Solution and Answer Guide

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Chapter 5

**\*5-1.** Describe in your own words why the confidence interval for the mean of five measurements is smaller than that for a single result.

**Solution:**

The distribution of means is narrower than the distribution of single results. Hence, the standard error of the mean of 5 measurements is smaller than the standard deviation of a single result. The mean is thus known with more confidence than is a single result.

**5-2.** Assuming a large number of measurements so that *s* is a good estimate of σ, determine what confidence level was used for each of the following confidence intervals.

**Solutions:**

**(a)** 2 5. 8*s*

*x*±*N*

Looking at Table 5-1, we find that for *z* = 2.58, CL = 99%

**(b)** 1 9. 6*s*

*x*±*N*

CL = 95%

**(c)** 3 2. 9*s*

*x*±*N*

CL = 99.9%

**(d)** *s*

*x*±*N*

CL = 68%

**5-3.** Discuss how the size of the confidence interval for the mean is influenced by the following (all the other factors are constant):

**Solutions:**

**(a)** the standard deviation σ.

Since *z*σ CI = ± *x*, *N* as the standard deviation, σ, increases the confidence interval increases.

\*Answers and solutions are provided in the Student Solutions Manual for questions and problems marked with an asterisk.

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**(b)** the sample size *N*.

as the sample size, *N*, increases the confidence interval decreases.

**(c)** the confidence level.

As the desired confidence level increases, *z* increases and thus the confidence interval increases.

**5-4.** Consider the following sets of replicate measurements:

**\*A B \*C D \*E F**

0.514 2.7 70.24 3.5 0.812 70.65

0.503 3.0 70.22 3.1 0.792 70.63

0.486 2.6 70.10 3.1 0.794 70.64

0.497 2.8 3.3 0.900 70.21

0.472 3.2 2.5

Calculate the mean and the standard deviation for each of these six data sets. Calculate the 95% confidence interval for each set of data. What does this interval mean?

**Solutions:**

For Set A

***xi x* 2*i***

0.514 0.2642

0.503 0.2530

0.486 0.2362

0.497 0.2470

0.472 0.2228

Σ*xi* = 2.472 Σ*x* 2*i* = 1.223

mean: *x*= 2.472/5 = 0.494

standard deviation: = 1.223 − ( ) 2.472 2/ 5

*s* = 0.016

5 1−

Since, for a small set of measurements we cannot be certain *s* is a good approximation of σ, we should use the *t* statistic for confidence intervals. From Table 5-3, at 95% confidence *t* for 4 degrees of freedom is 2.78, therefore for set A,

CI for μ = 0.494 ± ( )( ) 2.78 0.016

5 = 0.494 ± 0.020

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Similarly, for the other data sets, we obtain the results shown in the following table:

**A B C D E F**

*x*0.494 2.86 70.19 3.1 0.824 70.53 *s* 0.016 0.24 0.08 0.37 0.051 0.22 95% CI 0.494 ± 0.020 2.86 ± 0.30 70.19 ± 0.20 3.1 ± 0.46 0.824 ± 0.081 70.53 ± 0.34

The 95% confidence interval is the range within which the population mean is expected to lie with a 95% probability.

**5-5.** Calculate the 95% confidence interval for each set of data in Problem 5-4 if *s* is a good estimate of σ and has a value of \*set A, 0.015; set B, 0.30; \*set C, 0.070; set D, 0.20; \*set E, 0.0090; and set F, 0.15.

**Solutions:**

If *s* is a good estimate of σ then we can use *z* = 1.96 for the 95% confidence level. For set A, at the 95% confidence,

( ) 1.96 (0.015) CI for μ = 0.494 ± = 0.494 ± 0.013. Similarly for sets B–F, the limits are:  5

**A B C D E F**

**CI** 0.494 ± 0.013 2.86 ± 0.26 70.19 ± 0.079 3.1 ± 0.18 0.824 ± 0.009 70.53 ± 0.015

**5-6.** The last result in each set of data in Problem 5-4 may be an outlier. Apply the *Q* test (95% confidence level) to determine whether or not there is a statistical basis to reject the result.

**Solutions:**

0.472 − 0.486

For set A: *Q* = = 0.33 and *Q* 0.472 − 0.514 crit = 0.710 for 5 observations at the 95% confidence level.

Since *Q* < *Q*crit the outlier value 0.472 cannot be rejected with 95% confidence.

A B C D E F

*Q* 0.33 0.33 0.86 0.60 0.81 0.95 *Q*crit 0.710 0.710 0.970 0.710 0.829 0.829 Decision Keep Keep Keep Keep Keep Reject

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**\*** An atomic absorption method for the determination of the amount of iron present in

**5-7.**

used jet engine oil was found from pooling 30 triplicate analyses to have a standard deviation *s* = . 2 9 μg Fe/mL. If *s* is a good estimate of σ , calculate the 95% and 99% confidence intervals for the result 17. μ 2 g Fe/mL if it was based on (a) a single analysis, (b) the mean of two analyses, and (c) the mean of four analyses.

**Solutions:**

**(a)** 99% CI = 17.2 ± 2.58 ⋅ 2.9 = 17.2 ± 7.5 μg Fe/mL

95% CI = 17.2 ± 1.96 ⋅ 2.9 = 17.2 ± 5.7 μg Fe/mL

**(b)**

2.58 ⋅ 2.9 99% CI = 17.2 ± = 17.2 ± 5.3 μg Fe/mL 2

1.96⋅ 2.9 95% CI = 17.2 ± = 17.2 ± 4.0 μg Fe/mL 2

2.58 2.9 ⋅

**(c)** 99% CI = 17.2 ± = 17.2 ± 3.7 μg Fe/mL

4

1.96⋅2.9 95% CI = 17.2 ± = 17.2 ± 2.8 μg Fe/mL

4

**5-8.** An atomic absorption method for determination of copper in fuel samples yielded a pooled standard deviation of *s*pooled = . 0 19 μg Cu/mL ( *s* → σ ). The analysis of an oil from a reciprocating aircraft engine showed a copper content of 6 8. μ 7 g Cu/mL. Calculate the 95% and 99% confidence intervals for the result if it was based on (a) a single analysis, (b) the mean of 4 analyses, and (c) the mean of 16 analyses.

**Solutions:**

**(a)** 95% CI = 6.87 ± 1.96 ⋅ 0.19 = 6.87 ± 0.37 μg Cu/mL

99% CI = 6.87 ± 2.58 ⋅ 0.19 = 6.87 ± 0.49 μg Cu/mL

**(b)** 1.96 ⋅ 0.19 95% CI = 6.87 ± = 6.87 ± 0.19 μg Cu/mL

4

2.58 ⋅ 0.19 99% CI = 6.87 ± = 6.87 ± 0.25 μg Cu/mL

4

**(c)** 1.96 ⋅ 0.19 95% CI = 6.87 ± = 6.87 ± 0.09 μg Cu/mL

16

2.58 ⋅ 0.19 99% CI = 6.87 ± = 6.87 ± 0.12 μg Cu/mL

16

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**\*5-9.** How many replicate measurements are needed to decrease the 95% and 99% confidence limits for the analysis described in Problem 5-7 to ± . 1 9 μg Fe/mL?

**Solutions:**

1.96⋅ 2.9 1.9 = For a 95% CI, *N =* 8.9 ≅ 9

*N*

2.58 ⋅ 2.9 1.9 = For a 99% CI, *N =* 15.6 ≅ 16

*N*

**5-10.** How many replicate measurements are necessary to decrease the 95% and 99% confidence limits for the analysis described in Problem 5-8 to ± . 0 15 μg Cu/mL?

**Solutions:**

1.96 ⋅ 0.19 0.15 = For the 95% CI, *N =* 7

*N*

2.58 ⋅ 0.19 0.15 = For a 99% CI, *N =* 10.7 ≅ 11

*N*

**\*5-11.** A volumetric calcium analysis on triplicate samples of the blood serum of a patient believed to be suffering from a hyperparathyroid condition produced the following data: mmol Ca/L = . 3 15, 3.25, 3.26. What is the 95% confidence interval for the mean of the data, assuming

**Solutions:**

**(a)** no prior information about the precision of the analysis?

For the data set, *x*= 3.22 and *s* = 0.06

4.30⋅ 0.06 95% CI = 3.22 ± = 3.22 ± 0.15 meq Ca/L

3

**(b)** *s* → = σ 0.056 mmol Ca/L?

1.96⋅ 0.056 95% CI = 3.22 ± = 3.22 ± 0.06 meq Ca/L

3

**5-12.** A chemist obtained the following data for percent lindane in the triplicate analysis of an insecticide preparation: 7.23, 6.95, and 7.53. Calculate the 90% confidence interval for the mean of the three data, assuming that

**Solutions:**

**(a)** the only information about the precision of the method is the precision for the three analyses.

For the data set, *x*= 7.24 and *s* = 0.29

2.92 ⋅ 0.29 90% CI = 7.24 ± = 7.24 ± 0.49%

3lindane

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**(b)** on the basis of long experience with the method, it is believed that *s* → = σ 0.28% lindane.

1.64 ⋅ 0.28 90% CI = 7.24 ± = 7.24 ± 0.27 % lindane

3

**5-13.** A standard method for the determination of glucose in serum is reported to have a standard deviation of 0.36 mg/dL. If *s* = . 0 36 is a good estimate of σ , how many replicate determinations should be made in order for the mean for the analysis of a sample to be within

**Solutions:**

\***(a)** 0.3 mg/dL of the true mean 99% of the time?

2.58 ⋅ 0.36 0.3 = For the 99% CI, *N =* 9.6 ≅ 10

*N*

**(b)** 0.3 mg/dL of the true mean 95% of the time?

1.96 ⋅ 0.36 0.3 = *N*For the 95% CI, *N =* 5.6 ≅ 6

**(c)** 0.3 mg/dL of the true mean 90% of the time?

1.64 ⋅ 0.36 0.3 = *N*For the 90% CI, *N =* 3.9 or 4

**5-14.** 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 →σ = 4 ppt for carbon and 6 ppt for hydrogen. The means of the 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?

**Solution:**

This is a two-tailed test and from Table 5-1, *z*crit = 1.96 for the 95% confidence level. For carbon,

68.5 − 68.8

*z* = = −1.54 ≥ −1.96

0.004 ⋅68.8% / 2

Systematic error is NOT indicated at 95% confidence level.

For hydrogen, ≤ − 4.882 − 4.953

*z* = = −3.38 1.96

0.006 ⋅ 4.953% / 2

Systematic error IS indicated at 95% confidence level.

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**\*5-15.** A prosecuting attorney in a criminal case presented as principal evidence small fragments of glass found imbedded in the coat of the accused. The attorney claimed that the fragments were identical in composition to a rare Belgian stained glass window broken during the crime. The average of triplicate analyses for five elements in the glass are in the table. On the basis of these data, does the defendant have grounds for claiming reasonable doubt as to guilt? Use the 99% confidence level as a criterion for doubt.

**Concentration, ppm Standard Deviation**

**Element From Clothes From Window *s*** → σ

As 129 119 9.5

Co 0.53 0.60 0.025

La 3.92 3.52 0.20

Sb 2.75 2.71 0.25

Th 0.61 0.73 0.043

**Solution:**

This is a two-tailed test where *s* → σ and from Table 5-1, *z*crit = 2.58 for the 99% confidence level.

129 − 119 For As: *z* = = 1.28 ≤ 2.58

3 3 + 9.53 3⋅

No significant difference exists at the 99% confidence level.

Proceeding in a similar fashion for the other elements

**Element *z* Significant Difference?**

As 1.28 No

Co −3.43 Yes

La 2.45 No

Sb 0.20 No

Th −3.42 Yes

For two of the elements there is a significant difference, but for three there are not. Thus, the defendant might have grounds for claiming reasonable doubt. It would be prudent, however, to analyze other windows and show that these elements are good diagnostics for the rare window.

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**5-16.** 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.

**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

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.

**Solution:**

The null hypothesis is that μ = 5.0 ppm dissolved O2 and the alternative hypothesis is that μ < 5.0 ppm dissolved O2. This is a one-tailed test and from Table 5-1, *t*crit = 1.90 for the 95% confidence level and 7 degrees of freedom.

For the data set, *x*= 4.888 and *s* = 0.40

4.888 − 5.0 *t* = = −0.79 ≥ −1.900.40 / 8

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

**\*5-17.** The week 3 measurement in the data set of Problem 5-16 is suspected of being an outlier. Use the *Q* test to determine if the value can be rejected at the 95% confidence level.

**Solution:**

= 5.6 − 5.1

*Q* = 0.385

5.6 − 4.3 and *Q*crit for 8 observations at 95% confidence = 0.526.

Since *Q* < *Q*crit the outlier value 5.6 cannot be rejected at the 95% confidence level.

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**5-18.** Before agreeing to the purchase of a large order of solvent, a company wants to see conclusive evidence that the mean value of a particular impurity is less than 1.0 ppb. What hypotheses should be tested? What are the type I and type II errors in this situation?

**Solution:**

*H*0: μ = 1.0 ppb for the impurity: *H*a: μ < 1.0 ppb for the impurity. This is a one tailed test. The type I error for this situation would be that we reject the null hypothesis when, in fact, it is true, i.e. we decide the impurity is < 1.0 ppb at

some level of confidence when, in fact, it is not < 1.0 ppb. The type II error would be that we accept the null hypothesis when, in fact, it is false, i.e. we decide the impurity is not < 1.0 ppb at some level of confidence when, in fact, it is < 1.0 ppb.

**\*5-19.** The level of a pollutant in a river adjacent to a chemical plant is regularly monitored. Over a period of years, the normal level of the pollutant has been established by chemical analyses. Recently, the company has made several changes to the plant that appear to have increased the level of the pollutant. The Environmental Protection Agency (EPA) wants conclusive proof that the pollutant level has not increased. State the relevant null and alternative hypotheses, and describe the type I and type II errors that might occur in this situation.

**Solution:**

The null hypothesis is that for the pollutant the current level = the previous level (*H*0: μcurrent = μprevious). The alternative hypothesis is *H*a: μcurrent > μprevious. This would be a one-tailed test. The type I error for this situation would be that we reject the

null hypothesis when, in fact, it is true, i.e. we decide the level of the pollutant is > the previous level at some level of confidence when, in fact, it is not. The type II error would be that we accept the null hypothesis when, in fact, it is false, i.e. we decide the level of the pollutant = the previous level when, in fact, it is > than the previous level.

**5-20.** State quantitatively the null hypothesis *H*0 and the alternative hypothesis *H*a for the following situations, and describe the type I and type II errors. If these hypotheses were to be tested statistically, comment on whether a one- or two-tailed test would be involved for each case.

**Solutions:**

\***(a)** The mean values for Ca determinations by an ion-selective electrode method and by an EDTA titration differ substantially.

*H*0: μISE = μEDTA, *H*a: μISE ≠ μEDTA. This would be a two-tailed test. The type I error for this situation would be that we decide the methods do not agree when they do The type II error would be that we decide the methods agree when they do not.

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**(b)** Since this sample gave a concentration lower than the 6.39 ppm level certified by NIST, a systematic error must have occurred.

: μ = 6.39 ppm; *H*a: μ = < 6.39 ppm.

*H*0 This is a one-tailed test. The type I error for this situation would be that we reject *H*0 decide that a systematic error exists when it does not. The type II error would be that we accept *H*0 decide a systematic error does not exist when it does.

\***(c)** Results show that the batch-to-batch variation in the impurity content of Brand X acetonitrile is lower than Brand Y acetonitrile.

*H*0:σ σ 2 2

X Y = ; *H*a: σ2X < . This is a one-tailed test. The type I error would be that we

σ2Y

decide that σ2X < when it is not. The type II error would be that we decide that

σ2Y

σ2X = σ when actually 2Y σ σ 2 2

X Y < .

**(d)** The atomic absorption results obtained for Cd are less precise than the electrochemical results.

*H*0: σ2AA = σ2EC; *H*a: σ2AA < σ2EC. This is a one-tailed test. The type I error for this situation would be that we decide AA results are less precise than electrochemistry results, when the precision is the same. The type II error would be that we decide the precision is the same when they electrochemical results are more precise.

**\*5-21.** The homogeneity of the chloride level in a water sample from a lake was tested by analyzing portions drawn from the top and from near the bottom of the lake, with the following results in ppm Cl:

**Top Bottom**

26.30 26.22

26.43 26.32

26.28 26.20

26.19 26.11

26.49 26.42

**Solutions:**

**(a)** Apply the *t* test at the 95% confidence level to determine if the chloride level from the top of the lake is different from that at the bottom.

For the Top data set, *x*= 26.338

For the bottom data set, *x*= 26.254

*s*pooled = 0.1199

degrees of freedom = 5 + 5 − 2 = 8

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For 8 degrees of freedom at 95% confidence *t*crit = 2.31

= 26.338 − 26.254 *t* = 1.11

5 5 + 0.11995 5⋅

Since *t* < *t*crit, we conclude that no significant difference exists at 95% confidence level.

**(b)** If each row in the table were samples analyzed in top-bottom pairs, use the paired *t* test and determine whether there is a significant difference between the top and bottom values at the 95% confidence level.

From the data, *N* = 5, *d* = 0.084 and *s*d = 0.015166

For 4 degrees of freedom at 95% confidence *t* = 2.78

0.084 − 0 *t* = = 12.52

0.015 / 5

Since 12.52 > 2.78, a significant difference does exist at 95% confidence level.

**(c)** Why is a different conclusion drawn from using the paired *t* test than from just pooling the data and using the normal *t* test for differences in means?

The large sample to sample variability causes

*s*Top and *s*Bottom to be large and masks

the

differences between the samples taken from the top and the bottom.

**5-22.** Two different analytical methods were used to determine residual chlorine in sewage effluents. Both methods were used on the same samples, but each sample came from various locations with differing amounts of contact time with the effluent. Two methods were used to determine the concentration of Cl in mg/L, and the results are shown in the following table:

**Sample Method A Method B**

1 0.39 0.36

2 0.84 1.35

3 1.76 2.56

4 3.35 3.92

5 4.69 5.35

6 7.70 8.33

7 10.52 10.70

8 10.92 10.91

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**Solutions:**

**(a)** What type of *t* test should be used to compare the two methods and why?

A paired *t* test should definitely be used in this case due to the large variation in the Cl concentrations resulting from the various contact times and various locations from which the samples were obtained.

**(b)** Do the two methods give different results? State and test the appropriate hypotheses.

*H*0: μd = 0; *H*a: μA ≠ 0, where μd is the mean difference between the methods From the data *N* = 8, *d* = −0.414 and *s*d = 0.32

For 7 degrees of freedom at 90% confidence level, *t*crit = 1.90

0.414 − 0 *t* = = 3.65

0.32 / 8

Since *t* > *t*crit, a significant difference is indicated at the 90% confidence level

**(c)** Does the conclusion depend on whether the 90%, 95%, or 99% confidence levels are used?

For 7 degrees of freedom at 95% confidence level, *t*crit = 2.36

Therefore, a significant difference in the 2 methods exists at the 95% confidence level.

For 7 degrees of freedom at the 99% confidence level, *t*crit = 3.50

Thus, a significant difference is indicated even at the 99% confidence level. The conclusion does not depend on which of the three confidence levels is used.

**\*5-23.** Sir William Ramsey (Lord Rayleigh) prepared nitrogen samples by several different methods. The density of each sample was measured as the mass of gas required to fill a particular flask at a certain temperature and pressure. Masses of nitrogen samples prepared by decomposition of various nitrogen compounds were 2.29280, 2.29940, 2.29849, and 2.30054 g. Masses of “nitrogen” prepared by removing oxygen from air in various ways were 2.31001, 2.31163, and 2.31028 g. Is the density of nitrogen prepared from nitrogen compounds significantly different from that prepared from air? What are the chances of the conclusion being in error? (Study of this difference led to the discovery of the inert gases by Lord Rayleigh).

**Solution:**

For the first data set: *x*= 2.2978

For the second data set: *x*= 2.3106

*s*pooled = 0.0027

Degrees of freedom = 4 + 3 − 2 = 5

2.2978 − 2.3106 *t* = = −6.207

4 3 + 0.00274 3⋅

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For 5 degrees of freedom at the 99% confidence level, *t* = 4.03 and at the 99.9% confidence level, *t* = 6.87. Thus, we can be between 99% and 99.9% confident that the nitrogen prepared in the two ways is different. The Excel TDIST(x,df,tails) function can be used to calculate the probability of getting a *t* value of −6.207. In this case we find TDIST(6.207,5,2) = 0.0016. Therefore, we can be 99.84% confident that the nitrogen prepared in the two ways is different. There is a 0.16% probability of this conclusion being in error.

**5-24.** The phosphorous content in ppm was measured for three different soil locations. Five replicate determinations were made on each soil sample. A partial ANOVA table follows:

**Variation Source SS df MS F**

Between soils \_\_\_\_\_\_ \_\_\_\_\_\_ \_\_\_\_\_\_ \_\_\_\_\_\_

Within soils \_\_\_\_\_\_ \_\_\_\_\_\_ 0.0081

Total 0.374 \_\_\_\_\_\_

**Solutions:**

**(a)** Fill in the missing entries in the ANOVA table.

**Source SS df MS F** Between soils 0.374 − 0.0972 = 0.2768 3 − 1 = 2 0.2768/2 = 0.1384 0.1384/0.0081 = 17.09 Within soils 12 ⋅ 0.0081 = 0.0972 15 − 3 = 12 0.0081

Total 0.374 15 − 1 = 14

**(b)** State the null and alternative hypotheses.

*H*0: μsamp1 = μsamp2 = μsamp3; *H*a: at least two of the means differ.

**(c)** Do the three soils differ in phosphorous content at the 95% confidence level?

From Table 5-4 the *F* value for 12 degrees of freedom in the denominator and 2 degrees of freedom in the numerator at the 95% confidence level is 3.89. Since the *F* value calculated in the table exceeds *F* critical, we reject *H*0 and conclude that the phosphorous contents of the soil samples taken from the 3 locations are different.

**\*5-25.** The ascorbic acid concentration in mmol/L of five different brands of orange juice was measured. Six replicate samples of each brand were analyzed. The following partial ANOVA table was obtained.

**Variation Source SS df MS F**

Between juices \_\_\_\_\_\_ \_\_\_\_\_\_ \_\_\_\_\_\_ 8.45

Within juices \_\_\_\_\_\_ \_\_\_\_\_\_ 0.913

Total \_\_\_\_\_\_ \_\_\_\_\_\_

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**Solutions:**

**(a)** Fill in the missing entries in the table.

**Source SS df MS F** Between juices 4 ⋅ 7.715 = 30.86 5 − 1 = 4 0.913 ⋅ 8.45 = 7.715 8.45 Within juices 25 ⋅ 0.913 = 22.825 30 − 5 = 25 0.913

Total 30.86 + 22.82 = 53.68 30 − 1 = 29

**(b)** State the null and alternative hypotheses.

*H*0: μbrand1 = μbrand2 = μbrand3 = μbrand4 = μbrand5; *H*a: at least two of the means differ.

**(c)** Is there a difference in the ascorbic acid content of the five juices at the 95% confidence level?

The Excel FINV(prob,df1,df2) function can be used to calculate the *F* value for the above problem. In this case we find FINV(0.05,4,25) = 2.76. Since *F* calculated exceeds *F* critical, we reject the null hypothesis and conclude that the average ascorbic acid contents of the 5 brands of orange juice differ at the 95% confidence level.

**5-26.** Five different laboratories participated in an interlaboratory study involving determinations of the iron level in water samples. The following results are replicate determinations of Fe in ppm for laboratories A through E.

**Result No. Lab A Lab B Lab C Lab D Lab E**

1 10.3 9.5 10.1 8.6 10.6

2 11.4 9.9 10.0 9.3 10.5

3 9.8 9.6 10.4 9.2 11.1

**Solutions:**

**(a)** State the appropriate hypotheses.

*H*0: μLabA = μLabB = μLabC = μLabD = μLabE; *H*a: at least two of the means differ.

**(b)** Do the laboratories differ at the 95% confidence level? At the 99% confidence level (*F*crit = . 5 99 ?) At the 99.9% confidence level (*F*crit = . 11 28 ?)

See spreadsheet next page. From Table 5-4 the *F* value for 4 degrees of freedom in the numerator and 10 degrees of freedom in the denominator at 95% is 3.48. Since *F* calculated exceeds *F* tabulated we reject *H*0 and conclude that the laboratories differ at 95% confidence. We can also be 99% confident that the laboratories differ, but we cannot be 99.9% confident that the laboratories differ.

**(c)** Which laboratories are different from each other at the 95% confidence level?

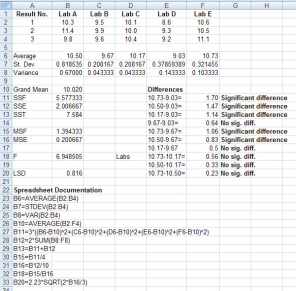
Based on the calculated LSD value laboratories A, C and E differ from laboratory D, but laboratory B does not. Laboratories E and A differ from laboratory B, but laboratory C does not. No significant difference exists between laboratories E and A.

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**Spreadsheet for Problem 5-26.**

****

**\*5-27.** Four analysts perform replicate sets of Hg determinations on the same analytical sample. The results in ppb Hg are shown in the following table:

**Determination Analyst 1 Analyst 2 Analyst 3 Analyst 4**

1 10.19 10.19 10.14 10.24

2 10.15 10.11 10.12 10.26

3 10.16 10.15 10.04 10.29

4 10.10 10.12 10.07 10.23

**Solutions:**

**(a)** State the appropriate hypotheses.

*H*0: μAnalyst1 = μAnalyst2 = μAnalyst3 = μAnalyst4; *H*a: at least two of the means differ.

**(b)** Do the analysts differ at the 95% confidence level? At the 99% confidence level (*F*crit = . 5 95 ?) At the 99.9% confidence level ( ) *F*crit = . 10 80 ?

See spreadsheet next page. From Table 5-4 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 exceeds *F* critical, we reject the null hypothesis and conclude that the analysts differ at 95% confidence. The *F* value calculated of 13.60 also exceeds the

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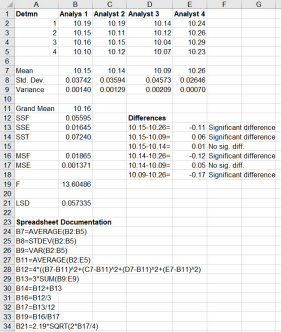
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critical values at the 99% and 99.9% confidence levels so that we can be certain that the analysts differ at these confidence levels.

**(c)** Which analysts differ from each other at the 95% confidence level?

Based on the calculated LSD value of 0.0573, there are significant differences between analysts 1 and 4, analysts 1 and 3, analysts 2 and 4, and analysts 3 and 4. There is no significant difference between analysts 1 and 2 and 2 and 3.

**Spreadsheet for Problem 5-27.**

****

**5-28.** 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

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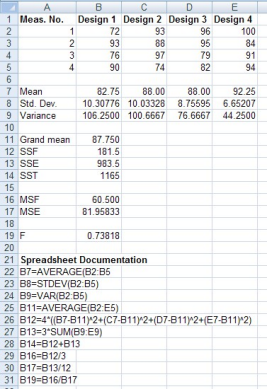
**Solutions:**

**(a)** State the appropriate hypotheses.

*H*0: μDes1 = μDes2 = μDes3 = μDes4; *H*a: at least two of the means differ.

**(b)** Do the flow cell designs differ at the 95% confidence level?

See spreadsheet.



From Table 5-4 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)** If a difference was detected in part (b), which designs differ from each other at the 95% confidence level?

No differences were detected.

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**\*5-29.** 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 next 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 39.1 45.9

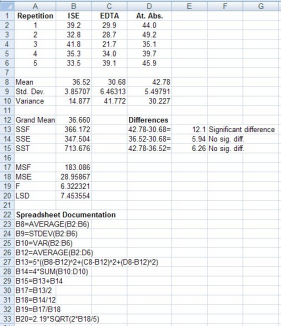
**Solutions:**

**(a)** State the null and alternative hypotheses.

*H*0: μISE = μEDTA = μAA; *H*a: at least two of the means differ.

**(b)** Determine whether there are differences in the three methods at the 95% confidence levels.

See spreadsheet.



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From Table 5-4 the *F* value for 2 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 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)** If a difference was found at the 95% confidence level, determine which methods differ from each other.

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.

**5-30.** 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.

**Solutions:**

**(a)** 51.27, 51.61, 51.84, 51.70

51.27 − 51.61

*Q* = = 0.596 and *Q* 51.84 − 51.27 crit for 4 observations at 95% confidence = 0.829. Since *Q* < *Q*crit the outlier value 51.27 cannot be rejected with 95% confidence.

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

7.388 − 7.295

*Q* = = 0.894 and *Q* 7.388 − 7.284 crit for 4 observations at 95% confidence = 0.829. Since *Q* > *Q*crit the outlier value 7.388 can be rejected with 95% confidence.

**\*5-31** 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.

**Solutions:**

**(a)** 95.10, 94.62, 94.70

95.10 − 94.70

= −

*Q* = 0.833

95.10 94.62and *Q*crit for 3 observations at 95% confidence = 0.970. Since *Q* < *Q*crit the outlier value 95.10 cannot be rejected with 95% confidence.

**(b)** 95.10, 94.62, 94.65, 94.70

95.10 − 94.70

= −

*Q* = 0.833

95.10 94.62 and *Q*crit for 4 observations at 95% confidence = 0.829. Since *Q* > *Q*crit the outlier value 95.10 can be rejected with 95% confidence.

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**5-32.** Determination of phosphorous in blood serum gave results of 4.40, 4.42, 4.60, 4.48, and 4.50 ppm P. Determine whether the 4.60 ppm result is an outlier or should be retained at the 95% confidence level.

4.60 − 4.50

*Q* = = 0.5 and *Q* 4.60 − 4.40 crit for 5 observations at 95% confidence = 0.710. Since *Q* < *Q*crit the value 4.60 ppm cannot be rejected with 95% confidence.

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