Solution and Answer Guide

Solution and Answer Guide: Skoog et al., *Fundamentals of Analytical Chemistry*, 10e, © 2022, 978-0-357-45039-0, Chapter 4: Random Errors in Chemical Analysis

Chapter 4

**4-1.** Define

**Answers:**

**\*(a)** sample standard deviation.

The *sample standard deviation* is the standard deviation of a sample of data. It applies to a small set of data from the population. It uses deviations from the experimental mean and the number of degrees or freedom *N* − 1 in place of the population mean μ and *N*.

**(b)** coefficient of variation.

The *coefficient of variation* is the percent relative standard deviation or ( *s ~~x~~*/ ) ⋅ 100%.

**\*(c)** variance.

The *variance* is the square of the standard deviation.

**(d)** standard error of the mean.

The *standard error of the mean* is the standard deviation of the mean and is given by the standard deviation of the data set divided by the square root of the number of measurements.

**4-2.** Differentiate between

**Answers:**

**\*(a)** parameter and statistic.

The term *parameter* refers to quantities such as the mean and standard deviation of a population or distribution of data. The term *statistic* refers to an estimate of a parameter that is made from a sample of data.

**(b)** population mean and sample mean.

The *population mean* is the true mean for the population of data. The *sample mean* is the arithmetic average of a limited sample drawn from the population.

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

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**\*(c)** random and systematic error.

*Random errors* result from uncontrolled variables in an experiment while *systematic errors* are those that can be ascribed to a particular cause and can usually be determined.

**(d)** accuracy and precision.

*Accuracy* represents the agreement between an experimentally measured value and the true or accepted value. *Precision* describes the agreement among measurements that have been performed in exactly the same way.

**4-3.** Distinguish between

**Answers:**

**\*(a)** the sample variance and the population variance.

The *sample variance s*2 is the variance of a sample drawn from the population. It is ∑ ) *N*( *x ~~x~~* − 2

*i*

given by

*s*2 = *i*=1 , *N* −1 where *x* is the sample mean.

The *population variance* σ2 is the variance of an entire population given by

∑ ) *N*( *x* − μ 2

*i*

σ2 = *i*=1 , *N* where μ is the population mean.

**(b)** the meaning of the word *sample* as it is used in a chemical and in a statistical sense.

In the chemical sense, a sample is what is taken for chemical analysis. In statistics a sample is a subset taken from the population used to infer information about the population.

**4-4.** What is the standard error of a mean? Why is the standard deviation of the mean lower than the standard deviation of the data points in a set?

**Solution:**

The standard error of a mean, *sm,* is the standard deviation of the set of data, *s,* divided by the square root of the number of data in the set, i.e. *s s m* = / *N*. The standard error of the mean *sm* is lower than the standard deviation of the data points in a set *s* because a set of data made up of means will have less spread than a set of data made up of data points. In the equations for *sm*, the denominator ( ) *N* always has a value greater than 1 so that *sm* will always be less than *s*.

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**\*4-5.** From the Gaussian (normal) error curve, what is the probability that a result from a population lies between 0 and +1σ of the mean? What is the probability of a result occurring that is between +1σ and +2σ of the mean?

**Answer:**

Since the probability that a result lies between −1σ and +1σ is 0.683, the probability that a result will lie between 0 and +1σ will be half this value or 0.342. The probability that a result will lie between +1σ and +2σ will be half the difference between the probability of the result being between −2σ and +2σ, and −1σ and +1σ, or ½ (0.954−0.683) = 0.136.

**4-6.** From the normal curve of error, find the probability that a result is outside the limits of ±2σ from the mean. What is the probability that a result has a more negative deviation from the mean than −2σ?

**Answer:**

Since the probability that a result lies between −2σ and +2σ is 0.954, the probability that a result will lie outside this range is (1 − 0.954) = 0.046. The probability that a result will be more negative than −2σ will be half this value, or 0.023.

**4-7.** Consider the following sets of replicate measurements:

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

9.5 55.35 0.612 5.7 20.63 0.972

8.5 55.32 0.592 4.2 20.65 0.943

9.1 55.20 0.694 5.6 20.64 0.986

9.3 0.700 4.8 20.51 0.937

9.1 5.0 0.954

For each set, calculate the (a) mean, (b) median, (c) spread or range, (d) standard deviation, and (e) coefficient of variation.

**Solutions:**

*xi x*2*i*

9.5 90.25

8.5 72.25

9.1 82.81

9.3 86.49

9.1 82.81

Σ*xi* = 45.5 Σ*x* 2*i* = 414.61

mean: *x*= 45.5/5 = 9.1

median = 9.1

spread: *w* = 9.5 − 8.5 = 1.0

standard deviation: = 414.61− ( ) 45.5 2/ 5

*s* = 0.37

5 1−

coefficient of variation: CV = (0.37/9.1) ⋅ 100% = 4.1%

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Results for Sets A through F, obtained in a similar way, are given in the following table.

A B C D E F **(a)** *x*9.1 55.29 0.650 5.1 20.61 0.958 **(b)** median 9.1 55.32 0.653 5.0 20.64 0.954 **(c)** *w* 1.0 0.15 0.108 1.5 0.14 0.049 **(d)** *s* 0.37 0.08 0.056 0.6 0.07 0.02 **(e)** CV, % 4.1 0.14 8.5 12.2 0.32 2.1

**4-8.** The accepted values for the sets of data in Problem 4-7 are **\***set A, 9.0; set B, 55.33; **\***set C, 0.630; set D, 5.4; **\***set E, 20.58; and set F, 0.965. For the mean of each set, calculate (a) the absolute error and (b) the relative error in parts per thousand.

**Solutions:**

For Set A, *E* = 9.1 − 9.0 = 0.1

*Er* = (0.1/9.0) ⋅ 1000 ppt = 11.1 ppt

Set B, *E* = −0.040 *Er* = −0.7 ppt

Set C, *E* = 0.0195 *Er* = 31 ppt

Set D, *E* = −0.34 *Er* = −63 ppt

Set E, *E* = 0.03 *Er* = 1.3 ppt

Set F, *E* = −0.007 *Er* = −6.8 ppt

**4-9.** Estimate the absolute deviation and the coefficient of variation for the results of the following calculations. Round each result so that it contains only significant digits. The numbers in parentheses are absolute standard deviations.

**Solutions:**

**\*(a)** *y* = 3 9. 5( ) ± . 0 03 + 0 9. 93(± . 0 001)

2 2 7. ± 025( ) 0.001 = 2.082

*s* = + ( ) 0.03 2 2

*y* (0.001) + (0.001)2= 0.030

CV = (0.03/−2.082) ⋅ 100% = −1.4%

*y* = −2.08(±0.03)

**(b)** *y* = 15.57( ) ± . 0 04 + 0.0037(± . 0 0001)

13. ± 59( ) 0.08 = 19.1637

*sy* = + ( ) 0.04 2 2 (0.0001) + (0.08)2= 0.089

CV = (0.089/19.1637) ⋅ 100% = 0.46%

*y* = 19.16(±0.09)

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**\*(c)** *y* = . 29 2( ) ±0.3 ⋅ 2.03(±0.02) ⋅10217

= . 5 93928⋅10216

*s* ⎛ ⎞ 0.3 2⎛ ⎞2

0.02 ⋅10−17 *y* = + ⎜ ⎟ ⎜ ⎟ ~~−~~ =

⎝ ⎠ ⎝ ⎠ ⋅ 1~~7~~ 0.01422

*y* 29.2 2.034 10

CV = (0.0142) ⋅ 100% = 1.42%

*sy* = (0.0142) ⋅ (5.93928 ⋅ 10−16) = 0.08446 ⋅ 10−16

*y* = 5.94(±0.08) ⋅ 10−16

**(d)**74 ( ) ±

= ± 6( ) 0 2

*y* 32 1 ⋅1. ± 964( ) 0.006

= . 122*,*830 9572

*sy* ⎛ ⎞ 1 2 2 2 ⎛ ⎞⎛ 0.006 ⎞2

= + ⎜ ⎟⎜ ⎟ + ⎜ ⎟ = 0.00510

*y* ⎝ ⎠ 326 ⎝ ⎠ 740 ⎝ 1.964 ⎠

CV = (0.00510) ⋅ 100% = 0.510%

*sy* = (0.00510) ⋅ (122830.9572) = 626

*y* = 1.228(±0.006) ⋅ 105

187( ) ± − 6 89(±3) *y* = = () ( ) 7 5. 559 1022

**\*(e)** ⋅

1240 ± + 1 57 ±8

*s* 2 2

num = + ( ) 6 ( ) 3 = 6.71 *y*num = 187 − 89 = 98

*s* = + ( )2 2

den 1 (8) = 8.06 *y*den = 1240 + 57 = 1297

*sy* ⎛ ⎞ 6.71 2 2 ⎛ 8.06 ⎞

= + ⎜ ⎟⎜ ⎟ = 0.0688

*y* ⎝ ⎠ 98 ⎝1297 ⎠

CV = (0.0688) ⋅ 100% = 6.88%

*sy* = (0.0688) ⋅ (0.075559) = 0.00520

*y* = 7.6(±0.5) ⋅ 10−2

**(f)**3 5. ± 6( ) 0.01

*y* = = ( ) 6.81992 ⋅1023

522 ±3

*sy* ⎛ ⎞ 0.01 2 2 ⎛ 3 ⎞

= + ⎜ ⎟⎜ ⎟ = 0.006397

*y* ⎝ ⎠ 3.56 ⎝ 522 ⎠

CV = (0.006397) ⋅ 100% = 0.6397%

*sy* = (0.006397) ⋅ (6.81992 ⋅ 10−3) = 4.36 ⋅ 10−5

*y* = 6.82(±0.04) ⋅ 10−3

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**4-10.** Estimate the absolute standard deviation and the coefficient of variation for the results of the following calculations. Round each result to include only significant figures. The numbers in parentheses are absolute standard deviations.

**Solutions:**

**\*(a)** 29 *y* = . 1 02( ) ±0 0. 2 ⋅1028 − 3 5. 4(±0 2. ) ⋅10

2 2

*s* = ⋅ ( ) − − 8 9

*y* 0.02 10 + (0.2⋅10 ) = 2.83⋅10−10

*y* = 1.02⋅10−8 − 3.54⋅10−9 = 6.66⋅10−9

2.83⋅10−10

CV = −~~9~~ ⋅ = 100% 4.25%

6.66 ⋅10

*y* = 6.7 ±0.3 ⋅ 10−9

**(b)** *y* = 90.31( ) ± . 0 08 − 89.32(± . 0 06)

+ . 0 200( ) ±0.004

*s* ( ) 08 2 2

*y* = + 0. (0.06) + (0.004)2= 0.10

*y* = 90.31 − 89.32 + 0.200 = 1.190

0.10 CV = ⋅ = 100% 8.41%

1.190

*y* = 1.2(±0.1)

**\*(c)** *y* = 0.0040( ) () ± . 0 0005 ⋅10.28 ± . 0 02

⋅ ± 347( ) 1

*sy* ⎛ ⎞ 0.0005 2 2 ⎛ 0.02 ⎞ ⎛ 1 ⎞

= + ⎜ ⎟⎜ ⎟ + ⎜ ⎟ = 0.1250

*y* ⎝ ⎠ 0.0040 ⎝10.28 ⎠ ⎝ 347 ⎠

CV = (0.1250) ⋅ 100% = 12.5%

*y* = 0.0040 ⋅ 10.28 ⋅ 347 = 14.27

*sy* = (0.125) ⋅ (14.27) = 1.78

*y* = 14(±2)

**(d)**223( ) ± . 0 03 ⋅10214

*y* =1. ± 47( ) 0.04 ⋅10216

*s* ⎛ ⎞2 2

*y* 0.03 ⋅ ⋅ 10− − 14 ⎛ 0.04 10 16 ⎞

= + ⎜ ⎟ − ~~− 14~~ ⎜ 1~~6~~ ⎟ = 0.0272

*y* ⎝ ⎠ 223 ⋅ ⋅ 10 ⎝ 1.47 10 ⎠

CV = (0.027) ⋅ 100% = 2.7%

*y* = 223⋅10−14 / 1.47⋅10−16 = 1.517 ⋅ 104

*s*y = (0.0272) ⋅ (1.517 ⋅ 104) = 0.0413 ⋅ 104

*y* = 1.52(±0.04) ⋅ 104

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**\*(e)**100( ) ±1

*y* = 2 1 ( ) ±

*sy* ⎛ ⎞ 1 1 2 2 ⎛ ⎞

= + ⎜ ⎟ ⎜⎟ = 0.500

*y* ⎝ ⎠ 100 ⎝ 2 ⎠

CV = (0.500) ⋅ 100% = 50.0%

*y* = 100 / 2 = 50.0

*sy* = (0.500) ⋅ (50.0) = 25

*y* = 50(±25)

**(f)**1. ± 49( ) 0.02 ⋅102 2 2 3 − 4. ± 97( ) 0.06 ⋅10 *y* = 27. ± 1 0 () ( .7 + 8.99 ±0.08)

( )2 2

*s* = ⋅ − − 2 3

−4

num 0.02 10 + (0.06 ⋅ 10 ) = 2.09 ⋅ 10

num = 0.0149 − 0.00497 = 0.00993

*s* =+= ( )2 2

den 0.7 (0.08) 0.704

den = 27.1 + 8.99 = 36.09

*s* ⎛ ⎞ 0.000209 2 2

*y* ⎛ 0.704 ⎞ = + ⎜ ⎟⎜ ⎟ = 0.0287

*y* ⎝ ⎠ 0.00993 ⎝ 36.09 ⎠

CV = (0.0287) ⋅ 100% = 2.87%

*y* = 0.00993/36.09 = 2.751 ⋅ 10−4

*sy* = (0.0287) ⋅ (2.751 ⋅ 10−4) = 7.895 ⋅ 10−6 *y* = 2.75(±0.08) ⋅ 10−4

**4-11.** Calculate the absolute standard deviation and the coefficient of variation for the results of the following calculations. Round each result to include only significant figures. The numbers in parentheses are absolute standard deviations.

**Solutions:**

**\*(a)** ⎤⎦ *y* = . log ⎡2 00( ) ±0.03 ⋅1024

⎣

*y* = log(2.00 ⋅ 10−4) = −3.6989 ( ) 0.434 ( ) 0.03 ⋅10−4

*s* =( ) 6.51 10−3

*y*2.00 ⋅10−~~4~~ = ⋅

*y* = −3.699 ±0.006

CV = (0.006/3.699) ⋅ 100% = 0.16%

**(b)** ⎤⎦ *y* = . log ⎡4 42( ) ±0.01 ⋅1037 ⎣

As in part (a): *y* = 37.645 ±0.001

CV = 0.003%

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**\*(c)** . )⎤⎦ *y* = . antilog ⎡1 200(±0 003 ⎣

*y* = antilog(1.200) = 15.849 *sy* = = ( ) 2.303 (0.003) 0.0069

*y*

*sy* = (0.0069)(15.849) = 0.11

CV = (0.11/15.8) ⋅ 100% = 0.69%

**(d)** ⎤⎦ *y* = . antilog ⎡49 54( ) ±0.04 ⎣ As in part (c): *y* = 3.5(±0.3) ⋅ 1049 CV = 9.2%

*y* = 15.8 ±0.1

**4-12.** Calculate the absolute standard deviation and the coefficient of variation for the results of the following calculations. Round each result to include only significant figures. The numbers in parentheses are absolute standard deviations.

**Solutions:**

**\*(a)** ⎤⎦3

*y* = . ⎡4 17( ) ±0.03 ⋅1024

⎣

*sy* ⎛ ⎞ 0.03⋅10−4

*y* = (4.17 ⋅ 10−4)3 = 7.251 ⋅ 10−11 .0216

= = 3 0 ⎜ ⎟

*y* ⎝ ⎠ 4.17 ⋅10−4

= (0.0216)(7.251 ⋅ 10−11) = 1.565 ⋅ 10−12 *y* = 7.3(±0.2) ⋅ 10−11

*sy*

CV = (1.565 ⋅ 10−12/7.251 ⋅ 10−11) ⋅ 100% = 2.2%

**(b)** ⎤⎦ *y* 2 1 4

= . ⎡ 936( ) ±0.002 */*

⎣

As in part (a): *y* = 1.3090(±0.0002)

CV = 0.02%

**\*4-13.** The standard deviation in measuring the diameter *d* of a sphere is ±0.02 cm. What is the standard deviation in the calculated volume *V* of the sphere if *d* = 2.35 cm?

**Solution:**

From the equation for the volume of a sphere, we have

4 4 3 ⎛ ⎞ *d* 3 3 4 ⎛ 2.35 ⎞ *V r* = = π π 3⎜ ⎟ = π ⎜ ⎟ = 6.80 cm

3 3 ⎝ ⎠ 2 3 ⎝ 2 ⎠

Hence, we may write

*sV sd* 0.02

= ⋅ 3 = 3 ⋅ = 0.0255

*V d* 2.35

*sV* = 6.80 ⋅ 0.0255 = 0.173

*V* = 6.8(±0.2) cm3

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**4-14.** 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 7.6 m. Calculate the volume in liters of the tank and the standard deviation of the result.

**Solution:**

The mean diameter of the tank is 5.2 + + 5.7 5.3 + 5.5 *d* = = 5.425 m4

∑*N*( ) *x ~~x~~* − 2

*i*

*s* = *i*=1

The standard deviation of the diameter is

*d* = 0.222 *N* −1

The mean height of the tank is 7.9 + + 7.8 7.6 *h* = = 7.767 m and *s*

3 *h* = 0.153

The volume of the tank is given by

222 2

⎛ ⎞ *d* 2 ⎛ ⎞ 5.425( ) ±0.

*V h* = ⋅ π π ⎜ ⎟ = 7.767(±0.153) ⋅ ⋅ ⎜ ⎟

⎝ ⎠ 2 ⎝ ⎠ 2

The error in the 3rd factor is given by

*s* ⎛ ⎞ 0 2

*y* .222 = = ⎜ ⎟ 0.0409 *y* = ½ (5.425) = 2.7125 *sy* = 0.0409 ⋅ 2.7125 = 0.111 *y* ⎝ ⎠ 5.425

*V* = 7.767(±0.153) ⋅ (3.14159) ⋅ (2.7125(±0.111))2

*sy* ⎛ ⎞ 0.111 = = 2⎜ ⎟ 0.0818 *y* = (2.7125)2 = 7.358 *s*

*y* 2.7125 *y* = (0.0818)(7.358) = 0.602 ⎝ ⎠ *V* = 7.767(±0.153) ⋅ (3.14159) ⋅ 7.358(±0.602)

Next, we propagate the error in volume by assuming the error in pi is negligible. *sy* ⎛ ⎞ 0.153 2 2 ⎛ ⎞ 0.602

= + ⎜ ⎟⎜ ⎟ = 0.0841 *y* = 7.767 ⋅ 3.14159 ⋅ 7.358 = 179.5

*y* ⎝ ⎠ 7.767 ⎝ ⎠ 7.358

*sy* = (0.0841)(179.5) = 15.09

*y* = 180(±20) m3

Converting to liters, we have

10 *V* = 180(±20) m3 00*L*

⋅*m*3 = 1.8(±0.2) ⋅ 105 *L*

**\*4-15.** In a volumetric determination of an analyte A, the data obtained and their standard deviations are as follows:

Initial buret reading 0.19 mL 0.02 mL

Final buret reading 9.26 mL 0.03 mL

Sample mass 45.0 mg 0.2 mg

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From the data, find the coefficient of variation of the final result for the %A that is obtained by using the equation that follows and assuming there is no uncertainty in the equivalent mass.

%A = titrant volume ⋅ equivalent mass ⋅ 100%/sample mass

**Solution:**

Since the titrant volume equals the final buret reading minus the initial buret reading, we can introduce the values given into the equation for %A.

%A = [9.26(±0.03) − 0.19(±0.02)] ⋅ equivalent weight ⋅ 100/[45.0(±0.2)]

Obtaining the value of the first factor and the error in the first factor

*s* = + ( ) 0.03 2 2

*y* (0.02) = 0.0361 *y* = 9.26 − 0.19 = 9.07

We can now obtain the relative error of the calculation

*s* 0.036 2 2

%A ⎛ ⎞⎛ 0.2 ⎞

= + ⎜ ⎟⎜ ⎟ = 0.00596

%A ⎝ ⎠ 9.07 ⎝ 45.0 ⎠

The coefficient of variation is then

CV = (0.00596) ⋅ 100% = 0.596% or 0.6%

**4-16.** Chapter 26 describes inductively coupled plasma atomic emission spectrometry. In that method, 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 as

*S k* = ′*e*2*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 ⋅ 10−23 J K−1). For an ICP of average temperature 7000 K and for Cu with an excitation energy of 6.12 ⋅ 10−19 J, how precisely does the ICP temperature need to be controlled for the coefficient of variation in the emission signal to be 1% or less?

**Solution:**

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

*e s* 2 2

*S* ⎛ ⎞ *s* ⎛ ⎞ *s*

≤ = 0.01 ⎜ ⎟ *k*′ + ⎜ ⎟ −*E k*/ *T*

*S k*′ ⎜ ⎟ ⎝ ⎠ *e*−*E k*~~/~~ *T*

⎝ ⎠

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

*e*−*E k*~~/~~ *T*From Table 4-4, we find *se*−*E k*/ *T*

*s*

0.01= *e*−*E k*/ *T*

−*E k*~~/~~ *~~T~~* = *s*

*e* −*E k*/ *T*

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*s*−*E/kT* can be determined by evaluation of the errors in each of the numbers. *s s* 222

−*E k*/ *T* ⎛⎞ ⎛⎞ ⎛⎞

= + ⎜ ⎟ *E s*⎜ *k s* ⎟ + ⎜ *T* ⎟ −*E k*/ *T* ⎝ ⎠ *E* ⎝ *k* ⎠ ⎝ *T* ⎠

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

⎛ ⎞ ⎛ ⎞ *s s* −

*T T* − − *E* ⎛ ⎞ 6.12 ⋅10 19

*s*−*E k* = ⋅= ⎜ ⎟ / *T* ⎜⎟ ⎜ ⎟ ( ) = 0.01 ⎜ ⎟ ⎝ ⎠ *T kT* ⎝ 7000 ⎠ 1.3807 ⋅10−23 ( ) 7000 ⎝ ⎠

Solving for *sT* gives:

*sT* ≤ 11.1 K

**\*4-17.** Chapter 22 shows that quantitative molecular absorption spectrometry is based on Beer’s law, which can be written as

2log = *T b*ε *c*X

where *T* is the transmittance of a solution of an analyte X, *b* is the thickness of the absorbing solution, *c* X is the molar concentration of X, and ε is an experimentally

determined constant. By measuring a series of standard solutions of X, ε*b* was found to have a value of 3312(±12) M−1, where the number in parentheses is the absolute standard deviation.

An unknown solution of X was measured in a cell identical to the one used to determine ε*b*. The replicate results were *T* = 0.213, 0.216, 0.208, and 0.214. Calculate (a) the molar concentration of the analyte *c*X, (b) the absolute standard deviation of the *c*X, and (c) the coefficient of variation of *c*X.

**Solutions:**

We first calculate the mean transmittance and the standard deviation of the mean.

⎛ 0.213 +++ 0.216 0.208 0.214 ⎞⎟⎠

mean *T* = ⎜ = 0.2128

⎝ 4

*sT* = 0.0034

**(a)** ⎛ ⎞ −log*T* −log( ) 0.2128

*c*X = ⎜ ⎟ = = 2.029⋅10−4 M

⎝ ⎠ ε*b* 3312

**(b)** For −log*T, sy* = (0.434)*sT*/*T* = 0.434 ⋅ (0.0034/0.2128) = 0.00693

−log(0.2128) = 0.672

− ± log*T* 0.672 0.00693

*c*X = = ε*b* 3312 ± 12

*s* 2 2

*C*X ⎛ ⎞ 0.00693 ⎛ 12 ⎞

= + ⎜ ⎟⎜ ⎟ = 0.0109

*c*X ⎝ ⎠ 0.672 ⎝ 3312 ⎠

*s* X ( ) 0.0109 ( ) 4 6

*C* = ⋅ 2.029 10− − = 2.22 ⋅ 10

**(c)** CV = (2.22 ⋅ 10−6/2.029 ⋅ 10−4) ⋅ 100% = 1.1%

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Solution and Answer Guide: Skoog et al., *Fundamentals of Analytical Chemistry*, 10e,

© 2022, 978-0-357-45039-0, Chapter 4: Random Errors in Chemical Analysis

**4-18.** Analysis of several plant-food preparations for potassium ion yielded the following data: **Sample Percent K**+

1 6.02, 6.04, 5.88, 6.06, 5.82

2 7.48, 7.47, 7.29

3 3.90, 3.96, 4.16, 3.96

4 4.48, 4.65, 4.68, 4.42

5 5.29, 5.13, 5.14, 5.28, 5.20

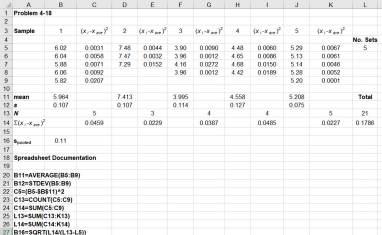
The preparations were randomly drawn from the same population.

**(a)** Find the mean and standard deviation *s* for each sample.

**(b)** Obtain the pooled value *s*pooled.

**Solutions:**

**(a)** and **(b)**

****

**(c)** Why is *s*pooled a better estimate of σ than the standard deviation from any one sample? **Answer:**

Pooling the variations in %K from the five samples gives a better estimate of σ because several data sets are used. Thus the pooled standard deviation uses a larger number of data points and can reflect variations that arise because of sample selection and sample preparation.

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**\*4-19.** Six bottles of wine of the same variety were analyzed for residual sugar content with the following results:

**Bottle Percent (w/v) Residual Sugar**

1 1.02, 0.84, 0.99

2 1.13, 1.02, 1.17, 1.02

3 1.12, 1.32, 1.13, 1.20, 1.25

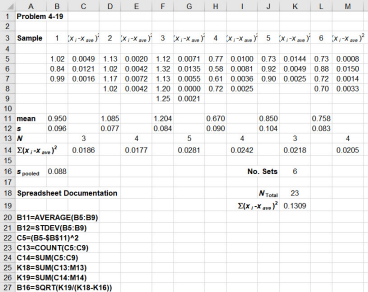
4 0.77, 0.58, 0.61, 0.72

5 0.73, 0.92, 0.90

6 0.73, 0.88, 0.72, 0.70

**(a)** Evaluate the standard deviation *s* for each set of data.

**Solution:**

****

The standard deviations are *s*1 = 0.096, *s*2 = 0.077, *s*3 = 0.084, *s*4 = 0.090, *s*5 = 0.104, *s*6 = 0.083

**(b)** Pool the data to obtain an absolute standard deviation for the method.

**Solution:**

*s*pooled = 0.088 or 0.09

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**4-20.** Nine samples of illicit heroin preparations were analyzed in duplicate by a gas chromatographic method. The samples can be assumed to have been drawn randomly from the same population. Pool the following data to establish an estimate of σ for the procedure.

**Sample Heroin, % Sample Heroin, %**

1 2.24, 2.27 6 1.07, 1.02

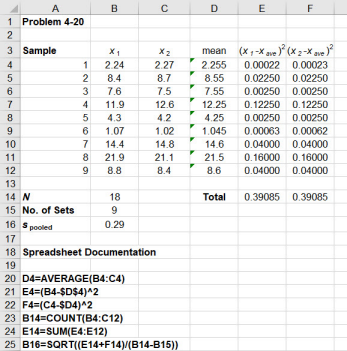
2 8.4, 8.7 7 14.4, 14.8

3 7.6, 7.5 8 21.9, 21.1

4 11.9, 12.6 9 8.8, 8.4

5 4.3, 4.2

**Solution:**

****

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**\*4-21.**

Calculate a pooled estimate of σ from the following spectrophotometric analysis for NTA (nitrilotriacetic acid) in water from the Ohio River:

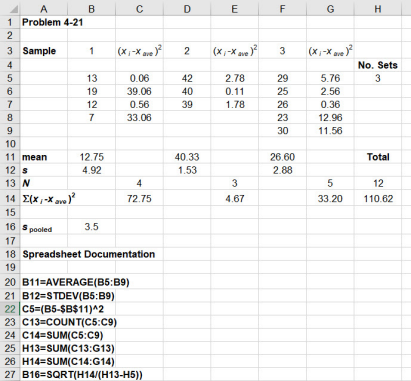
**Sample NTA, ppb**

1 13, 19, 12, 7

2 42, 40, 39

3 29, 25, 26, 23, 30

**Solution:**

****

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**4-22.** Go to **http://dx.doi.org/10.18434/T43G6C**, where you will find a link to the NIST Statistical Reference Datasets site. Find the Dataset Archives, locate the Univariate Summary Statistics section, and select the Mavro data set. This actual data set is the result of a study by NIST chemist Radu Mavrodineaunu. His study was to determine a certified transmittance value for an optical filter. Click on the ASCII format data file. The data set at the bottom of the page contains 50 transmittance values collected by Mavrodineaunu. Once you have the data on the screen, use your mouse to highlight only the 50 transmittance values, and click on Edit/Copy (or use Ctrl-C) to place the data on the clipboard. Then start Excel with a clean spreadsheet, and click on Edit/Paste (Ctrl-V) to insert the data in column B. Now, find the mean and standard deviation, and compare your values to those presented when you click on Certified Values on the NIST web page. Be sure to increase the displayed number of digits in your spreadsheet so that you can compare all the digits. Comment on any differences between your results and the certified values. Suggest possible sources for the differences.

**Solution:**

**Excel value NIST value**

**Mean** 2.001856000000000 2.001856000000000

**SD** 0.000429123454003085 0.000429123454003053

The means are the same in both cases. There is some difference, however, in the standard deviations in the last two digits. The differences could arise because of the different algorithms used to calculate the SD and to roundoff errors in the calculations. The first 16 digits are identical.

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