	3.8	3.8
3.5	3.0	2.9	3.4	4.3	5.5	5.5
4.5	4.5	1.1	2.0	5.8	4.2	4.9
2.2	3.1	2.9	3.4	4.0	5.3	4.5

(a) Determine if the between-laboratory variability is significantly greater than the within-laboratory variability at $\alpha = 0.05$. If the between-laboratory variability is significant, then determine the source(s) of that variability.

(b) Estimate values for σ_{rand}^2 and for σ_{syst}^2 .

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