Guidelines on Determining and Reporting Significant Figures in Chemical Measurements (Handbook)

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I dedicate this handbook with love to my beautiful, understanding, and caring wife, Linda "Mai Nkosi" Govere; our

two lovely deep-thinking daughters, Alexandra Shungudzo and Saunsuray Muchadei; and their ever calculating and

determined brother, Nkosilathi Tendaishe.

E.M.G.

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Preface

The five basic factors that affect the quality of chemical measurements are sample collection, preservation, processing, analysis, and data reporting. Improper actions on any of the five factors may result in poor data from which poor judgments or decisions could be made. To improve quality of sample data there ought to be clear guidelines for performing all the five factors. This handbook is aimed at addressing one of the five factors, namely data reporting. The main purpose of this handbook is to provide the theory and practice of determining, and intelligently reporting and interpreting significant figures in chemical measurements. From a review of literature, it appears that many authors have forgotten or simply pay little attention to the importance of assigning proper significant figures to multi-digit, computer-generated results. Such ignorance or carelessness tends to result in misinforming the end users of the reported results and may lead to incorrect data-based decisions. Thus this handbook serves as a quality assurance and quality control tool on significant figures. In preparing this handbook, an attempt was made to detail general and specific aspects of significant figures. A practical rather than a theoretical approach was followed. Even though computations are nowadays done using calculators and computers, the guidelines in this handbook are presented as an explanation of how those numbers are determined rather than how one should do the calculations. Detailed guidelines that can be carried out with minimum of difficulty by mathematically less sophisticated clients are presented. Because of the way the information is presented, this handbook is a valuable resource for teaching in schools and colleges, for training at research and extension support science laboratories, and as a reference for scientists and publishers.

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Unit 1: **Introduction**

This world is a world full of numbers and the value of any number depends on the significant digits within that number. A measured value has little or no true meaning and thus, it is useless, unless the figures (digits) in that value were deemed to be significant and the significant figures were properly determined and reported. Significant figures are especially important in the field of analytical chemistry and the fields to which it is applied such as agriculture, engineering, medicine, food science, environmental science, natural resources management, and ecology. Errors in reporting significant figures are being noticed even in prestigious research journals *(1-3)*. A casual examination of published literature indicates that numerous authors are not giving proper attention to significant figures. It is especially common to see calculated values having too many significant figures. That shows that a significant number of people, who generate data, use the data, review research articles, and edit journals, may need theoretical and practical guidelines in determining, reporting, and interpreting significant figures. The fact that errors in reporting data exists among highly educated personnel may indicate that significant figures as a subject matter is getting a fairly cursory treatment or a brief review at the college level with the expectation that students will have learned how to deal with significant figures in their high school coursework. It appears that as instructors try to balance the amount of material they want to cover with the amount of time in a semester, less and less time is devoted to significant figures.

Deciding the appropriate number of significant figures for the reporting of numerical data is not an obvious or easy task. This handbook presents a detailed account of the meaning, theory, and practice of determining and reporting significant figures. It is hoped that these guidelines will enable laboratory analysts and principal research investigators to intelligently report and interpret those multi-digit results from calculators and computers we have come to take for granted. Even though computations are nowadays done using calculators and computers, the guidelines in this handbook are presented as an explanation of how those numbers are determined rather than how one should do the calculations. The goal is that students, teachers, laboratory technicians, researchers, and publishers should decide the appropriate number of significant figures on the basis of scholarly considerations rather than arbitrary reasons of habit.

Unit 2: **Learning Objectives**

After studying this handbook, you should be able to:

1. Define the concept of significant figures.

2. List the reasons why significant figures are important.

3. Apply guidelines on determining significant figures in chemical measurements.

4. Apply guidelines on determining significant figures in mathematical calculations.

5. Apply guidelines on rounding off chemical measurements and their calculated results.

6. Appropriately compute uncertainties and report values with their estimated uncertainties.

7. Apply guidelines on reporting significant figures in graph interpretation.

8. Use significant figures as a quality control objective.

9. Aspire to improve the quality of scientific meaning and decision making by properly determining, reporting, and interpreting significant figures in measurements and their calculated values.

10. Be able to answer practice questions given in Appendix A.

Unit 3: **The Definition of Significant Figures**

Quantitative analytical chemical data are mainly reported using the real number system called the *decimal system* (See Appendix B: The Main Number System Used In Reporting Chemical Measurements, for details). In the decimal number system, any of the ten Arabic numerals (symbols) 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 is a **digit**. For instance, a number 152 has three digits 1, 5, and 2. The word **figure** is used in the same sense as the word digit. It is a character or symbol denoting a number. A **number** is an expression of quantity. A digit alone or in combination serves to express a number. The digits that can be considered correct in the approximate representation of a quantity, whether measured or computed, and that are essential to conveying a numerical value to its full precision are called **significant figures**. **Precision** is a measure of the reproducibility or how closeness of replicated (repeated) measurements (made under same prescribed conditions). Precision should not be confused with **accuracy** that refers to how close a particular measurement is to the true or correct value. Therefore, the concept of significant figures applies only to measurements - quantities and their computations which are subject to error. A **measurement** can be defined as the approximate numerical value of a physical quantity obtained by comparison with an accepted scale *(4)*. It does not apply to integers because integers are exact numbers (values). Exact **numbers** are counting numbers. They indicate how many of something is present. They are not measurements made with instruments nor do they affect the accuracy of a calculation or the precision of the expression *(5)*. For example, in a statement: "The soil solution test shows that there are only 7 of the 16 plant essential nutrients present", the number 7 and 16 are integers and not measurements.

The term "**significant figures**" is used to describe some judgment of the number of reportable digits in a result. Under the **significant figure convention** all decimal numbers are assumed to be significant ones *(4)*. A value is made up of significant figures when it contains all digits known to be true and one last digit that is in doubt *(6)*. For instance, a value reported as 45.474 mg C contains five significant figures, of which four digits, 45.47 are certain but the last digit 4 is not. Taylor *(7)* defined significant figure as a term that refers to rounding a numerical value (datum) to the number of digits consistent with the confidence that can be placed in it. Anderson *(8)* described significant figures as the digits in a number that give information about the degree of certainty in a measured or calculated value. Mathematically, a significant figure can be defined as any of the digits 1, 2, 3, 4, 5, 6, 7, 8, 9, and 0

when it does not merely locate the decimal point *(9)*. For example, the zeros in 3004 are significant whereas the ones in 0.0064 and 2800 are not.

Unit 4: **Importance of Determining Significant Figures**

In quantitative chemical analysis, assigning proper significant figures to analytical results is very important because of the reasons given below.

1. Significant figures reflect the precision of a measurement and analytical instrument. The greater the number of significant figures the more precise the measurement. For example, the mass of KCl used to make 100 mL of 1 *M* KCl reported as 7.4551 g would imply an analytical balance was used as opposed to a top-loading (ordinary balance) because the former has four to five significant figures to the right of the decimal point (precision of ± 0.0001 to ± 0.00001 g) and the latter has zero to three significant figures to the right of the decimal point (precision of ± 0.1 to ± 0.001 g).

2. Significant figures reflect the precision of the reported values. They help us avoid reckless use of too many digits that may convey false sense of the precision of the numerical value. Thus understanding significant figures is necessary in order to report a realistic answer. For example, reporting a temperature reading as 53.24637 $^{\circ}$C would make one wonder how one could have gotten that level of precision from a thermometer. However, we can be certain that the temperature was above 50 $^{\circ}$C. Thus, the number of significant figures used in a measured value tells us its degree of precision.

3. Significant figures tell something about the appropriateness of the analytical method. They help us think about inherent precision of the measuring instrument or device. For example, a result reported as 2.800×10^{3} g indicates a four-place precision and implies a balance used to weigh the sample had a tolerance of ± 1 g. If the result were reported as 2800 g, the degree of uncertainty would not be obvious.

4. The number of digits employed to express the numerical value can convey some idea of the uncertainty in the numerical value of a measurement. **Implied uncertainty** can be computed from **stand-alone significant figures** (measurement-based quantities for which the uncertainty are not given directly, and must be inferred from the number of significant figures used to represent them). For example, a value of 4.6 mg L^{-1} is understood to mean 4.6 ± 0.1 (some would say even up to 4.6 ± 0.2 or 0.3). The 0.1, 0.2 or 0.3 is the implied uncertainty. The **implied relative uncertainty** for 0.1 is $^{0.1}\!/_{4.6} = ^{1}\!/_{46} = 2.2\%$.

5. Proper application of significant figures avoids underestimating or overestimating the experimental results or measurements. Too few digits in the reporting of numerical values rob the user of valuable information by losing meaningful digits. On the other hand, too many digits result in retaining meaningless digits.

6. Assigning proper significant figures to measurements and their calculated results helps to avoid making erroneous, misleading, and costly decisions based on reported data.

7. Significant figures tell us the last digit or at most the last two digits that may change (in precision) on further experimentation.

8. Significant figures reveal the difference between exact numbers of mathematics and the limited precision of measured values.

9. Significant figures indicate the level of discrimination in calculating quantities of variables. This use of significant figures was well demonstrated by Mitchell *(10)* when he queried researchers who had determined skeletal age in 765 ethnically diverse children using a standard method whose narrowest levels of discrimination were 1 month in the case of skeletal age of individual bones, and three months when considering the entire hand. The researchers calculated their results to the nearest 0.001 of a year instead of to the nearest month or 0.08 of a year.

10. Proper use of significant figures may help in definitions and applications of scientific terms. For example, the definition of the unit to express pressure is Pascal (Pa). One atmosphere (atm) and 1 bar are not the same but close; 101,325 Pa equal 1 atm, and 1 bar equals 10^5 Pa. The difference is in the 6 significant figures in the value 101,325. If we round 101,325 to one significant figure we could end up distorting the definitions. We would end up saying 1 bar equals 1 atm. That wouldn't be precise or accurate. Therefore significant figures give significant meaning to a value.

11. Significant figures allow for comparability of results because proper use of significant figures adds clarity and degree of equivalence (comparability) of measurement results. This is very important in global decision-making and cross-fertilization of ideas between industries, institutions, and nations.

Unit 5: **Guidelines on Determining Significant Figures in Chemical Measurements**

Each digit in a number has a value according to its place in the number. Not all **place-values** are significant. In **place-value systems**, the value of the symbol depends upon the position or place of the symbol in the representation. The most commonly used number system is the **decimal-positional number system**, the decimal referring to the use of ten symbols - 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9, to construct all numbers. In reporting laboratory results, decision has to be made as to what is a significant figure, in other words, what is the number of reportable digits in a result. This decision can only be made based on the sensitivity and reliability of the analytical method and instrument employed in generating the results. Application of the analytical results is another factor in deciding significant figures. Only meaningful digits should be retained in the reported laboratory value. Assuming Table 1 contains properly reported measurements or their computed values, the following are guidelines that can be used to determine the number of significant figures:

Guideline 1. Digits from 1 to 9 that are in a value represent significant figures regardless of the position of any decimal points. In other words, all non-zero digits are significant. Thus all values in column A of Table 1 have five significant figures.

Guideline 2. Values containing zeros that are bounded on either side by a number from 1 to 9 represent significant figures. Thus all values in column B have five significant figures because the zeros between two other significant digits are significant.

Guideline 3. Zeros after a decimal point that has a digit between 1 and 9 on its left are significant figures. In other words, zeros at the end of a number are significant if they are to the right of the decimal point. Thus all values in column C have five significant figures.

Guideline 4. Zeros after a decimal point that has no digits from 1 to 9 before it, are not significant. These zeros precede the first non-zero digit and position the decimal point. Thus values in Column D have five significant figures.

Guideline 5. Zeros before a decimal point with no other preceding digits from 1 to 9 are not significant. Thus values in Column E have five significant figures. Usually a lone zero preceding a decimal point is

written for "cosmetic" *(11)* and functional purposes. The zero makes it easier to notice the presence of the decimal point.

Guideline 6. Zeros at the end (final zeros) of a number are not significant if the number is written without decimal point. Examples for this guideline are given in Column F. However, most people say these zeros are unclear as to the number of significant figures and usually assume the "worst" case when working with such numbers.

Guideline 7. Zeros at the end (final zeros) of a number are significant if the number is written with a decimal point using **scientific** or **engineering notation** to show the significant digits. In **scientific notation**, the number is written with one non-zero digit to the left of the decimal point and an integer exponent or power of ten. For example arsenic in tap water given as 0.17456 ppb can be presented as 0.17456 µg L^{-1} or 1.7456×10^{-7} g L^{-1} in scientific notation.   (A number that is raised to a power is called a **base.** Numbers other than ten can be used as bases). **Engineering notation** is another form of exponential notation in which the number is written with one, two, or three digits to the left of the decimal point and the integer exponent is always expressed as a number divisible by three. For example, the 1.7456×10^{-7} g L^{-1} in scientific notation would be expressed as 174.56×10^{-9} g L^{-1} in engineering notation. Significant digits are those in the coefficient, not in the power of ten. For instance, given the value 400 g L^{-1}, one cannot tell if the number was measured to the nearest unit, ten, or hundred. Using *Guideline 6* we would assume one significant figure in 400 g L^{-1}. However, to remove confusion, we can use scientific notation to show significant digits. Not only does scientific notation better represent significant figures, but it also makes mathematical manipulation easier. The value, 400 g L^{-1} written as 4.00×10^2 g L^{-1}, means there are 3 significant figures in the reported value. However, if written as 4.0×10^2 then there are 2 significant figures. In other words, if the zeros can be omitted when converting a value to the scientific form, then the zeros are not significant *(6)*. It should also be noted that 4.0×10^2 implies uncertainty of $\pm 0.1 \times 10^2$. Thus 6.6×10^2 nm implies uncertainty of $\pm 0.1 \times 10^2$ nm (660 ± 10 nm). Column G gives values (written using scientific notation) and their significant figures. Please note that standard position for the decimal place when using scientific notation is always just after the first non-zero digit in the number counting from the left. An alternative to the use of scientific notation is to put a decimal point after the zero, for example, 6700**.** ^{o}C, but this is rarely done *(9)*. Another alternative is to put an underscore at the last significant zero *(8)*.

For example, 670<u>0</u> $^{\mathrm{o}}$C would indicate that the zeros up to the one underscored are significant. Also this is rarely done. Clase *(12)* suggested using a "?" or "*" symbols to indicate "unknown" digits. For instance, a 0.893226 g weight measured on a top-loading balance (readability ± 0.001 g) would have 3 unknown digits, e.g., 0.893??? g or 0.893*** g compared to a microbalance (readability ± 0.000001 g), e.g., 0.893226 g. Again, the use of the symbol ? or * is rarely done.

Additional examples that demonstrate assignment of significant figures on chemical measurements are given in Table 2.

Table 1. Data for illustrating guidelines in determining significant figures (S.F.).

Column A	Column B	Column C	Column D	Column E	Column F		Column G	
78736	78706	7873.0	0.078736	0.078736	70000	1 S.F.	7×10^4	1 S.F.
7873.6	787.06	707.00	0.0078736	00.70706	78000	2 S.F.	7.0×10^4	2 S.F.
787.36	78.006	78.000	0.00078736	000.70036	78700	3 S.F.	7.00×10^4	3 S.F.
78.736	70.006	7.8000	0.000078736	0000.78700	78730	4. S.F.	7.000×10^4	4. S.F.
7.8736	7.0006	7.0000	0.0000078736	000.78030	78736	5 S.F.	7.0000×10^4	5 S.F.
0.78736	0.70606	0.70000	0.00000078736	00.078736	787360	5 S.F.	7.00000×10^5	6 S.F.

Table 2. Examples showing significant digits in chemical measurements.

Measured Chemical Parameter	Measurement Result	Measurement Units	Significant digits
Volume of 2 *M* HCl	100.0	mL	4
Weight of empty crucible	21.0045	g	6
Molarity of NaOH solution	0.00500	*M* (moles L^{-1})	3
Dissociation constant for HPO$_4^{2-}$	7.1×10^{-13}		2
	710×10^{-15}		2
Compressed gas regulator pressure range	10 – 400	psig (pounds per square inch gauge)	1
Voltage on voltmeter	300	V (volts)	1
Electrical resistance on ohmeter	1200	Ω (ohms)	2
Electrical current on ammeter	0.50	A (ampere)	2
Amount of arsenic in water	0.1700	μμg L^{-1}	4
	0.1700	ppb (parts per billion)	4
	0.1700	ng mL^{-1}	4
	0.0000001700	ppm (parts per million)	4
Conductivity	720.0010	μS (micro siemens)	7
Freezing temperature point of pure liquid water	0	$^{\circ}$C (Celsius)	1
	273.15	K (Kelvin)	5
Radiation absorbed dose	10	rd (rad)	1
Frequency of radiation	4.0206×10^{14}	sec^{-1}	5
Wavelength of radiation	0.0000202	cm	3
	202	nm	3
	0.000000202	m	3
Wavelength on a diffractometer	1.0510	Å (angstrom)	5
Molar absorptivity	210	L mol^{-1} cm^{-1}	2
Absorbance	0.600		3
Rest mass of the electron	9.1090×10^{-28}	g	5
	910.90×10^{-30}	g	5
Electrical charge	$160.217\ 764\ 62 \times 10^{-21}$	C (coulomb)	11
Air flow volume per unit time	10	cfm (cubic feet per minute)	1
	17	m^3 hr^{-1}	2
	283.3	L min^{-1}	4

Unit 6: **Guidelines on Determining Significant Figures in Mathematical Calculations**

Special care must be taken in presenting significant figures of calculated values. Take for instance the same measured value 17894 $\mu g\ L^{-1}$ reported as 17.9 mg L^{-1} and 1.79 x 10^4 $\mu g\ L^{-1}$; how can one tell what the correct value is? In a published article that appeared in *Clinical Pharmacology and Therapeutics* journal, Levy *(2)* pointed out the author of the article measured data in three significant figures (values ranging from 170 to 632 mL min^{-1}) but reported the mean value as 356.36 mL min^{-1}. The reported mean indicated an enhancement of precision one-hundredfold. Even though increasing the number of significant figures in the process of mathematical operations is usually an unintended careless error, its consequences may not be distinguishable from the intentional and therefore unethical alteration of data.

Under the significant figure convention, the fundamental principle concerning significant figures in calculations is that the calculated quantity can be no more precise than the data used in the calculation, and the reported result should reflect this fact *(11)*. In any calculation, the number of significant figures is dictated by the **least precise factor** in the calculation. (A chain is only as strong as its weakest link). For multiplication or division, the least precise factor is the value whose total number of significant figures is the smallest; whereas with addition or subtraction, the least precise factor is the value whose total number of digits to the right of decimal is the smallest. Thus, in general, the result of a multiplication or division problem has the same total number of significant figures as the number with the fewest significant figures used in the calculation; whereas the result to an addition or subtraction problem has the same number of digits to the right of the decimal point as the number with the fewest such digits that is used in the calculation *(13)*. The following are specific guidelines that can be used to determine the number of significant figures in calculations under the **significant figure convention.** Note that while computations are done with calculators and computers the following computation guidelines are presented as an explanation of how those numbers are determined rather than how you should do the calculations.

Guideline 1. When performing multiplication or division of numbers in exponential operations, identify the **mantissa** and the **exponent**. Mantissa is a **significand**, that is, an integer or fixed-point multiplied by a base to some integer power (the **exponent**). In computers the base is usually 2 and in scientific notation it is usually 10. When the base is 2, it is the binary analog of scientific notation in base 10.

The **Exponent** is the number of times a quantity is multiplied by itself. Chemists express small numbers by using exponential figures, e.g. $[H^+] = 5.75 \times 10^{-7}$ *M*. The 5.75 is the mantissa and the –7 is the exponent. **Exponentiation** is a process generalized from repeated multiplication, in much the same way that multiplication is a process generalized from repeated addition. The next operation after exponentiation is **tetration**. As an example, for a number 15,

$15 + 15 = 2*15$ Addition to Multiplication

$15*15 = 15^2$ Multiplication to Exponentiation

$15^{15} = 15 \uparrow\uparrow 2$ Exponentiation to Tetration

Two standard exponential notations, scientific and engineering are used to express exponential numbers. In **scientific notation**, the mantissa has one non-zero digit to the left of the decimal point that is multiplied by an integer exponent, which is a power of ten. In **Engineering notation,** the mantissa can have one, two, or three digits to the left of the decimal point and the integer exponent is always expressed as a number divisible by three. The mantissa contains *all* and *only* the significant figures. The mantissa with the fewest significant figures is the least precise factor that controls the number of significant numbers in the calculated result of multiplication or division calculations. When multiplying numbers in exponential notations, get the **product** of the mantissas and determine the final exponent by adding all exponents. For example, $(7 \times 10^4)*(7.29 \times 10^{-2})*(6.027 \times 10^3) = (7*7.29*6.027) \times$

$10^{(4 + -2 + 3)} = 300 \times 10^5 = 3 \times 10^7$ (scientific notation) or 30×10^6 (engineering notation). Since 7×10^4 has only one significant figure, these results are expressed with only one significant figure. When dividing numbers in exponential notations get the **quotient** of mantissas and get the final exponent by subtracting exponents in the divisor from exponents in the dividend. For example, $(7.29 \times 10^{-2})/(6.027 \times 10^3) = (7.29/6.027) \times 10^{(-2 + -3)} = 1.2096 \times 10^{-5} = 1.21 \times 10^{-5}$ (in scientific notation) or 12.1×10^{-6} (in engineering notation). The three significant digits in 7.29×10^{-2} determine the number of significant digits in the result. If two factors have the same number of significant figures, the lesser precise factor is the one whose **mantissa** is the smaller of the two *(14)*. Now try this example.

The absorbance of a 0.00123 % (w/v) solution of diazoanthide at a wavelength of 527 nm is 0.624. What would be the absorbance of 0.00100 % (w/v) solution at 527 nm?

Solution: The absorbance is obtained by proportionality:

$$Absorbance: \quad \frac{0.624}{0.00123\%} = \frac{X}{0.00100\%}$$

$$\frac{0.624}{0.00123\%} \, x \, \frac{0.00100\%}{1} = 0.507 \ \text{(3 S.F.) not 0.507317073 (9 S.F.)}$$

We can use the scientific (and engineering) notation to express the small percentage values as shown below.

The absorbance of a $1.23 \ x \ 10^{-3}$ % (w/v) solution of diazoanthide at a wavelength of 527 nm is 0.624. What would be the absorbance of $1.00 \ x \ 10^{-3}$ % (w/v) solution at 527 nm? Solution: The absorbance is obtained by proportionality:

$$Absorbance: \quad \frac{0.624}{1.23 \ x \ 10^{-3} \, \%} = \frac{X}{1.00 \ x \ 10^{-3} \, \%}$$

$$\frac{0.624}{1.23 \ x \ 10^{-3} \, \%} \, x \, \frac{1.00 \ x \, 10^{-3} \, \%}{1}$$

$$\frac{0.624}{1.23\%} \, x \, \frac{1.00\%}{1} = 0.507$$

Note that the exponents (–3) are divisible by 3 and therefore both the scientific and engineering notations are the same.

Guideline 2. When performing addition or subtraction of numbers in exponential notation the exponents are adjusted so that they are the same. The mantissas are then added and the common exponent is appended. Suppose you are comparing the effects of alumina (Al_2O_3) and a humic substance on the rate of disappearance of active phosphorus in soil solution as part of a larger experiment to reduce water pollution. To do this you determined the time it took for the added phosphorus to reach half concentration ($t_{1/2}$ in seconds) in the soil solution. Average results showed:

Alumina treatment: $At_{1/2} = 3.06 \times 10^5$ s

Humic substance treatment: $Ht_{1/2} = 20.92 \times 10^4$ s

Which one of the two treatments would be more effective in reducing phosphorus migration into underground water?

To have a clear comparison, it's easiest to adjust exponents of the two treatments so that they are the same. The mantissas are then subtracted and the common exponent is appended to see the differences in $t_{1/2}$.

Alumina treatment: $At_{1/2} = 3.06 \times 10^5$ s

Humic substance treatment: $Ht_{1/2} = 2.092 \times 10^5$ s

The humic substance adsorbs phosphorus from soil solution at a faster rate because $Ht_{1/2}$ is smaller than $At_{1/2}$. The difference between $At_{1/2}$ and $Ht_{1/2}$ was 0.97×10^5 s ($3.06 - 2.092 = 0.968 = 0.97$). The mantissa in the result of addition or subtraction calculation will have the same number of digits to the right of the decimal point as the mantissa with the fewest such digits used in the calculation process.

The following example gives a scenario in which one of the numbers added in exponential notation has an exponent significantly smaller than the others: $(7 \times 10^4) + (7.29 \times 10^{-2}) + (6.027 \times 10^3) = (70 \times 10^3) + (0.0000729 \times 10^3) + (6.027 \times 10^3) = (70 + 0.0000729 + 6.027) \times 10^3 = 76.0270729 \times 10^3 = 76 \times 10^3 = 8 \times 10^4$ (rounded off based on mantissa with one significant digit, 7 in the number 7 x 10^4). From this example, it can be seen that taking a number with uncertainty and adding a number smaller than that uncertainty means that, in the end when the answer is rounded off, nothing has happened. Thus, when two or three numbers are added or subtracted in exponential notation and one has an exponent significantly smaller than the others, you can just ignore it.

Guideline 3. When performing calculations that involve a mixture of numbers in exponential and non-exponential notation, consider the numbers that are not in exponential form as mantissas with a zero exponent (for

example 2.4 can be considered as 2.4 x 10^0 because any number to the power zero gives a value of 1) and then use guidelines 1 and 2 above while following the order of mathematical operations (brackets, multiplication, division, addition and subtraction).

Guideline 4. When taking logarithms, such as converting [Ca^+] to pCa, or [H^+] to pH or transmittance to absorbance, the number of digits to the right of the decimal in the result must equal the number of significant figures in the original number. For example, if H^+ = 1.05 x 10^{-7}, then pH = -log (1.05 x 10^{-7}) = 6.979. Note that the decimal 0.979 in 6.979 has the same number of digits (3) as the mantissa, 1.05.

Guideline 5. When performing a series of multiplications, carry all digits through the operations, the minimum of which should be two digits beyond the last digit of the multiplier with the most significant figures. Round off the product to the number of significant digits of the multiplier with the fewest significant digits. Thus, the reported result should have no more significant figures than the factor with the fewest significant figures. For example, the volume of a soil aggregate 2.214 cm x 4.04 cm x 10.00 cm = 89.4456 cm^3 = 89.4 cm^3. The value with the fewest significant figures is 4.04. It has three.

Guideline 6. When performing a series of divisions, use all digits of the **dividend** (the number being divided) and **divisor** (the number used to divide). Round off the **quotient** to the number of significant digits of the dividend or divisor with the fewest significant digits (the least precise factor). For instance,

$$\frac{2.601 * 50.0}{55.1 * 0.070} = 33.718 = 34$$

The divisor 0.070 has two significant figures causing the quotient (33.718) to have two significant figures 3 and 4. However, if you were to divide 398.7 g of soil into 13 equal sub-samples. You find the answer as follows:

$$\frac{398.7 \, g}{13} = 30.67 \, g$$

The number 13 is an exact **counting number**. It does not play any part in determining significant numbers. It is not a measurement but an **integral number**. Also, when converting one measurement to another, such as converting cubic meters to cubic feet, bars to pascals, milligrams to kilograms, grams to moles of a chemical compound, etc., we determine significant figures based on the measurement values not the conversion factors. **Conversion factors** are definitions and not meas-

urements. By definition there are 2.2046 lb per 1 kg, 4.1840 J per 1 cal, 101,325 Pa per 1 atm, 60 s per min, 0 K = -273.15 ^{0}C, and 1 eV = 1.602 x 10^{19} J. An attempt should be made to enter conversion factors to several more significant places than other factors. Likewise, constants in equations, which come from definitions, cannot be least precise factors. For example, Bragg's law used in X-ray diffraction spectroscopy used to determine crystal structures is given as:

$$n\lambda = 2d \sin\theta$$

In the equation, n is an integer (1, 2, 3, ….), and the order of diffraction; λ (Greek letter, lambda) is the wavelength in angstroms (Å); d is the interplanar spacing in angstroms; and θ (Greek letter, theta) is the diffraction angle in degrees. The n and 2 in the equation cannot be least precise factors. Another example is the magnitude of kinetic energy, E_k, of an object, which depends on its mass, m, and speed, v:

$$E_k = \frac{1}{2}mv^2$$

In this equation, the ½ cannot be a least precise factor.

Guideline 7. When adding numbers, carry all digits during additions. Round off the **sum** to the same number of decimal places as the **addend** with the fewest decimal places. That is, the number of digits to the right of the decimal point in the answer is determined by the measurement that has the least number of digits to the right of the decimal point. For instance, 48.0 g clay + 19.144 g silt + 32.00 g sand + 6.02 g organic matter = 105.2 g soil sample.

Guideline 8. When subtracting a series of numbers, carry all digits during the subtractions. Round off the final result to the same number of decimal places as the number in the series with the fewest decimal places. For instance, 64.44 - 84.6249 = - 20.18. From this example and the one given in Guidelines 7, it can be seen that in adding or subtracting, the concern is not with significant figures but with the digits to the right of the decimal point. The measurement with the fewest such digits dictates the number of significant figures *(15)*.

Guideline 9. When determining the number of significant figures in an experimental slope and intercept, the number of significant figures in the intercept should be the same as those in the original measured data *(16)*. In determining slope of a linear equation from two points on a line e.g. (x_1, y_1) and (x_2, y_2), the slope m of the line can be defined as rise over run:

$$m = \frac{y_2 - y_1}{x_2 - x_1} \quad or \quad \frac{y_1 - y_2}{x_1 - x_2} \quad where \quad x_1 \neq x_2$$

Under significant figure convention, the number of significant figures of the slope is dictated by the factor with the fewest significant figures. For example during thermogravimetric analysis (TA) the weight of a heated substance decreased linearly from 170.4 µg at 0 °C to 160.4 µg at 2041 °C. The rate of change, m, in mass per temperature is given by:

(170.4 µg - 160.4 µg) / (2041 °C - 0 °C) = 10.0 / 2040 = 0.00490 µg / °C

Another example would be the determination of calibration constants. For example, we have a liquid known to have a kinematic viscosity of 22.72 cS at 25 °C and capillary viscometer reading of 125 sec. If an unknown liquid was then tested with the same viscometer and found to give a time of 155 sec, we would compute the kinematic viscosity of the unknown liquid as follows:

Calibration constant = 22.72 cS /125 sec = 0.18176 cS sec^{-1}

Kinematic viscosity of unknown = (0.18176 cS sec^{-1})(155 sec)= 28.2 cS

Guideline 10.   When transforming numerical results, the number of significant figures in the transformed data should be the same as the significant figures in the untransformed results because the level of precision does not change in the transformed values *(17)*. Take for example potentiometric determination of Ca^{2+} yielding 6 µg mL^{-1} transformed to a log 6. If the log transformation were reported as 0.778 instead of 0.8, this would imply uncertainty of the transformed value has shifted from 1 part in 6 (16.7%) to 1 part in 778 (0.128%). The improved precision in the transformed datum is grossly inaccurate.

Guideline 11.   For statistically analyzed numerical results, rounding off final values for a report may be decided based on the minimum significant difference of the compared values *(18)*. Take, for instance, in a research that was comparing two nitrate-nitrogen sources N1-NO_3^- and N2-NO_3^- as fertilizers for ornamental plants, the results showed mean values of 2.24 µg mL^{-1} NO_3^- for N1-NO_3^- and 2.05 µg mL^{-1} NO_3^- for N2-NO_3^- in soil extracts treated with the two sources. The difference between the two fertilizers is 2.24 µg mL^{-1} - 2.05 µg mL^{-1} = 0.19 µg mL^{-1}. If the value 2.24 µg mL^{-1} NO_3^- were rounded off to 2 significant figures, we would have 2.2 µg mL^{-1} NO_3^-. If the value 2.05 µg mL^{-1} NO_3^- were also rounded off to 2 significant figures, we would have 2.1 µg mL^{-1} NO_3^-. The difference between the rounded off values is 2.2 µg mL^{-1} - 2.1 µg mL^{-1} = 0.1 µg mL^{-1}. By rounding off to 2 significant figures, true differences as little as 0.1 or as much as 0.19 may be lost. However, if from a statistical

standpoint, the minimum difference deemed significant was 0.19 or greater, then, the extra significant figures (decimal places) add no interpretative information. On the other hand, statistical difference of less than 0.19 would add interpretative meaning to the results. According to Garland, Nibler, and Shoemaker *(19),* the number of figures to retain in experimental raw data and preliminary calculations should exceed a certain minimum.

Guideline 12. When performing multi-step calculations apply the described guidelines above in the following order of mathematical operations:

1st Parentheses, brackets, or braces, are calculated from the inside out.

2nd Exponents are computed.

3rd Multiplication calculations are done.

4th Division calculations are carried.

5th and 6th Addition and subtraction operations are done.

For example: GC measurements of phenol concentration in 10 swine slurry samples collected from the swine producers in the Commonwealth of Pennsylvania were: 6.5, 6.6, 6.7, 6.8, 7.1, 7.3, 7.4, 7.7, 7.7, 7.7 mg L^{-1}. The sample estimate of the standard deviation of the measurements can be calculated using the formula:

$$s = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}$$

We calculate what is in the parentheses, brackets, or braces, starting from the inside out.

$$\left(\sum x^2\right) = 513.27$$

$$\left(\sum x\right)^2 = (715)^2$$

$$(n-1) = (10-1)$$

Then we compute the second "layer" as follows:

$$10\left(\sum x^2\right) = 10(513.27)$$

$$\left(\sum x\right)^2 = (715)^2$$

$$10(n-1) = 10(10-1) = 9$$

to have

$$s = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}} = \sqrt{\frac{10(513.27) - (71.5)^2}{10(10-1)}} = \sqrt{\frac{10(513.27) - (5112.25)}{10(9)}}.$$

Then we do the multiplication within the square root sign to get:

$$\sqrt{\frac{(5132.7 - 5112.25)}{90}}$$

Then we perform the subtraction to get the ratio $\dfrac{20.45}{90}$.

$$= \sqrt{\frac{20.45}{90}} = \sqrt{0.227222} = 0.476678 = 0.5 \ mg \ L^{-1}$$

The final answer is 0.5 mg L^{-1} because it is rounded off. The rounding off was based on the subtraction rule applied to 5132.7 – 5112.25. When subtracting a series of numbers, we carry all digits during the subtractions and then round off the final result to the same number of decimal places as the number in the series with the fewest decimal places (5132.7 has one decimal place). The value 90 is an integer (counting number) that does not control the significant digits in the final value. Therefore the final result was rounded to 0.5.

To give another example, if we were to calculate the **standard score**, or **z score** (the number of standard deviations that a given value x is above or below the mean) for a phenol measurement of 7.6 mg L^{-1} we would have:

$$z = \frac{x - \bar{x}}{s} = \frac{x - \bar{x}}{\sqrt{\dfrac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}} = \frac{7.6 - 7.15}{0.476678} = \frac{0.45}{0.47668} = 0.9$$

The square root of any value, x, can be written using brackets as $(x)^{1/2}$.

There are several things to note in the above computations:

▪   The order of mathematical computations was followed.

▪   Rounding to significant figures was done at the end, after all calculations.

- The final answer is 0.9 and not 0.94 because 7.6 – 7.15 gives a value with one significant figure (0.4) based on subtraction and addition guidelines on determining significant figures.

Unit 7: **Guidelines on Rounding Off Chemical Measurements and Their Calculated Results**

Significant figure can be viewed as a term that refers to rounding a numerical value to the number of digits consistent with the confidence that can be placed in it. Thus, the number of significant figures is said to be the number of digits remaining when the data is so rounded *(7)*. **Rounding-off** a value is dropping all digits that are not significant. Significant figures are the ones you are sure of except the rightmost one, which is normally taken to be uncertain within half a unit. This ensures that reported data have no more digits than are justified by their precision and manufacturer's instrumental specification, and therefore are not misleading or depriving end users of important interpretative information. The following is a list of guidelines that should be used in rounding off chemical measurements *(6-7, 20)*:

Guideline 1. First determine the **rounding digit** and the **decision digit**. The **rounding digit** is the digit in the last position you keep, and the **decision digit** is the digit in the first position you discard, that is, the digit immediately after the one to be retained *(20)*. For example, suppose you measure microbial biomass carbon in a soil extract and you get a **9.3049** mg L^{-1} reading from a TOC analyzer. If the decision is to retain three significant figures, then digit **0** is the rounding digit and **4** is the decision digit. When two or more figures are to the right of the last rounding digit, they are considered as a group in rounding decisions *(7)*. Thus the digits **49** are considered as a group in rounding decisions. Since numerical data are often obtained with more digits than are justified by the instrumental accuracy or precision, the first thing to do in rounding-off is therefore to determine the number of digits you want to keep consistent with the level of confidence that can be ascribed. As said earlier, the decision should be based upon detection limits of the instrument, manufacturer's specifications, test measurements to determine precision, other reports, experience, and the client's specification. Details are given below.

Guideline 2. If the decision **digit** is less than 5, it is dropped and the rounding digit is retained unchanged. For example: 7.57499 become 7.57 to three significant figures. The digit **7** in **57** is the rounding digit and the group **4**99 is the decision digit and it is less than **5**00; it is therefore dropped. Let's look again at the previous example in Guideline 1. The measured microbial biomass carbon was **9.3049**

mg L^{-1}. The decision group was **49** and since it is less than **5**0, it is drooped off and we have our final result reported as **9.30** mg L^{-1}. Table 3 below gives more examples on rounding digits, decision digits, and decision groups shown in bold font.

Table 3. Examples of rounding digit, decision digit, and decision groups used in rounding off results.

Sample ID	TOC Conc. (mg L^{-1})	Desired Significant figures, TOC Conc. (mg L^{-1})	Rounding Digit (in bold)	Decision digit (in bold)	Decision Group (in bold)	Reported Result, TOC Conc. (mg L^{-1})
Hdwd N-150	9.1188	1	**9**.1188	9.**1**188	9.**1188**	**9**
Hdwd N-151	9.1500	2	9.**1**500	9.1**5**00	9.1**500**	**9.2**
Hdwd N-152	10.9980	3	10.**9**980	10.9**9**80	10.9**980**	**11.0**
Hdwd N-153	8.9791	4	8.97**9**1	8.979**1**	none	**8.979**
Hdwd N-154	9.3049	5	9.304**9**	none	none	**9.3049**
Hdwd N-155	11.0173	6	11.017**3**	none	none	**11.0173**

Guideline 3. If the decision digit is greater than 5, the rounding digit is increased by 1. For example: 7.57602 become 7.5**8** to three significant figures. The digit **7** in 5**7** is the rounding digit and the group **602** is the decision group and it is greater that 500; the rounding digit is therefore increased by 1 to make 8. Another example: 7.575001 would become 7.58 because the decision group 5001 is greater than 500. See more examples given in Table 3 above. For example, the first number in TOC concentration in column 2 of the Table 3 was measured and found to be **9.1188** mg L^{-1}. The desired significant figures for the measurement were 1. The rounding digit was **9**, the decision digit was **1** and the decision group was **1188**. The final reported result was **9** mg L^{-1}.

Guideline 4. If the decision digit is exactly 5 (that is, there are no figures other than zeros beyond the five), and the rounding digit is an **even number** (a number divisible by 2 with no remainder), the rounding digit is left unchanged. For example: **7.54500** become **7.54** to three significant figures. The digit 4 is the even rounding digit and the group 500 is the decision digit and it is equal to 5; the rounding digit is therefore retained unchanged.

Guideline 5. If the decision digit is exactly 5 (that is, there are no figures other than zeros beyond the five), and the rounding digit is an **odd number** (a number when divided by 2 leaves a remainder), the rounding digit is increased by 1. For example: 7.55500 become 7.56 to three significant figures. The third digit 5 is the odd rounding digit and the group 500 is the decision group and it is equal to 500; the rounding digit is therefore increased by 1 to make 6. Another way of stating Guideline 5 is that when rounding involves 5 exactly, round to the even number. In Table 3, the second measured value was **9.1500** mg L^{-1}. Rounding the value to two significant figures resulted in a reported value of **9.2** mg L^{-1}. Because some people believe there is no statistical reason for this rule, and while others may not be familiar with the more extensive rules since these are not commonly taught in primary and secondary school curricula, many authors choose not to follow Guidelines 3, 4, and 5. Instead they follow the Guideline: *If the decision digit is 5 or greater, the rounding digit is increased by 1.* However, The National Institute of Science Technology (NIST) of the U.S. Commerce Department's Technology Administration *(21)* considers even/odd rounding of numbers described in Guidelines 4 and 5 above as providing a more balanced distribution of results.

Guideline 6. If the inherent accuracy of the analytical instrument or measuring device is known, round off the results to reflect the accuracy of the instrument. The measuring device with the least accuracy will determine the significant figures of the final result (reported value). Table 4a and 4b give the accuracy, recovery, precision, and limits of error of the instrument before analysis of environmental or treatment samples. Based on these parameters, the desired quality control objectives for treatment samples were established. For example, accuracy values of 85.0 %, 90.0 %, and 90.0 % were selected for Infrared (IR) detector, and 5 mg L^{-1} and 45 mg L^{-1} working standards, respectively. Results of analysis whose recovery was below 90 % or above 110% were not accepted. The results whose accuracy was between 90 % and 110 % were rounded off to the nearest tenth because the limits of errors for both accuracy and precision *[measured value x (1-% recovery)]* or *[measured value x (1-% precision)]* were below ½ of a unit measure (Table 4b).

Guideline 7. When combining (adding) sets of results with the same measurement units, round off the final result such that the number of digits to the right of the decimal point in the final result is the same as the result that has the least number of digits to the right of the decimal point.

Guideline 8. When performing a series of calculations that rely on a relatively small difference in two values, for example, calculation of variance and standard deviation, the procedure is to carry several extra figures through the calculations and then to round off the final answer to the proper number of significant figures that would make detection of small differences possible. This will avoid the loss of all significance. Table 5a shows values of arsenic results that Jim B. Voit (Laboratory Manager, Water Evaluation Laboratory, 1400, Brush Row Rd., P.O. Box 1004, Wilberforce, OH 45384, U.S.A.; tel.: 937-376-6193; fax: 937-376-6192; e-mail: JimVoit@csu.ces.edu. http://www.iscpubs.com/articles/aln/n0202voi.pdf) analyzed in order to determine the suitability of an analytical procedure for the analysis of drinking water samples. Note the standard deviations have extra digits beyond the rounding digits in the measured arsenic values. Rounding off standard deviations to, for example, one or two decimal places as demonstrated in Table 5b would mask the differences between measured arsenic values within and across columns, and between standard deviations.

Table 4a. Example of guidelines on rounding off chemical measurements based on accuracy of the instrument.

Soil Core Extractions for Microbial Biomass Carbon- Harvard Forest
Date Samples Collected 11/ 6/00
Soil 0.5 M K_2SO_4 extracts, Processed 11/17-11/2000
Analytical Chemist: Ephraim Govere, Dynamac Corp
Date Samples Analyzed Dec 13/00
Samples diluted 5X except blank.
The results were adjusted for dilution
A = Environmental Sample   B = Duplicate   S = Spiked Sample
File = CHEM\Total Organic Carbon\Microbial_C_110600.xls

QA/QC Results at the Beginning of Environmental Samples Analysis					
Sample ID	Expected TOC Conc. (mg L^{-1})	Measured TOC Conc. (mg L^{-1})	Difference (%)	Accuracy (%)	Desired QC Objectives (%)
IR DETECTOR mV for 5 ppm	100.00	110.2160	10.2%	90.7%	85.0%
Standard 5 mg L^{-1}	5.00	4.75612	-4.9%	95.1%	90.0%
Standard 45 mg L^{-1}	45.00	42.6350	-5.3%	94.7%	90.0%

QA/QC Results for Environmental Samples						
Sample ID	Soil Wt. (g)	K$_2$SO$_4$ Extract Soln. (g)	QA/QC Sample Type	TOC Conc. (mg L^{-1})	Recovery (%)	Precision (%)
Hdwd N-150	15.02	60.59	A	9.1188		
Hdwd N-151	15.03	60.59	B	9.1552		99.7%
Hdwd N-152	15.04	60.59	S	10.9980	98.8%	
Hdwd N-153	15.01	62.93	A	8.9791		
Hdwd N-154	15.00	62.93	B	9.3049		97.5%
Hdwd N-155	15.03	62.93	S	11.0173	98.9%	
Blank	0	61.89	A	0.49733		

QA/QC Results of Internal Standards to Measure Drift				
Sample ID	Initial Value at Beginning of Analysis	Value at end of Analysis	Difference (%)	Accuracy (%)
Standard 45 mg L^{-1}	42.6350	42.8036	0.004	99.6%

Table 4b. Limit of errors for measured values.

QA/QC Results for Environmental Samples				
			Limit of Error (mg L^{-1})	
Sample ID	Measured Value (mg L^{-1})	Reported Value (mg L^{-1})	Accuracy	Precision
Hdwd N-150	9.12	9.1	0.11	0.03
Hdwd N-151	9.16	9.2	0.11	0.03
Hdwd N-152	11.00	11.0	0.13	0.03
Hdwd N-153	8.98	9.0	0.10	0.22
Hdwd N-154	9.30	9.3	0.10	0.23
Hdwd N-155	11.02	11.0	0.12	0.28

Table 5a. An example of rounding off standard deviations (SD) relative to measured values from which the SD are calculated.

Sample type Matrix	IDL (0.5 ppb) Type I reagent water	MDL (0.5 ppb) Tap water	LFM (5.0 ppb) Tap water	Sample Tap water
Duplicate sample de-terminations (μg L^{-1})	0.46	0.80	4.90	0.24
	0.50	0.74	5.43	0.09
	0.52	0.63	5.20	0.20
	0.36	0.64	5.22	0.01
	0.38	0.70	5.35	–0.03
	0.47	0.53	4.98	0.03
	0.55	0.68	5.33	0.17
	0.54	0.58	5.15	
Mean	0.47	0.66	5.20	0.10
SD	**0.06521**	**0.08225**	**0.1709**	**0.09866**

IDL = Instrument detection limit check sample using Type 1 reagent water fortified with arsenic at a level 2.5 x that of the expected or desired detection limit.

MDL = Method detection limit check sample using tap water fortified with arsenic at a level 2.5 x that of the expected or desired detection limit

LFM = A laboratory-fortified matrix sample using Cincinnati tap water fortified with arsenic at a level similar to that of laboratory-fortified blank.

Table 5b. Rounded off standard deviations to various decimal places.

Standard Deviations				Decimal Places
0.06521	0.08225	0.17090	0.09866	4
0.065	0.082	0.171	0.099	3
0.07	0.08	0.17	0.10	2
0.1	0.1	0.2	0.1	1

Guideline 9. When the results have been properly rounded off using the guidelines above, any further rounding should be decided and asked for by the user of the results (the client) from consideration of the uses to which she or he may put the results. For example, many service laboratories such as those performing soil analyses for farmers may "scoop" a certain volume of soil for analysis, whereas a research laboratory may use a more precise measuring device such as an analytical balance. The farmer may be interested in knowing how many tons per hectare of lime she should apply to the farm. The margin of error is relatively large and may not have dire consequences on crops. On the other hand, a researcher investigating a new drug dosage for people suffering from high blood pressure may want to find critical differences among treatments and therefore wants more refined data. The error associated with the wrong dosage could mean life or death, or a malpractice suit or imprisonment, or all of the above. However, no matter how the results will be used, rounding should not result in over-interpretation or under-interpretation. The fundamental principle underlying a consideration of significant figures is that the result of a calculation should also reflect the accuracy of the methods and measuring devices expected from the experiment or operations upon which the calculation is based *(3)*. Knowing the tolerances of measuring devices and validation of methods are critical to obtaining good data (Table 4). Appendix C gives tolerances of volumetric glassware, pipets, graduated cylinders, micropipettors, dispensers, burets, and analytical balances.

Unit 8: **Guidelines on Reporting a Value and Its Estimated Uncertainty**

An intrinsic feature that every quantitative measurement carries is the uncertainty associated with it caused by measurement errors. Uncertainty can be defined as a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the **measurand** such as (mass, amount, number, or volume) concentration of an analyte *(22-23)*. Since knowledge of the measurement uncertainty implies increased confidence in the validity of a measurement, one of the essential skills of a laboratory analyst is the ability to correctly determine and intelligently report measurement uncertainties. Sources of uncertainty include sampling, storage conditions, instrument effects, reagent purity, measurement conditions, sample effects, computational effects, blank correction, operator effects, and random effects *(24)*. Skoog *(25)* grouped measurement errors into two broad categories: **determinate** and **indeterminate**.

Determinate errors are those that can potentially be isolated, identified, accounted for, and corrected. They include

1. instrumental errors

2. method errors

3. personal errors

Sources of **instrumental errors** include increased circuit resistance, vibration, electronic faults, and temperature effects on detectors. **Method errors** may arise from the chemical and physical condition of reagents and reactions. They may include contamination of reagents, instability of reagents, chemical interference and incomplete reactions. **Personal errors** include blunders by laboratory personnel. The errors may be from:

1. Measuring the wrong sample.

2. Transcription or transposing measured values.

3. Misreading a scale.

4. Mechanical loss.

Determinate errors are systematic. Systematic errors are constant no matter how many measurements are made. The errors are always of the same sign and magnitude and produce the same **bias**. Bias is a consistent deviation of measured values from the true or expected value.

Indeterminate errors in instrumental measurements are those random errors that manifest themselves in a form of small, random fluctuations that are not detectable individually but have cumulative effect that is recognized as noise and is taken care of by methods of statistics. Unlike **systematic errors**, **random errors** vary in sign and magnitude and are unpredictable. Random errors average out and approach zero if enough measurements are made. Thus because of the presence of indeterminate errors, there is a consensus that the reporting of measurements and calculated values from them should indicate the measurement itself or the calculated value and an estimate of the measurement uncertainties.

Instead of using the **significant figure convention** in expressing measurements and calculations from them by **stand-alone significant figures** (measurement-based quantities for which the uncertainties are not given directly, and must be inferred from the number of significant figures used to represent them), Reilly *(4)* suggested an alternative approach that recognizes the presence of errors in measurements. He suggested writing measurements and numbers derived from them in the form: $x \pm u_x$ where x is the measurement or value calculated from it and u_x represents the uncertainty or error magnitude in it. The u_x is the number ordinarily used in stating how much error is expected. Calculating and expressing measurements in this way is more flexible than the significant figure convention because u_x is not restricted to a value of five. Thus, Reilly's approach shows how big an error is likely to occur in measurement than to know its maximum possible value as is the case in the significant figure convention approach. In fact, the Institute of Reference Materials and Measurements founded the International Measurement Evaluation Program (IMEP) as an awareness program and as a tool to show the true state of chemical measurement results, both to practitioners and end users of chemical results. One of IMEP's requirements in reporting results is that measured values are reported with their uncertainties *(26)*. Reilly *(4)* suggested the following guidelines in calculating and expressing uncertainty in decimal numbers.

Guideline 1. All mathematical numbers such as e, π, etc., should be expressed using the significant figure convention.

Guideline 2. Enough extra digits should be carried in all arithmetical calculations that the rounded results would not be changed if more were carried. This usually requires two or three extra digits. This guideline is easily followed because many people do not write down (rightly so) intermediate answers in a

multi-step calculation; they carry the entire calculated number in the computer or calculator and write the final answer.

Guideline 3. The significant figure convention should never be applied for the purpose of expressing uncertainty in measurements or results of calculations on them. As defined earlier in Unit 3, significant digits or significant figures are digits read from the measuring instrument plus one doubtful digit estimated by the observer. This is different from measurement of uncertainty. Uncertainty is usually called experimental error. When an accepted or standard value of the physical quantity is known, the percent error is calculated to compare an experimental measurement with a standard. This is expressed as percent accuracy in Table 4a. It can be seen from Table 4a that when a known quantity of standard e.g. 5.00 mg L^{-1} was measured on an analyzer, a concentration of 4.765612 mg L^{-1} total organic carbon was read from the instrument. The significant figure for this reading was 4.76 mg L^{-1}. The percent difference or percent error was - 4.9 %, and the percent accuracy was 95.1 %. In Table 4a percent difference was computed as follows:

$$ Percent\ Error = 100 \left(\frac{Experimental\ value\ \ -\ \ Standard\ value}{Standard\ value} \right) $$

When there is no standard, two or more experimental measurements can be used to determine percent difference. By subtracting the percent difference from 100 %, we get precision. Table 4a gives the percent precision values. The calculation is:

$$ Percent\ Error = 100 \left(\frac{Larger\ experimental\ value\ \ -\ \ Smaller\ experimental\ value}{Average\ experimental\ value} \right) $$

From the above discussion, it can be seen that significant figure convention should never be applied for the purpose of expressing uncertainty in measurements or results of calculations on them. Determination of significant digits in measured values and determination of uncertainties of measured values are different processes. A more detailed discussion of uncertainty is covered below.

Guideline 4. Measurements and the results of calculations on them should be presented by showing the decimal number plus or minus its uncertainty, for example, $x \pm u_x$. If u_x is the standard deviation, then it is the uncertainty of the result x_i and is called **standard uncertainty** (23-24). If we have a result P $\pm u_p$ where u_p is a value obtained by combining standard uncertainties following Guidelines 5 and 6 given below, then, u_p is called **combined standard uncertainty**. If we multiply the combined uncertainty value by a **coverage factor**, a level of confidence factor (usually 2 or 3) e.g. (2 x u_p) for 95%, and (3 x u_p) for 99% confidence level, we get what is called **expanded uncertainty** (22-24). The best way to determine uncertainty is by statistical treatment of the data.

Guideline 5. The uncertainty in the sum or difference of uncertain numbers is found as the square root of the sum of the squares of the uncertainty in the individual numbers. Thus,

$$u_{(x1+x2+...+xn)} \text{ or } u_{(x1-x2-...-xn)} = \left\{ (u_{x1})^2 + (u_{x2})^2 + ... + (u_{xn})^2 \right\}^{1/2} \rightarrow \text{uncertainty in the sum or difference.}$$

For example: Given the equation for computing the result, *P*, as: $P = x - y + z$

Where: P is the result, and x, y, z are measurements and have the following values:

Measurements:
$$x = 10.3 \pm 0.1$$
$$y = 9.34 \pm 0.07$$
$$z = 3.026 \pm 0.002$$

P would be determined as follows:

$P = (10.3 \pm 0.1) - (9.34 \pm 0.07) + (3.026 \pm 0.002)$

$= (10.3 - 9.34 + 3.026) \pm \{(0.1)^2 + (0.07)^2 \pm (0.002)^2\}^{1/2} = \textbf{4.0} \pm \textbf{0.1}$

The expanded uncertainty (2 x 0.1) indicates that 95% of the time, the true value is equally likely to occur anywhere over the interval from [4.0 - (2 x 0.1] to [4.0 + (2 x 0.1)] = 3.8 to 4.2. The result **4.0 ± 0.1** can also be reported as a value and its relative uncertainty or percent of the measured value as follows: $P = \textbf{4.0} \pm \textbf{2.5\%}$

To further demonstrate the process of determining significant figures, we can add constants to the equation: $P = ax - by + cz$

		Measurements:			Constants:	
		$x = 10.3 \pm 0.1$			$a = 5$	
		$y = 9.34 \pm 0.07$			$b = -3$	
		$z = 3.026 \pm 0.002$			$c = 2$	

Measurement Variable	Constant (*C*)	Measurement (*M*)	Uncertainty (U)	*C**M	*C**U	*C**U Squared
x	5	10.3	0.1	51.50	0.5	0.25
y	-3	9.34	0.07	-(-28.02)	-0.21	0.0441
z	2	3.026	0.002	6.0520	0.004	0.000016000

Sum of Squares of Uncertainties (SSU)   =   0.29412
Calculated result *P* (Sum of *C**M)   =   85.572
Calculated Uncertainty Value (Square root of SSU)   =   0.54232

Proper significant figures for calculated result *P*   =   **85.6**
Proper significant figures for calculated uncertainty value   =   **0.5**

Result with its propagated uncertainties of measurements   =   **85.6 ± 0.5**
Result with its percent propagated uncertainties of measurements   =   **85.6 ± 0.6 %**

The value reported as 85.6 ± 0.5 or without ± as 85.6 because the uncertainty is in the tenths place. This is the same result the simple rule of tenths being limiting in the three factors. Varavuk (1986) suggested that when given the sum and its uncertainty, the sum is rounded off one digit less than the digits of the highest uncertainty (least precise) value. For example, given a sum and its uncertainty as 63.372 ± 0.0555 mL, an imprecision of ± 0.0555 mL means that all digits at the hundredths place and beyond are uncertain. Thus, 63.372 mL is rounded to the nearest hundredth: 63.37. If the sum and its uncertainty were 63.372 ± 0.555 mL it would mean that all digits beyond the tenths place are uncertain. We would round the sum to the nearest tenth, 63.4.

Guideline 6. The relative uncertainty in the **product** or **quotient** of uncertain numbers is the square root of the sum of the squares of the relative uncertainties in the individual numbers. Thus given $y = x_1 * x_2 * ... * x_n$ or $y = x_1/x_2$, the relative uncertainty is given as;

$$u_{(y)} = y \left\{ \left(\frac{u_{x1}}{x_1} \right)^2 + \left(\frac{u_{x2}}{x_2} \right)^2 + ... + \left(\frac{u_{xn}}{x_n} \right)^2 \right\}^{1/2} \text{ -> uncertainty in a product or quotient}$$

The product or quotient and its uncertainty can be given as:

$$y \pm u_{(y)} = y \left\{ 1 \pm \left[\sum_{i=1}^{n} \left(\frac{u_{xi}}{x_i} \right)^2 \right]^{1/2} \right\}$$

For example, if $P = (18.3 \pm 0.1)/(22.34 \pm 0.27)$

then

$$P \pm u_{(P)} = \frac{(18.3 \pm 0.1)}{(22.34 \pm 0.27)} = \frac{(18.3)}{(22.34)} \left\{ 1 \pm \left[\left(\frac{0.1}{18.3} \right)^2 + \left(\frac{0.27}{22.34} \right)^2 \right]^{1/2} \right\} = 0.819 \pm 0.025$$

The general rule for the uncertainty in a general function $f(x_1, x_2, \ldots x_n)$, where the x's are uncertain quantities is given by

$$u(f) = \left[\sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} u(x_i) \right)^2 \right]^{1/2}$$

To illustrate the use of the formula for a general function let

$P = (50 \pm 30) \exp(-0.22 \pm 0.04)$

$$P \pm u_{(P)} = 50 \exp(-0.22) \pm \left\{ [\exp(-0.22)x30]^2 + [-501\exp(-0.22)x0.04]^2 \right\}^{1/2}$$
$$= (40.1259 \pm 24.12908)$$

Step by step calculations are shown below.

50*EXP(-0.22)	40.1259
(EXP(-0.22)*30)^2	579.6328
(-50*EXP(-0.22)*0.04)^2	2.5761
SQRT(579.632779 + 2.576145684)	24.1290
P ± u(P)	**40.1259 ± 24.12908**

The value would be reported as: **$P \pm u_{(P)} = 40 \pm 20$**

Guideline 7. Provided that the numbers used in expressing uncertainty are arithmetically correct, there is no harm except awkwardness in showing too many figures; if too few are shown, however, the uncertainty may not be shown precisely enough. Ordinarily, the uncertainty should be shown with two to four arithmetically correct figures, disregarding leading zeros, and the number itself shown with a total number of figures to conform to the uncertainty. The number of figures in x and u_x should be large enough that the range is described finely enough. For example, $u_x = 1.4$ and $u_x = 1$ represents a 40% range difference. Thus rounding 1.4 to 1 would make the description too coarse.

Guideline 8. When reporting a value and its estimated uncertainty, the relative magnitude of the uncertainty compared with the result should dictate the number of significant figures with which the result should be reported. The uncertainty should be reported with one or two significant figures with a value between 3 and 30 whatever the place value *(1)*. Table 6 gives examples of inappropriate and appropriate rounding of values with their estimated uncertainties.

Table 6. Examples of inappropriate and appropriate rounding of values and their estimated uncertainties.

Inappropriate Published Value	Appropriate Rounding	†Significant Digits in Uncertainty
771 ± 135	$(7.7 \pm 1.4) \times 10^2$	14
65.9 ± 10.1	$(6.6 \pm 1.0) \times 10^1$	10
$e^{-(646 \pm 69)/T}$	$e^{-(650 \pm 70)/T}$	7
1.79 ± 0.78	1.8 ± 0.8	8
$e^{(8450 \pm 850)/T}$	$e^{(8400 \pm 800)/T}$	8
$(1.4488 \pm 0.0290) \times 10^{-46}$	$(1.449 \pm 0.029) \times 10^{-46}$	29
-19.9998 SE‡ 0.100842	-20.00 SE 0.10	10

†This column indicates that uncertainty values have one or two significant figures with a value between 3 and 30 whatever the place value *(1)*.

‡ SE = standard error

The following are examples presented by The National Institute of Science Technology (NIST) of the U.S. Commerce Department's Technology Administration *(21).* They illustrate what NIST considers the proper method of reporting uncertainties. The NIST guideline is that uncertainties should have no more than two significant figures. The examples are reworked to further illustrate and help understand what is presented in Table 6.

NIST Example A

Suppose the correction for a weight is computed to be 1.3578 mg and the uncertainty is 0.5775 mg.

- Based on NIST, first, round the uncertainty to two significant figures, that is, 0.58 mg. Then state the correction as 1.36 mg. Notice that the uncertainty and the correction express the same number of decimal places. Report the correction as 1.36 mg ± 0.58 mg.

- Based on Table 6, the NIST answer is incorrect. The correct result is 1.4 ± 0.6 mg. The uncertainty value 0.6 has one significant figure (6) that is between 3 and 30.

NIST Example B

The volume of a given flask is computed to be 2000.714431 mL and the uncertainty is 0.084024 mL.

- Based on NIST, first, round the uncertainty to two significant figures, that is, 0.084 mL. (Do not count the first zero after the decimal point.) Round the calculated volume to the same number of decimal places as the uncertainty statement, that is, 2000.714 mL. Report the volume as 2000.714 mL ± 0.084 mL.

- Based on Table 6, the NIST answer is incorrect. The correct result is 2000.71 ± 0.08 mL. The uncertainty value 0.08 has one significant figure (8) that is between 3 and 30.

NIST Example C

The correction for a weight is computed to be 4.3415 mg and the uncertainty is 2.0478 mg.

- Based on NIST, first, round the uncertainty to two significant figures, that is, 2.0 mg. (Notice that two significant figures are shown. The zero is a significant figure since it follows a non-zero number.) Then, round the correction to the same number of decimal places as the

uncertainty statement, that is, 4.3 mg. Report the correction as 4.3 mg ± 2.0 mg.

- Based on Table 6, the NIST answer is correct. The uncertainty value 2.0 has two significant figures (20) that are between 3 and 30.

NIST Example D

The correction for a weight is computed to be 285.41 mg and the uncertainty is 102.98 mg.

- Based on NIST, because this uncertainty is a large number, we first convert both values to the next larger commonly reported unit (i.e., 0.28541 g and 0.10298 g respectively). First, round the uncertainty to 0.10 g. (The first nonzero digit (1) is the first significant figure and the remaining digits are rounded to the nearest number following the first nonzero digit.) Then, round the correction to the point where the rounding occurred in the uncertainty statement. Round the correction to 0.29 g. Report the correction as 0.29 g ± 0.10 g.
- Based on Table 6, the NIST answer is correct. The uncertainty value 0.10 has two significant figures (10) that are between 3 and 30.

NIST Example E

The correction for a weight is computed to be 285.41 mg and the uncertainty is 33.4875 mg.

- Based on NIST, first, round the uncertainty to two significant figures, that is 33 mg. Then, round the correction to the same number of decimal places as the uncertainty statement, that is, 285 mg. Report the correction as 285 mg ± 33 mg.
- Based on Table 6, the NIST answer is incorrect. The correct result is 280 ± 30 mg. The uncertainty value 30 has one significant figure (3) that is between 3 and 30.

NIST Example F

The length of a calibrated interval is computed to be 9.9994558 ft and the uncertainty is 0.0035617 in.

- Based on NIST, first, make sure both values are reported in the same unit (i.e., convert the uncertainty to ft, 0.000296808 ft.) Then, round the value to two significant figures, that is, 0.00030 ft. Then, round the length of the interval to the same number of decimal places as

the uncertainty value, that is, 9.99946 ft. Report the length of the interval as 9.99946 ft ± 0.00030 ft.

- Based on Table 6, the NIST answer is correct. The uncertainty value 0.00030 has one significant figure (3) that is between 3 and 30.

Guideline 9. Round individual datum to 25% of the expected standard deviation per observation for recording and statistical analyses, and published treatment means to 10% of their standard errors *(27).* Standard deviation indicates how widely sample observations are distributed around the mean. In Unit 6, Guideline 12, the standard deviation of a sample with 10 observations was found to be 0.5 mg L^{-1}. This means that 95 % of the 10 observations (two standard deviations) have average values that range from [7.2 - (2 x 0.5] to [7.2 + (2*0.5)] = 6.2 to 8.2 mg L^{-1} and 99 % of the sets (three standard deviations) have average values that range from [7.2 - (3 x 0.5] to [7.2 + (3*0.5)] mg L^{-1} = 5.7 to 8.7 mg L^{-1} assuming a normal (bell-shaped) distribution. Sample standard deviation tells us how widely the spread or distribution of the observations is around the sample mean, but it does not tell us how closely the sample mean estimates the population mean. Standard error of the mean (SE) when used for normal (samples of any size) and non normal distributions (best with sample sizes >30), can estimate how accurately a sample mean estimates the population mean. In our example, the standard error of the mean would be computed as:

$$SE = \frac{SD}{\sqrt{n}} = \frac{0.5}{\sqrt{10}} = 0.16$$

Where SD is the standard deviation. The value of 0.16 indicated that 95% of the time, the true value is equally likely to occur anywhere over the interval from [7.2 -(2 x 0.16] to [7.2 + (2 x 0.16)] mg L^{-1} = 6.9 to 7.5 mg L^{-1}.

Based on this example, 25 % of 0.5 (standard deviation) is 0.125. That would mean that all digits in observation measurements beyond the tenths place are estimates or uncertain. Thus our observations should not have a value like 7.13 mg L^{-1} but rounded to 7.1 mg L^{-1}. Similarly 10 % of 0.16 (standard error of the mean) is 0.016. This means that digits beyond the hundredths place in the treatment mean are uncertain. Thus we can write the treatment mean as 7.15 mg L^{-1}.

Unit 9: **Guidelines on Reporting Significant Figures in Graph Interpretation**

Graphs are common in science literature. Chemical measurements can be presented or illustrated using graphs, and data can be extracted from graphs. The style and format of the graphs depend upon their intended purposes. The two most used graphs in analytical chemistry are computational graphs and display graphs. Computational graphs are used to extract numeric results from the data. Calibration graphs are typical examples. From the computational graphs, prediction (computational) equations are derived and used to extract numerical results. Display graphs present data sets from experiments. Display graphs are the ones most seen in laboratory reports, research journals, and scientific proceedings. A pictorial graph is used when display graphs are thought to be too complex, especially when one wants to simplify information, let's say in a textbook, or for a presentation to a target group not very familiar with the subject matter. Thus the purpose of a pictorial graph is to simplify and clearly illustrate a concept, a trend, or relationship between variables. No attempt is made to show data points or errors on pictorial graphs. However, display graphs and computational graphs should clearly show the size of the experimental uncertainties (errors) in each plotted point. This can be done in several ways, the most common being standard deviation bars and standard error bars. (Computation of these errors was illustrated in Unit 8). In Figure 1 below, the plotted point is represented as a dot, square, or triangular mark or any mark. The range of uncertainty at each datum point is shown by the extent of the vertical and horizontal bars going through datum point. The error bar types shown in 1A of Figure 1 are suitable where the error is entirely in one variable, or where the errors in both variables have been lumped together. If we are interested in showing the error in each variable explicitly, the datum point would have the extent of both vertical and horizontal bar as illustrated in 2A to 3B in Figure 1. When the uncertainties have a symmetric distribution about the mean, the error bars extend equally on either side of the points as shown in 2A, 2B and 2C in Figure1. If the data distributions are not symmetric, the plotted points will not be centrally located in the range of uncertainty and the error bars might look like those labeled 3A and 3B in Figure1. Data that are presented in display graphs and data derived from computational graphs should have appropriate significant figures. The following are guidelines on significant figures in graph construction and interpretation. The guidelines are based on Graham's *(16)* publication.

Guideline 1. The ordinate (vertical coordinate) and the abscissa (horizontal coordinate) should have the same

number of decimal places as the original rounded data for the ordinate and abscissa, respectively. For

example the data set in Table 7 is illustrated in Figure 2. The numbers of cycles (the independent

variable) in the Table are integer numbers and so are the abscissa (horizontal) numbers in the graph.

The ordinate (vertical) numbers in the graph are rounded to two decimal places and so are the num-

bers in Table 7.
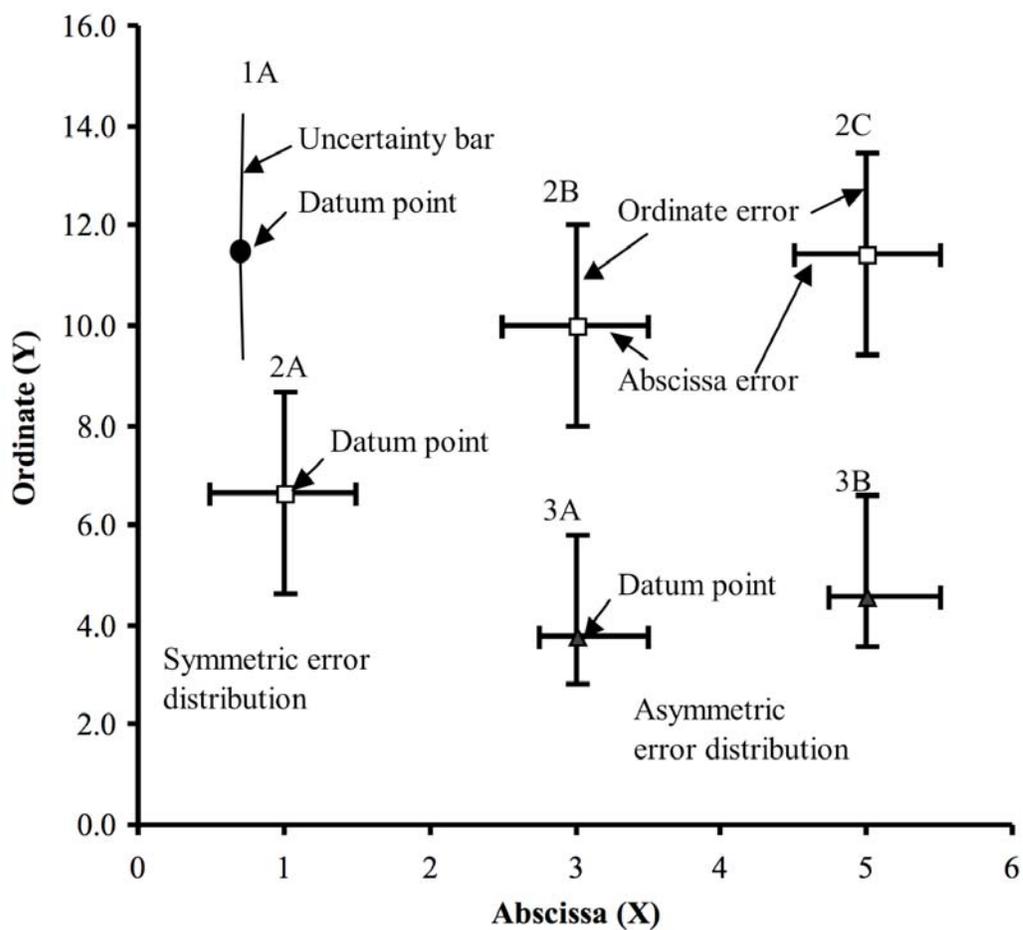
Figure 1. Illustration of plotted data points with uncertainty bars. The point on 2A has a Y uncertainty of ± 2 and X uncertainty of ± 1. The plotted points on 3A and 3B are not centrally located in the range of uncertainty and the error bars.

Table 7. Mean phenol concentration in swine slurry treated with horseradish deodorants.

	Cycles				
Horseradish Deodorants	1	2	3	4	5
NoHR&P = No HR and no peroxides	12.08	8.00	10.35	12.16	9.69
HR+HP = 20 L swine slurry + 2 kg HR + 68 mM HP	6.64	7.73	10.00	10.12	11.42
HR+CP = 20 L swine slurry + 2 kg HR + 34 mM CP	1.34	2.61	3.80	3.56	4.58
Standard Errors	3.099	1.754	2.128	2.596	2.056

☰ **NoHR&P = No HR and no peroxides**
☐ **HR+HP = 20 L swine slurry + 2 kg HR + 68 mM HP**
▨ **HR+CP = 20 L swine slurry + 2 kg HR + 34 mM CP**
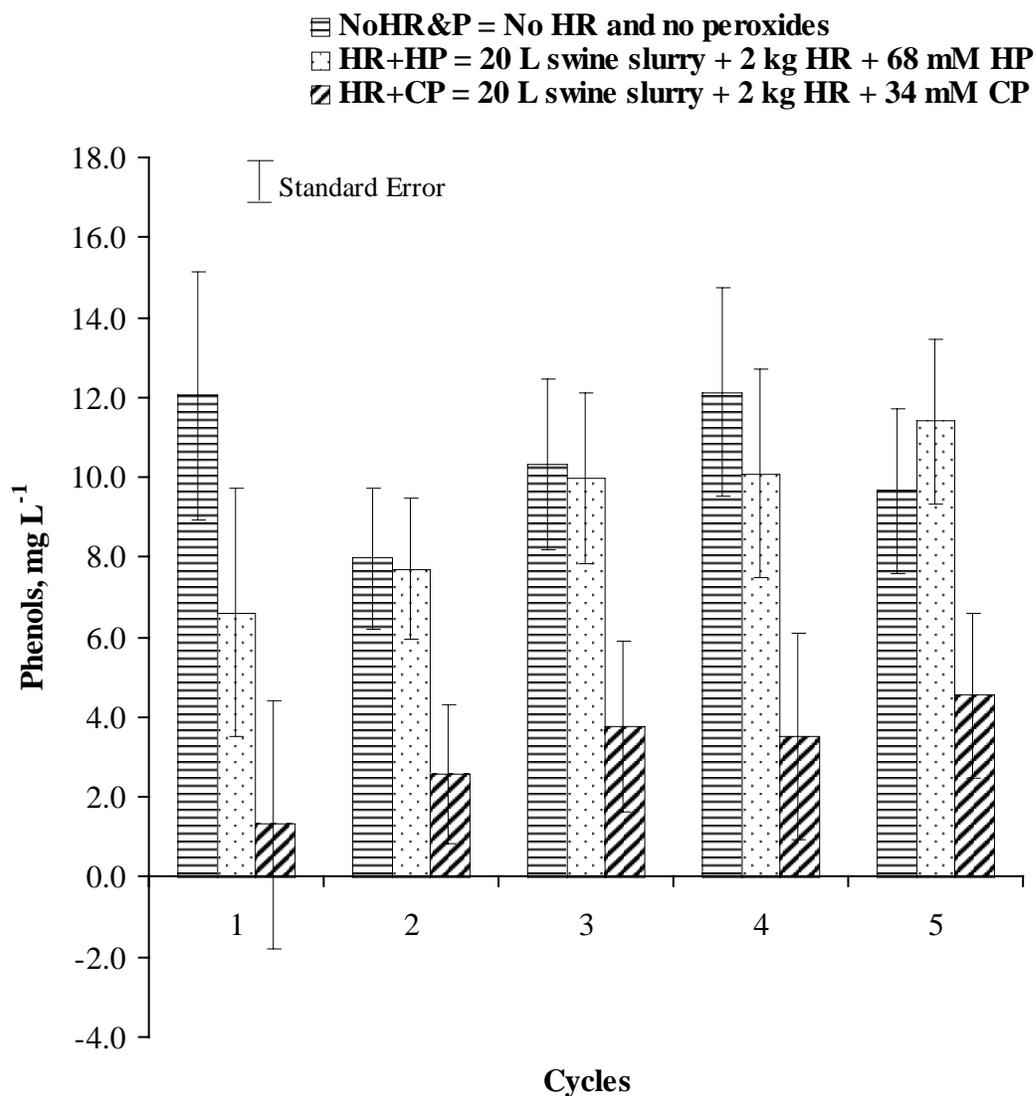
Figure 2. Effects of recycling horseradish (HR) on concentrations of phenols in swine slurry (SS) treated with horseradish + hydrogen peroxide (HR+HP), and horseradish + calcium peroxide (HR+CP) treatments.

Guideline 2. The scale or interval for the ordinate and abscissa should have the same precision level as the original data sets. As an example, data in Table 7 is graphed in Figure 2. The horizontal coordinate values in Figure 2 are 1, 2, 3, 4, and 5; the scale should be an integer and not a decimal value. That means you cannot, for example, have 0.5 as the interval for the graph or have a mark on abscissa showing 2.5. The data for the ordinate is rounded to two decimal places in Table 7, whereas in Figure 2 is rounded to only one decimal place. This is an example of incorrect way of presenting data in a graph. Both data in the Table 7 and in the graph should have the same decimal places. Table 7 has too many significant figures.

Guideline 3. The scale chosen for the ordinate and abscissa should be sufficiently expanded to show slight trends and differences. The standard error range for the ordinate is from about 2 to 3 (Table 7). Thus 2 units were chosen as the interval of the ordinate in order to show slight trends and differences (Figure 3).

Guideline 4. If the error bars represent error estimates smaller than the maximum (average deviation, standard deviation, standard error, etc.), then the line of "best fit" (fitted curve) need not pass within all of the error bars but just most of them. (The best fit line in Figure 3 is within all error bars.)

Guideline 5. The number of significant figures in the slope or intercept should be within the precision range of the original data. The number of significant figures quoted for a given slope or intercept should be consistent with the uncertainty in the measurement. From Figure 2, it would be inappropriate to quote the results as Phenol = 6 ± 3.099 mg L^{-1} for phenol concentration as affected by the HR+HP treatment because of too few significant figures in the results compared to the uncertainties. It would equally be wrong to express the result as Phenol = 6.641 ± 3 mg L^{-1} because of too many significant figures in the results compared to the uncertainties. However, giving the best estimate of the next significant figure after the one limited by the uncertainty, for example 6.64 ± 3.1 mg L^{-1} is acceptable. Because they are estimates, it is usually a good practice to write uncertainties using one significant figure, or in some cases, (for very high precision measurements, for example) with two significant figures.
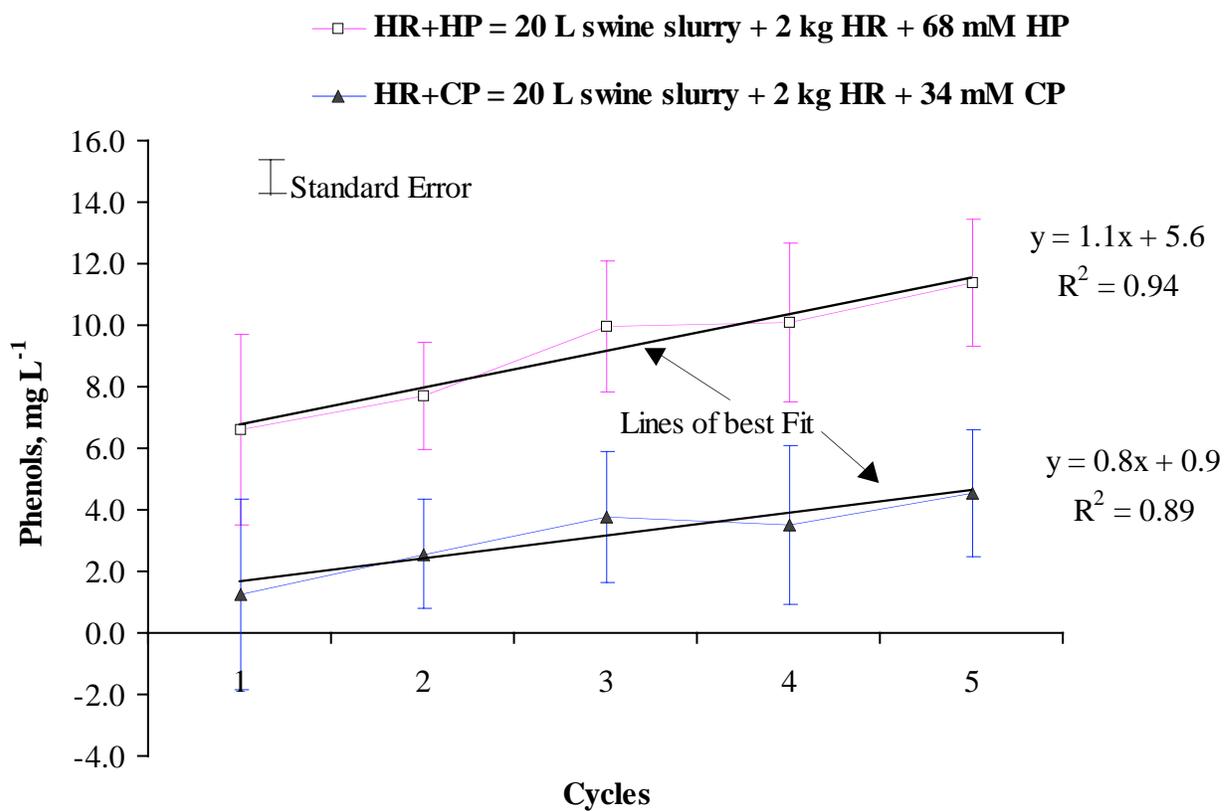
Figure 3. Effects of recycling horseradish (HR) on concentrations of phenols in swine slurry (SS) treated with horse-radish + hydrogen peroxide (HR+HP), and horseradish + calcium peroxide (HR+CP) treatments.

Guideline 6. The uncertainties in the slope and intercept should be shown in the prediction equation. For example, in a linear model $y = mx + b$, the prediction equation based on the original data should be presented in the form:

$$y = (m \pm \Delta m)x + (b \pm \Delta b)$$

Where Δm is the uncertainty in quantity m, and $\Delta\Delta b$ is the uncertainty in quantity b. A graph of this nature has three uncertainties:

1. Uncertainty (Δc) in the vertical line, c. The $\Delta\Delta c$ is deviation from a vertical line, c (not from a point but vertical from the line).

2. Uncertainty (Δb) in the ordinate intercept, b.

3. Uncertainty (Δm) in the slope, m.

The uncertainties: Δc, Δm and Δb are computed as follows:

$$\Delta c = \delta_{\Delta y *}\sqrt{\frac{\pi}{N}}$$

Where subscript Δy indicates the standard deviation in the values of the deviations from the line, not in the y values themselves, and the $\delta_{\Delta y}$ is the mean absolute deviation.

$$\Delta m = \frac{\delta_{|x-\bar{x}||\Delta y|}}{\dfrac{\sum x^2}{N} - \left(\dfrac{\sum x}{N}\right)^2}\sqrt{\frac{\pi}{N}}$$

$$\Delta b \quad = \quad \sqrt{(\Delta c)^2 + (\bar{x}\Delta m)^2}$$

Table 8 below is a table of data from Graham *(16)* that illustrates the computation of the factors in the above equations.

Table 8. Example of data for computing uncertainties in a graph.

x	y (given)	y (best-fit)	$\lVert x - \bar{x} \rVert$	x^2	$\lvert \Delta \rvert \Delta y \rVert$	$\lVert x - \bar{x} \rVert \lvert \Delta y \rVert$
10	3.48	3.43	4.5	100	0.05	0.225
11	3.57	3.55	3.5	121	0.02	0.070
12	3.61	3.68	2.5	144	0.07	0.175
13	3.79	3.80	1.5	169	0.01	0.015
14	3.89	3.92	0.5	196	0.03	0.015
15	4.06	4.05	0.5	225	0.01	0.005
16	4.19	4.17	1.5	256	0.02	0.030
17	4.25	4.29	2.5	289	0.04	0.100
18	4.47	4.42	3.5	324	0.05	0.175
19	4.53	4.54	4.5	361	0.01	0.045
$\bar{x}$ and $\left(\sum \frac{x}{N}\right)^2$				$\left(\sum x^2\right)\big/ N$	$\delta_{\lvert \Delta y \rvert}$	$\delta_{\lvert x - \bar{x} \rVert \lvert \Delta y \rvert}$
14.5 and 210.25				218.5	0.031	0.0855

Unit 10: **Use of Significant Figures as a Quality Control Objective**

Every quantitative measurement carries with it a degree of uncertainty whose magnitude depends on the nature of the measuring device and the skill with which the device is used. The detection limits of measurements for every measuring instrument and glassware automatically set the limits on the number of significant digits to which a value can be rounded-off. Anyone making a measurement has a responsibility to indicate the uncertainty associated with it. Significant figures (meaningful digits obtained in measurement) describe the degree of confidence in a measurement. With the present "computer disease", additional digits that have no meaning but merely add printing costs and obscure true meaning of data, are pumped into laboratory reports and published literature. In addition to costs and distortion of facts, the additional digits add more difficulty in evaluating the data and may even cast doubt on the value of the research itself *(3)*. While a number of readers have pointed out the non-use and misuse of significant figures in published journals, there are no indications that the problem is declining. Many authors are not paying adequate attention to significant figures. To curb this problem, **quality control objectives** that include significant figures as one of the objective criteria, should be in place at data generation points. These points include sample collection and processing, chemical preparation, and instrumental analysis. The significant figures of the final reported measurements or their calculated values should be based on all the **analytical critical path measurements (ACriPaM)**. The **ACriPaM** are measurements that are critical in obtaining precise and accurate results. In analytical chemistry the critical path measurements are mostly:

weight measurements: these include weights of samples, standards, and reagents.

volume measurements: these include volumes of samples, standards, and reagents.

instrumental measurements: these include concentrations, absorbance, transmittance, electric potentials, refractive indexes, temperature, pressure, or any desired form of measurement. Table 9 gives the ACriPaM for determining total organic and inorganic carbon in soil solutions. It is from AcriPaM that justifiable significant figures in measurement results are derived. A good **standard operating procedure** (**SOP**) or standard method of analysis should indicate the significant figures to which the measurements or their calculated results were rounded. Levy *(2)* suggested that authors should state in the Methods section the specific significant figures to which data were rounded.

To the laboratory analyst, the SOP should not only give percent accuracy, precision, and completeness, but should include ACriPaM that indicate tolerance or limits of error of measuring devices and analytical instruments as indication of uncertainties. Measuring devices with high tolerance have more unknown digits as compared to the devices with low tolerance. Appendix C gives selected measuring devices and their tolerances (uncertainties). It is from such information that ACriPaM are constructed.

A survey of literature and SOP's indicates that ACriPaM are non-existent. A most reasonable approach is defining uncertainty as the standard error of the mean and expressing chemical measurements with their component uncertainty. What are common are **stand-alone significant figures**. Stand-alone significant figures are measurement-based quantities for which the uncertainties are not given directly and must be inferred from the number of significant figures used to represent them. According to Field (1986), stand-alone significant figures are a fact of life. In their absence, it is not possible to implement Reilly's *(4)* guidelines presented earlier (see Unit 8). Reilly's guidelines are based on measurements whose component uncertainties are known. How then can one assess the quality (correctness) of stand-alone significant figures? Fields *(14)* suggested the following guidelines in form of "rules" that can be applied as quality control checks for stand-alone significant figures:

Guideline 1. **The Simple Rule:** The number of significant figures in a **product** (quantity obtained by multiplying measurements) or **quotient** (quantity obtained by dividing measurements) is equal to that of the least precise factor (the quantity with the least number of significant figures). The Simple Rule is essentially unbiased when it is used correctly but can give absurd results. According to Fields *(14),* when the component uncertainties of a multiplication or division calculation are not known, the Simple Rule can be expected to give unreasonable results about 25% of the time. To illustrate the weakness of the Simple Rule, Fields showed that the uncertainty of a quotient 0.990 obtained from

$1.01/1.020$ is 0.001, and the **implied relative uncertainty** (**IRU**) of the quotient

$\left(0.001/0.990 \ = \ 1/990 \ = \ 0.1\% \right)$ and that of the least precise factor (LPF)

$\left(0.01/1.01 \ = \ 1/101 \ = \ 1\% \right)$ differed by a factor of ten $\left(1/0.1 \ = \ 10 \right).$

Guideline 2. **The Least Precise Factor Root Rule**: Given P = IRU of the product, Q = IRU of the quotient, and L = IRU of the least precise factor, the product or quotient has been rounded to the correct number of significant figures if $\frac{1}{\sqrt{10}} < \frac{P}{L} < \sqrt{10}$. In comparing these relationships, one should express all numbers in **scientific notation** e.g. 0.0345 would be 3.45×10^{-2} where 3.45 is the mantissa, (2) find the LPF, (3) compare the mantissa of the answer and the LPF, divide the large mantissa by the smaller mantissa. If the quotient is $\geq \sqrt{10}$, then adjust the number of significant figures in the answer mantissa such that the smaller mantissa has one more significant figure than the larger. The LPF Root Rule significantly reduces the discrepancy between the IRU of the product or quotient and the LPF. According to Fields, the LPF Root Rule says that in most cases we can and should adjust the number of significant figures in the product or quotient such that uncertainty in the product or quotient is 0.3162 to 3.162 times the uncertainty of the LPF. The Pinkerton-Gleit Rule

$$\left| \log \frac{1}{IRU(LPF)} - \log \frac{1}{IRU(result)} \right| < 0.5 \text{ can be used to test if the product or quo-}$$

tient has been rounded correctly.

Guideline 3. **The 1-5 2-8 Rules:** If the precise factor begins with a "1" and the product or quotient begins with "5", "6", "7", "8" or "9" (or vice-versa) then give the quantity beginning with "1" one more significant figure than the other quantity. If the LPF begins with a "2" and the product or quotient begins "8" or "9" (or vice-versa) then give the quantity beginning with "2" one more significant figure than the other quantity. If none of the two conditions above applies, then use the Simple Rule.

Guideline 4. **The Three Rule:** Fields *(14)* summarized the Three Rule as follows: Locate the LPF and calculate its relative uncertainty using the ±1 convention. Convert the product or quotient to scientific notation, and multiply its mantissa by the relative uncertainty. This is the uncertainty of the product mantissa. Note the position (relative to the decimal point) of the first (non-zero) digit in the uncertainty of the product mantissa. Tentatively assume that the last significant digit of the product mantissa will be in the same position. Note the value of the first (non-zero) digit in the uncertainty of the product mantissa. If it is "1" or "2", everything is OK. Otherwise if it is "3" or more, then round off one more digit.

In deciding which rule to use, one should bear in mind that the fundamental idea behind any valid significant rule is that the percent uncertainty of the product or quotient will approximate that of the LPF in a calculation. Therefore, the number of significant figures used to express the product or quotient must imply an uncertainty, which is as close as possible to that implied by the LPF.

To illustrate the above rules let us assume that a freshman chemist analyzed total organic carbon (TOC) and got the following results: infrared detector analytical = 1.43 mV. Concentration conversion factor = 4.098 µg/mV. The freshman analyst gives the result as = 1.43*4.098 = 5.86014 µg TOC. Now as a quality control manager you want to tell the freshman chemist the significant figure rule to apply for the TOC instrument.

Table 9. Analytical Critical Path Measurements (ACriPaM) used to assign significant figure to total organic and inorganic carbon data generated using OI Analytical Model 700 TOC Analyzer.

Analytical Activity	Quantity Measured	Measurement Units		Measuring In-strument	Percent Tolerance	Limit of Error	
Preparing Standards							
1 Weighing standard reagents:							
sodium carbonate, primary standard	mass	0.8825	g	Mettler Toledo Professional Level, UMT/MT Series Microbal-ance	0.05%	1.0	ug
potassium acid phthalate, NBS reference	mass	0.2126	g	Mettler Toledo Professional Level, UMT/MT Series Microbal-ance	0.05%	1.0	ug
nicotinic acid	mass	0.01708	g	Mettler Toledo Professional Level, UMT/MT Series Microbal-ance	0.05%	1.0	ug
2 Making stock standard solutions							
Disolve 0.8825 g sodium carbonate in 100 mL volumetric flask and bring up to the mark with 18 megohm RO water.	volume	100	mL	Class A volu-metric flask	0.08%	0.08	mL
Desolve 0.2126 g potassium acid phtha-late in 100 mL volumetric flask and bring up to the mark with 18 megohm RO wa-ter.	volume	100	mL	Class A volu-metric flask	0.08%	0.08	mL
Desolve 0.01708 g nicotinic in 10 mL volumetric flask and bring up to the mark with 18 megohm RO water.	volume	10	mL	Class A volu-metric flask	0.2%	0.02	mL
3 Making working standard solutions							
Measure out 5 ml of the 1000 mg/l stock standard for TIC and TOC using a cali-brated Oxford pipet and place in a 1 liter volumetric flask and bring up to the mark with 18 megohm RO water (5 ppm TIC and TOC calibration std.).	volume	5000	uL	Adjustable vol-ume pipettors Series 2100	0.6%	30	uL
Measure out 4.5 ml of the 1000 mg/L stock standard for TIC and TOC using a calibrated Oxford pipet and place in a 1 liter volumetric flask and bring up to the mark with 18 megohm RO water (4.5 ppm TIC and TOC check std.).	volume	4500	uL	Adjustable vol-ume pipettors Series 2100	0.7%	30	uL
Measure out 300 uL of the 1000 mg/L stock standard for TIC and TOC using a calibrated Oxford pipet and place in a 1 liter volumetric flask and bring up to the mark with 18 megohm RO water (0.3 ppm TIC and TOC check std.).	volume	300	uL	Adjustable vol-ume pipettors Series 2100	2%	6	uL

Measure out 50 uL of the 1000 mg/L stock nicotinic acid using a calibrated Oxford pipet and place in a 10 mL volumetric flask and bring up to the mark with 18 megohm RO water (5 ppm TOC check std.).	volume	300	uL	Adjustable volume pipettors Series 2100	2%	6	uL
Making Spiked Sample Solutions							
Measure out 10 mL (5 + 5 mL) of sample using calibrated Oxford pipet and place in a sample vial.	volume	5000	uL	Adjustable volume pipettors Series 2100	1%	30	uL
Measure out 20 uL of the 1000 mg/L stock standard for TIC and TOC using a calibrated Oxford pipet and place into 10 mL sample solution (2 ppm TIC and TOC expected recovery).	volume	20	uL	Adjustable volume pipettors Series 2100	1%	0.2	uL
Measuring TIC and TOC Concentrations							
TOC range 4 ppb C to 10,000 ppm C	conc.	4 ppb - 10,000	ppm	OI Model 700 TOC Analyzer	2%	2	ppb
TIC range 1 ppb C to 10,000 ppm C	conc.	1 ppb - 10,000	ppm	OI Model 700 TOC Analyzer	1%	0.5	ppb
Data Quality Objectives							
TOC check standard (nicotinic-TOC) 5 ppm	conc.	5.0	ppm	OI Model 700 TOC Analyzer	10%	0.5	ppm
TOC and TIC check standard 0.3 ppm	conc.	0.3	ppm	OI Model 700 TOC Analyzer	50%	0.15	ppm
TOC and TIC check standard 45 ppm	conc.	45.0	ppm	OI Model 700 TOC Analyzer	10%	4.5	ppm

Simple Rule: $1.43*4.098 = 5.86$. The LPF has three significant figures, thus we round off the product to 5.86.

The LPF Root Rule:
$$\frac{\dfrac{1}{586}}{\dfrac{1}{143}} \; = \; 0.244 \quad < \quad \sqrt{10}$$

Based on the LPF Rule, the quotient is less than square root of ten. The number of significant figures in 5.86 need not be adjusted.

The 1-5 2-8 Rules: the LPF (1.43) begins with a "1" and the product begins with a "5", we therefore give the quantity with "1" one more significant figure. To give 1.43 one more significant than 5.86, we have to reduce 5.86 to 5.9. Thus the properly rounded product is 5.9.

The Three Rule: The uncertainty of the product mantissa is $\dfrac{1}{143} * 5.86014 = 0.04098$.

Because the uncertainty of the product mantissa is not "1" or "2", but "4" which is "3" or more, we therefore round off one more digit of the product to get 5.9 instead of 5.86.

For quality control purposes, it is not necessary to apply all the rules. However, an SOP or methodology should indicate the rule applied in checking and assigning significant figures to chemical measurements and calculated values from them. Table 10 gives an example of Quality Control in terms of Data Quality Objectives (DQO) that should be part of a standard operating procedure (laboratory method).

Table 10. Data quality objectives for Model 700 TOC analyzer.

Analyte	Range	Significant Figures		Accuracy	Precision	Completeness
		SF Rule	No of SF			
TOC or TIC	5.00 ppm	Simple	3	±10%	±10%	±5%
TOC or TIC	0.250 ppm	Simple	3	±50%	±50%	±5%

Unit 11: **Summary**

The digits that can be considered correct in the approximate representation of a quantity, whether measured or computed, and that are essential to conveying the numeral value to its full precision are called **significant figures**. Proper determining and reporting of significant figures avoids underestimating or overestimating the experimental results or measurements. Too few digits in the reporting of numerical values rob the user of valuable information by losing meaningful digits. On the other hand, too many digits result in retaining meaningless digits. Thus, proper application of significant figures allows for comparability of results because it adds clarity and degree of equivalence (comparability) of measurement results. This is very important in global decision-making and cross-fertilization of ideas between industries, institutions and nations. The following are some of the main points presented in this handbook that we should keep in mind when determining and reporting significant figures in chemical measurements:

1. All non-zero digits that are in a value and all zeros that are bounded on either side by a number from 1 to 9 are significant digits. Unless written in exponential notation, zeros to the right of nonzero digits may or may not be significant digits. Zeros before a decimal point with no other preceding digits from 1 to 9, and zeros that precede the first non-zero digit and position the decimal point are not significant digits.

2. When performing multiplication or division the product or quotient should have the same total number of significant figures as the measurement with the least significant figures used in the calculation. In multiplication or division of numbers in exponential notation, the result will have the same number of significant figures with those in the mantissa with fewest significant figures (the least precise factor). Conversion or counting numbers used in the calculations do not affect the significant digits of the result.

3. When adding or subtracting measurements, the sum or difference will have the same number of digits to the right of the decimal point as the number with the least such digits used in the calculation. When performing addition or subtraction of numbers in exponential notation the exponents are adjusted so that they are the same; the mantissas are then added and the common exponent is appended.

4. When taking logarithm of a measurement, the mantissa of the result should have same number of digits to the right of the decimal point as the number of significant digits in the original measurement.

5. When performing multi-step calculations apply the multiplication and division, and the addition and subtraction guidelines in the following order of mathematical operations:

    1st Parentheses, brackets, or braces, are calculated from the inside out.

2nd Exponents are computed.

3rd Multiplication calculations are done.

4th Division calculations are carried.

5th and 6th Addition and subtraction operations are done.

6. When rounding off, an acceptable rule is to increase the last significant digit by one if the quantity being discarded is more than half a unit, and leave alone if it is less than half. If the discarded quantity is exactly half a unit exactly, round the number so that the last digit is even.

7. In the propagation of uncertainties, the uncertainty in the sum or difference of uncertain numbers is found as the square root of the sum of the squares of the uncertainty in the individual numbers, whereas the relative uncertainty in the product or quotient of uncertain numbers is the square root of the sum of the squares of the relative uncertainties in the individual numbers.

8. When reporting a value and its estimated uncertainty, the relative magnitude of the uncertainty compared with the result should dictate the number of significant figures with which the result should be reported.

9. Data that are presented in display graphs and data derived from computational graphs should have appropriate significant figures and the graphs should clearly show the size of the experimental uncertainties (errors) in each plotted point.

10. Standard Operating Procedures or analytical protocols should indicate not only accuracy and precision, but also the number of significant figures in their data quality objectives. These significant figures in the results should be verified using some verification rules such as The Simple Rule, The Least Precise Factor Root Rule, The 1-5, 2-8 Rules, or The Three Rule.

The concept of significant figures ranks high among many topics that cause problems for beginning science students, laboratory technicians, and also educators and authors. Deciding the appropriate number of significant figures for the reporting of numerical data is a key step in communicating scientific information and is not an obvious or easy task. This handbook has provided step-by-step procedures for determining and reporting significant figures of measurements. It is hoped that those who utilize this handbook will be able to decide the appropriate number of significant figures of measurements based on scholarly considerations rather than arbitrary reasons of habit.

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Appendix A: Practice Questions

(Answers to the practice questions are given in Appendix D)

1. Define the following terms:
   a) Significant figures
   b) Precision
   c) Accuracy
   d) Implied relative uncertainty
   e) Least precise factor

2. What is the difference between the following terms?
   a) Scientific notation vs. engineering notation?
   b) Rounding digit vs. decision digit?
   c) Determinate vs. indeterminate errors?
   d) Mantissa vs. exponent?
   e) Limit of error vs. percent tolerance?

3. List five reasons why it is important to determine significant figures in chemical measurements.

4. Complete the following sentences by filling in *significant* or *not significant* in the black spaces.
   a) Digits from 1 to 9 in a value are _____regardless of the position of any decimal points.
   b) Zeros at the end of a number are_____ if they are to the right of the decimal point.
   c) Zeros before a decimal point with no other preceding digits from 1 to 9 are _____.
   d) Zeros at the end (final zeros) of a number are _____if the number is written with a decimal point using **scientific** or **engineering notation** to show the significant digits.
   e) If the zeros can be omitted when converting a value to the scientific form, then those zeros are _____.

5. Given the following measurements in columns one and three give their respective number of significant figures (SF) in columns two and four.

Measurement ($\mu g\ L^{-1}$)	Number of SF.	Measurement ($\mu g\ L^{-1}$)	Number of SF.
1000		35.34???	
1000		0.00	
0.010		3,700.	
0.01		1×10^{-2}	
0.001		7.873×10^{7}	

6. The speed of light in a vacuum is c = 299 792 458 m/s. Write the value to 1 significant and 4 significant figures using the scientific notation and the engineering notation.

7. Write the value 444,000 using (a) scientific notation and (b) engineering notation.

8. Correctly round off to two significant figures:
   a) Find the number of kg in 2.55 mg.
   b) The sum of 3.01 + 2234.3350 = ?
   c) The difference of 2234.0 – 3.01 = ?
   d) The product of 3.01 x 2234.3350 =?
   e) The quotient of 3.01/2234.3350 = ?
   f) The Log 3.01 = ?

9. The quantity Δz is called the absolute error while $\Delta z/z$ is called the relative error or fractional uncertainty. Percentage error is the fractional error multiplied by 100%. In practice, either the percentage error or the absolute error may be provided. Thus in machining an engine part, the tolerance is usually given as an absolute error, while electronic

components are usually given with a percentage tolerance. You are using a Serialized (Graduated) Class A Cylinders to measure 2000 mL of solution, refer to the table in Appendix C and find:
a) Absolute error, and
b) Relative error in measured volume.

10. Find the answers to the following problems and write the final result with its appropriate significant numbers for the measurement and for its uncertainty (Relly, 1992).

a) Addition and subtraction:
$(42.63 \pm 0.21) - (1.0 \pm 0.05) + (14.0 \pm 0.3)$

b) Multiplication and division:
$$\frac{2\pi(10.623 \pm 0.500)}{129 \pm 15}$$

c) Exponential
$(2.31 \pm 0.26)\exp(-1.31 \pm 0.08)$

11. The principal investigator (PI) in the lab you work under has asked you to perform the following task:

Weigh 7.000 ±0.1 g of fresh soil into a snap-cap cup.
Explain what you understand by that instruction in terms of the level of precision required in the measurement. Include a comment on the SF of the value (7.000 g) and its error term (±0.1 g). Suppose you asked the PI for more instruction and she sends back to you the following instructions:
Weigh 7.000 ±0.1 g of fresh soil into a snap-cap cup. Write down the weight of soil to 3 decimal places.

Is this instruction better that the first one? Why or why not?

12. You are looking at a digital pressure gauge with a reading of 225.4 pounds per square inch (psi). If the pressure gauge has an inherent precision of ± 1%, what would be your reported value? Indicate the real "guessed number" in 225.4. Based on the "guessed number" what value would you report as the pressure? *(28)*.

13. By convention, the last digit of a number is the one that was obtained with some uncertainty, *i.e.* it was estimated. Given the numbers in a table below, and based on the significant figures alone, give units and range in which the true value could vary. The first measurement in the first row was done for you.

Measurement (mL)	Graduated Increment (mL)	Range of True Value (mL)
25	1	24 - 26
25.0		
25.5		
25.555		
0.002		
0.0001		
2,500		
2.565		

14. Given two reported (rounded) values: 15.3 g and 15.376 g, which of two measurements were taken on a more precise balance? What is the smallest unit (readability) of each of the two balances used to measure the two weights?

15. Suppose that a 5,300-gal tank is being filled with liquid by a pump that delivers 10.50 gal min^{-1} when the tank is empty, decreasing linearly to 7.52 gal min^{-1} when the tank is full. How long does it take to fill the tank?

($dV/dt = 10.50 - 2.98\ V/V_0$ where V represents volume and t time).

16. Find the uncertainty of the sum of the following using Vatavuk's approach and Reilly's approach:

17.242 ± 0.0005
$0.73 \quad \pm 0.005$
$45.4 \quad \pm 0.05$

Use the uncertainty for each approach to round the sum. Compare the two approaches and select and justify one approach.

17. Given the following relationship between variable x and y. Determine the linear relationship by constructing a linear equation. Write the equation in the form:

$$ y = (m \pm \Delta m)x + (b \pm \Delta b) $$

where $\Delta\Delta m$ is the uncertainty in quantity m; and $\Delta\Delta b$ is the uncertainty in quantity b. (Hint: Although there are 10 y values, each given to two decimal places, the accuracy of these values is less than their precision.)

Independent Variable x	Dependent Variable y
10	4.48
11	3.52
12	3.61
13	3.79
14	3.89
15	4.06
16	4.19
17	4.25
18	4.47
19	4.53

18. Calculate and express the answer in the $y \pm u(y)$ in which $u(y)$ is the uncertainty in y (Refer to Reilly *(4)* if you fail to solve the problem).

$(42.63 \pm 0.31) - (1.0 \pm 0.05) + (14.0 \pm 0.3)$

$[2\pi(10.623 \pm 0.500)]/(129 \pm 15)$

19. William M. Vatavuk *(9)*, a chemical engineer and specialist in the cost-analysis of air-pollution-control systems presented the following data in an attempt to illustrate how to round mathematical results.

Estimating operation and maintenance cost

Cost Item	Unit cost	Annual Quantity	Annual cost		
Operation labor	$12.5/h	25,300 hr	$316,250	±	1,890
Supervisory labor	15.0/h	5,200 h	78,000	±	1,010
Maintenance labor	14.1/h	6,300 h	88,000	±	1,020
Maintenance materials			7,000	±	500
Electricity	0.056/kWh	133,000 kWh	7,448	±	94
Steam	$5.2/10^3$ lb	12.72×10^6 lb	66,144	±	662
Natural gas	$3.5/10^6$ BTU	15.2×10^9 BTU	53,200	±	935
Cooling water	$0.35/10^3$ gal	11.5×10^6 gal	4,025	±	75
Raw material A	2.53/lb	75,000 lb	189,750	±	1,640
Raw material B	0.752/lb	23,000 lb	17,296	±	388
Overhead	75% of total labor		362,310	±	2,419

Annual production = *150,000 ± 5,000 lb*	**Total O & M**	**$1,190,253**	**10,633**

	Rounded	**1,190,000**	
	O & M/lb	**7.93502**	**0.073**
	Rounded	**7.90**	

According to Caballero and Harris *(1)*, when reporting a value and its estimated uncertainty, the uncertainty should be reported with one or two significant figures with a value between 3 and 30 whatever the place value (see Table 6). Based on the guidelines by Caballero and Harris rewrite the annual cost values and their uncertainties properly and round the total operation and maintenance cost (Total O & M) and the operation and maintenance cost per pound (O & M/lb) based on your new calculations.

20. Evaluate results of your chemical measurements and judge if you followed the guidelines on determining and reporting significant figures.

21. Kundu and his coworkers *(29)* studied the removal of arsenic in water using hardened paste of Portland cement. They used two kinetic equations to estimate the pore diffusion coefficient as defined in Eq. (1) or the film diffusion coefficient as defined in Eq. (2), assuming the spherical geometry of the adsorbent.

$$t_{(1/2)}=0.030r^2/D_p \text{---(1)}$$
$$t_{(1/2)}=0.23r\delta/D_f\times(C_o/C_e) \text{---(2)}$$

Eqs. (1) and (2) are called half-time equations where r is the radius of the adsorbent in cm, $\underline{\delta}$ is the thickness of the water film adhered to the adsorbent in cm, D_p and D_f are the pore and film diffusion coefficients, respectively in cm^2 s^{-1}, C_o and C_e are the concentration of the metal ions on the adsorbent and in solution at equilibrium respectively and $t_{(1/2)}$ is the time required to bring down the metal concentration to half the initial concentration in seconds.

The D_p and D_f values can be calculated for different initial concentrations assuming $\delta = 0.001$ and the values obtained are presented in a table below. If film diffusion is the rate limiting step, the value of film diffusion coefficient (D_f) should be between 10^{-6} and 10^{-8} cm^2/s, but on the other hand, if the pore diffusion is in the rate limiting step, the pore diffusion coefficient (D_p) should be in the range of 10^{-11} and 10^{-13} cm^2/s for heavy metals.

(a) Calculate diffusion coefficient (D_f and D_p) from first order data for the determination of rate-limiting step using data presented in the table below and present your answer in scientific and engineering notation.

(b) Which one (pore diffusion or film diffusion) is the rate-limiting step for the Kundu et. al.*(29)* study?

Initial conc. (C_0) in ppm	Equilibrium conc. (C_e) in ppm	First order rate constant, K_1 (S^{-1})	Time to reach half conc. $t_{1/2}$ (S)	Mean geometric radius r (cm)	Film diffusion coefficient D_f (cm^2 s^{-1})	Pore diffusion coefficient D_p (cm^2 s^{-1})
0.2	0.053	6.51×10^{-6}	1.06×10^{5}	0.245	?	?
0.5	0.106	8.05×10^{-6}	0.860×10^{5}	0.245	?	?

Calculate D_p and D_f values for different initial concentrations assuming $\delta = 0.001$.

Appendix B: The Main Number System Used In Reporting Chemical Measurements

The main number systems used in quantitative analysis are the **real number system** and the **complex number system** *(30)*. Quantitative analytical chemical data are reported in the real number system. The real number system has the following subsets:

1. Negative and non-negative numbers
2. Natural numbers
3. Whole numbers
4. Integers
5. Fractions
6. Rational numbers
7. Irrational numbers

Negative numbers are values less than zero (e.g. -80), and **non-negative numbers** are values greater than or equal to zero (e.g. 80). However, an **absolute value** of a negative number is its non-negative value. The absolute value of a real number is its magnitude. **Magnitude** can be defined as the distance between two numbers on a number line. Thus the **absolute value** of -80 is 80; mathematically presented as $|-80| = 80$.

The simplest number system comprises the **natural numbers**. Natural numbers are positive real numbers used in counting discrete objects. The numbers {0, 1, 2, 3, 4, 5 ...} are a set of **counting** or **integral numbers** known as natural numbers. Thus a natural number is one of the counting numbers: a number that can represent the cardinality of a finite set of objects. **Cardinality** refers to cardinal number which is a number that designates the manyness of a set of objects, but not the order in which they are arranged. For instance, 48 samples, the 48 is a cardinal number. The numbers {1, 2, 3, 4, 5 ...} are **whole numbers**. The whole numbers, their negative equivalents and the zero, comprise the **integers**. Thus the numbers {...-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5 ...} are a set of integers. Thus integer numbers are an extension of natural numbers by way of including negatives of the natural numbers. When numbers are expressed as ratios (fractions) of integers or equivalently as terminating, or repeating, decimals, they are called **rational numbers** *(20)*. Examples of rational numbers are:

$$\frac{4}{1} = 4.000...; \qquad \frac{1}{2} = 0.5000...; \qquad \frac{4}{3} = 1.333...; \qquad \frac{8}{25} = 0.32000...; \qquad \frac{3}{11} = 0.272727...;$$

$$\frac{5}{7} = 0.714285714285714285...$$

From the given examples, it can be seen that rational numbers have repeating decimals; that is, from some point the decimals consists entirely of zeros or else a fixed finite string of digits that is repeated over and over. From the previous example,

$$\frac{4}{1} = 4.000...$$

it can be concluded that every integer is a rational number because integer X can be written as

$$\frac{X}{1} \ .$$

It can be seen that rational numbers, e.g.

$$\frac{8}{25} \quad \text{or} \quad \frac{4}{3}$$

are just ordinary fractions. A **fraction** is a number that expresses a ratio. Fractions have integers as both numerator and denominator. Fractions can further be characterized as **proper fractions** e.g. $\frac{8}{25}$ or **improper fractions** e.g. $\frac{4}{3}$.

Improper fractions can be written as mixed numbers e.g. $\frac{4}{3}$ can be changed to a mixed number $1\frac{1}{3}$.

Numbers not expressible as ratios of integers are called **irrational numbers**. Irrational numbers are represented by decimals that are infinite and non-repeating. For instance, the number π, which is the area of a circle the radius of which is one, has a value of 3.14159265358979323846..., has a non-terminating and non-repeating decimal expansion.

Similarly the decimal expansion of the number $\sqrt{2}$, which is the length of the diagonal of a square (or the hypotenuse of an isosceles right triangle) the side of which has length equal to 1, is a non-terminating quantity, 1.41421356237... The number e, the base of the natural logarithms, is an irrational number too $\{ e = 2.71828... \}$. Other examples of irrational numbers are:

$$1 + \sqrt{2} \; ; \quad \sqrt[3]{7} \; ; \quad \sqrt{3} \; ; \quad -\sqrt{5} \; ; \quad \cos 19^{\circ}; \quad \frac{1 + \sqrt{5}}{2} \; .$$

From the discussion above, a real number can be a natural number, whole number, integer, rational number or irrational number. For real numbers a and b, the number $a + bi$ is a **complex number**, where $i = \sqrt{-1}$. Complex numbers are called **imaginary** numbers when $b \neq 0$, and **pure imaginary numbers** when $a = 0$ and $b \neq 0$. The set of real numbers is a subset of the set of complex numbers because every real number a can be written as a complex number using $b = 0$. That is, for every real number a, you can write $a = a + 0i$. Therefore, it can be stated that every number is a complex number; a complex number is the sum of a real number and an imaginary number, the latter itself equal to the product of a real number with i (the square root of -1); a real number is either a rational number or irrational number; a rational number may be either an integer or a fraction, while an irrational number may be either an **algebraic number** (as are all rational numbers) or a **transcendental number** such as π or e^x. Quantitative analytical chemical results are mainly reported using the ***decimal system***. The decimal system uses ten different **figures** or **digits** 0, 1, 2, 3, 4, 5, 6, 7, 8, 9. The digits can stand-alone or can be arranged to make an analytical value. A decimal system is a real number system.

Appendix C: Tolerances Of Measuring Devices

Tolerances on Class A Volumetric Flasks

Capacity (mL)	Limit of Error (mL)†	Percent Tolerance (%)‡
10	0.02	0.2
25	0.03	0.12
50	0.05	0.1
100	0.08	0.08
200	0.10	0.05
250	0.12	0.048
500	0.20	0.040
1000	0.30	0.03
2000	0.50	0.025

†Limit of error as specified by manufacturer

‡Percent tolerance $= \dfrac{Limit\ of\ Error}{Capacity} * 100$

Note that the larger flasks have a tolerance of 0.1% or better, while the smaller ones are less accurate. Smaller flasks are also more difficult to use and more fragile. It is better to avoid them whenever possible. They may have to be used for very small samples or with expensive solvents.

Tolerances on Class A Volumetric Pipets (Transfer Pipets)

Capacity (mL)	Limit of Error (mL)	Percent Tolerance (%)
1	0.006	0.6
2	0.006	0.3
3	0.010	0.33
4	0.010	0.25
5	0.010	0.2
10	0.020	0.2
20	0.030	0.15
25	0.030	0.12
50	0.050	0.1
100	0.080	0.08
200	0.100	0.05

Usually volumetric transfer pipets range in size from 1.0 to 100 mL. They are used to deliver a specified volume of liquid into a container. Usually the volumetric pipet is calibrated to deliver (TD). Do not blow out (or otherwise remove) the last drop of material remaining in the tip. Allow the tip to touch the surface of the liquid in the receiving flask, so a little more liquid drains out from the tip: if this is inconvenient, touch the side of the receiver with the tip of the pipet to drain out nearly the same amount. Note that the accuracy is 0.33% or better for 2 mL or larger pipets. The 1 mL volumetric pipet is not used when high precision is required since its precision is only 0.6%, i.e. 1 mL ± 0.006 mL.

Tolerances on Measuring Graduated Pipets

Capacity (mL)	Limit of Error (mL)	Percent Tolerance (%) (full capacity)
0.1	0.005	5
0.2	0.008	4

0.5	0.02	4
1.0	0.02	2
2.0	0.06	3
5.0	0.07	1.4
10.0	0.07	0.7
25.0	0.10	0.4

A transfer pipet will measure only a single exact quantity, e.g. 5.00 ml ± 0.01 mL. For non-integer volume, e.g., 4.6 mL, a measuring pipet, graduated cylinder or buret may be used. The most common measuring pipets are 1, 2, 5, and 10 mL. The smallest measuring pipet capable of measuring the required volume should be chosen, e.g., a 5 mL pipet for 2.7 mL, if precision is important.

Tolerances on Measuring Serialized (Graduated) Class A Cylinders

Capacity (mL) †	Subdivision (mL)	Limit of Error (mL)	Percent Tolerance (%)
10	0.2	0.1	1.0
25	0.5	0.3	1.2
50	1	0.4	0.8
100	1	0.6	0.6
250	2	1.4	0.56
500	5	2.6	0.52
1000	10	5.0	0.5
2000	20	10.0	0.5

†Kimax*Brand serialized Class A cylinders with certificates of traceability and calibration (Fisher Scientific, 2000/2001 p. 475).

Measuring cylinders may be calibrated "To Contain" but are usually calibrated "To Deliver". Measuring cylinders are seldom used by chemists for precise measurement; however they are often adequate in non-critical procedures, for example in measuring the volume of a reagent. The smallest cylinder that will contain the measured volume will give the greatest accuracy.

Tolerances on Micropipettors

Capacity (µL)	Subdivision (µL)	Limit of Error ((µL)	Percent Tolerance (%)
Adjustable Volume Series 2100 Pipettors†			
0.1 – 2.5	0.002	0.012 – 0.035	12.0 – 1.4
0.5 – 10	.0.01	0.025 – 0.1	5.0 – 1.0
2 – 20	0.02	0.12 – 0.2	5.0 – 1.0
10 – 100	0.1	0.03 – 1.6	3.0 – 0.8
20 – 200	0.2	1.0 – 1.2	2.5 – 0.6
100 – 1000	1.0	3.0 – 6.0	3.0 – 0.6
500 - 5000	5.0	12 - 30	2.4 – 0.6
Adjustable Volume Series 2000 Pipettors‡			
0.1 – 2.5	0.002	0.012 – 0.035	12.0 – 1.4
0.5 – 10	.0.01	0.025 – 0.1	5.0 – 1.0
2 – 20	0.02	0.12 – 0.2	5.0 – 1.0
10 – 100	0.1	0.25 – 1.6	2.5 – 0.8
50 – 200	0.2	0.5 – 1.2	1.0 – 0.6
100 – 1000	1.0	1.6 – 6.0	1.6 – 0.6
500 - 5000	2.0	7.5 - 30	1.5 – 0.6
Fixed Volume Series 2000 Pipettors‡			
1		0.025	2.5
2		0.04	2.0
5		0.075	1.5

10	0.1	1.0
15	0.15	1.0
20	0.16	0.8
25	0.20	0.8
30	0.24	0.8
40	0.32	0.8
50	0.35	0.7
75	0.52	0.7
80	0.56	0.7
90	0.63	0.7
100	0.60	0.6
150	0.90	0.6
200	1.2	0.6
250	1.5	0.6
300	1.8	0.6
400	2.4	0.6
500	3.0	0.6
750	4.5	0.6
800	4.8	0.6
900	5.4	0.6
1000	6.0	0.6
1500	9.0	0.6
2000	1.2	0.06
2500	1.5	0.06

†Brinkmann Eppendorf Series 2100 adjustable volume pipettors (Fisher Scientific, Fisher Catalog 200/01 p.1330).
‡Brinkmann Eppendorf Series 2000 fixed volume pipettors (Fisher Scientific, Fisher Catalog 200/01 p.1329).

These pipets are calibrated "To Contain" the specific volume rather than "To Deliver" it. This means all their contents must be injected into the container.

Tolerances on Bottle-Top Dispensers

Capacity (mL) †	Subdivision (mL)	Limit of Error ((mL)	Percent Tolerance (%)
0.2 – 2.9	0.1	0.5	250 – 17
0.5 – 5.9	0.1	0.2	40 – 3.4
1.0 - 10.9	0.1	0.2	20 – 1.8
2 – 20.9	0.1	0.2	10 – 0.1
10 – 59	0.1	0.2	2.0 – 0.3
10 – 109	1.0	0.2	2.0 – 0.2

†Fisher/Wheaton Adjustable-Volume Bottle-Top Dispensers(Fisher Scientific, Fisher Catalog 200/01 p.1330).

Tolerances on Class A Burets

Capacity (mL) †	Subdivision (mL)	Limit of Error (mL)	Percent Tolerance (%)
10	0.05	0.02	0.2
25	0.1	0.03	0.12
50	0.1	0.05	0.1
100	0.2	0.10	0.1

†Kimax* brand Class A Precision bore buret with PTFE stopcocks (manual burets), Fisher Catalog 200/01 p.232).

A buret is the most accurate instrument for measurement of non-integer volumes. A class A buret has a tolerance of 0.1% to 0.2% of its total volume when properly used. The readings for 50 mL Class A burets should include a least significant digit within ± 0.01 mL, e.g., 30.62 mL.

Tolerances on Analytical Balances

Readability	Weighing Capacity	Linearity (Limit of Error)	Stabilization Time (s)	External Calibration Weight (g)
		Microbalance†		
0.1μμg	2100μμg	1.0μμg	10 - 16	2
1.0μg	5100μμg	4.0μμg	9 - 12	5
		Top-Loading Balance‡		
0.001 g	210 g	0.002 g	1.5 – 3	200
0.001 g	510 g	0.002 g	1.5 – 3	500
0.001 g	810 g	0.002 g	3 - 5	500
0.001 g	1210 g	0.002 g	3 - 5	1000

†Mettler Toledo Professional Level, UMT/MT Series Microbalance (VWR Catalog 2000/2001, p. 60)
‡Mettler Toledo Professional Level, PR Precision Top-Loading Balance (VWR Catalog 2000/2001, p. 61)

Appendix D – Answers To Problems In Appendix A.

1. Define the following terms:
    a) Significant figures (See Unit 4)
    b) Precision (See Unit 4)
    c) Accuracy (See Unit 4)
    d) Implied relative uncertainty (See Unit 5)
    e) Least precise factor (See Unit 7)

2. What is the difference between the following terms?
    a) Scientific notation vs. engineering notation? (See Unit 4)
    b) Rounding digit vs. decision digit? (See Unit 8)
    c) Determinate vs. indeterminate errors? (See Unit 9)
    d) Mantissa vs. exponent? (See Unit 6)
    e) Limit of error vs. percent tolerance?
        • (Percent Tolerance = (Limit of Error/Capacity)*100
        • (Percent tolerance x Capacity = Limit of error)

3. List five reasons why it is important to determine significant figures in chemical measurements. (See Unit 5)

4. Complete the following sentences by filling in *significant* or *not significant* in the black spaces.
    a). Digits from 1 to 9 in a value are *significant* regardless of the position of any decimal points.
    b). Zeros at the end of a number are *significant* if they are to the right of the decimal point.
    c). Zeros before a decimal point with no other preceding digits from 1 to 9 are *not significant*.
    d). Zeros at the end (final zeros) of a number are *significant* if the number is written with a decimal point using scientific or engineering notation to show the significant digits.
    e). If the zeros can be omitted when converting a value to the scientific form, then those zeros are *not significant*.

5. Given the following measurements in columns one and three give their respective number of significant figures (SF) in columns two and four.

Measurement (μg L^{-1})	Number of SF.	Measurement (μg L^{-1})	Number of SF.
1000	*1*	35.34???	*4*
1000	*3*	0.00	*2*

0.010	*2*	3,700.	*4*
0.01	*1*	1×10^{-2}	*1*
0.001	*1*	7.873×10^{7}	*4*

6. For 1 significant figure: Scientific notation = (3×10^{8}); Engineering notation = (300×10^{6});
For 4 significant figures: Scientific notation = 2.998×10^{8}; Engineering notation = 299.8×10^{6}.

7. (a) Scientific notation = 4.44×10^{5} and (b) engineering notation = 444×10^{3} (Note that the non-significant zeros were dropped in the final mantissa).

8.
   a) 2.6×10^{-6}
   b) 2237.34
   c) 2231.0
   d) 6730
   e) 0.00135
   f) 0.479

9.
   a) Absolute error = 10/2000 = 0.005
   b) Relative error = 0.005/2000 = 2.5×10^{-6}

10.
   a) 55.6 ± 0.37
   b) 0.517 ± 0.0649
   c) 0.6233 ± 0.0861

11. The instructions give both the precision required and the requested range of valued permissible. The value 7.000 indicates the degree of precision required (± 0.001). The 0.1 g indicated the permissible range of measurements. Measurements between 6.900 and 7.100 are acceptable. Measurements outside this range are not. The second instruction is redundant because the value 7.000 already indicates three decimal places and four significant figures. The only improvement I would make would be

   Weigh 7 ±0.1 g to the nearest 0.001g of fresh soil into a snap-cap cup.

12. The real guessed number is 225.4. The reading of $225.4 \pm 1\% = 225.4 \pm 2$ which becomes around 223 to 228 psi. You may therefore want to report the value as 225 as opposed to 225.4 *(28)*.

13.

Measurement (mL)	Graduated Increment (mL)	Range of True Value (mL)	
		Lower value	Upper value
25	1	24	26
25	0.1	24.9	25.1
25.5	0.5	25.0	26.0
25.555	0.005	25.550	25.560
0.002	0.001	0.001	0.003
0.0001	0.0001	0.0000	0.0002
2,500	100	2,400	2,600

| 2.565 | 0.005 | 2.560 | 2.570 |

14. The balance that was used to weigh15.376 g, readability = 0.001 g.

15. 590 min *(9)*.

16. Vatavuk = 63.4 ± 0.05 because imprecision of 0.0503 means that all digits at the 100th and beyond are uncertain. Reilly = 63.4 ± 0.05. There is no difference in the two approaches. The results are the same.

17. $y = (m \pm \Delta m)x + (b \pm \Delta b)$

$y = (0.12 \pm 0.000062)x + (2.2 \pm 0.0056)$

18. (See Reilly *(4)*)
        a) 55.63 ± 0.37
        b) 0.5174 ± 0.0649

19. Estimating operation and maintenance cost

Cost Item	Unit cost	Annual Quantity	Annual Cost, Appropriate Rounding ($)		Uncertainty
Operation labor	$12.5/h	25,300 hr	(3.16 ±	0.019) x 10^5	19
Supervisory labor	15.0/h	5,200 h	(7.8 ±	0.10) x 10^4	10
Maintenance labor	14.1/h	6,300 h	(8.8 ±	0.10) x 10^4	10
Maintenance materials			(7.0 ±	0.5) x 10^3	5
Electricity	0.056/kWh	133,000 kWh	(7.4 ±	0.09) x 10^3	9
Steam	5.2/10^3 lb	12.72 x 10^6 lb	(6.6 ±	0.07) x 10^4	7
Natural gas	3.5/10^6 BTU	15.2 x 10^9 BTU	(5.3 ±	0.09) x 10^4	9
Cooling water	0.35/10^3 gal	11.5 x 10^6 gal	(4.0 ±	0.08) x 10^3	8
Raw material A	2.53/lb	75,000 lb	(1.90 ±	0.016) x 10^5	16
Raw material B	0.752/lb	23,000 lb	(1.7 ±	0.04) x 10^4	4
Overhead	75% of total labor		(3.6 ±	0.024) x 10^5	24

Annual production		**Total O & M**	**$1,186,400** ±	**$3,957**
(1.5 ± 0.05) x 10^5 lb		**Rounded**	**$1,186,400** ±	**$4,000**
		O & M/lb	**7.90933** ±	**0.02638**
		Rounded	**7.9** ±	**0.026**

20. The new calculations showed that there were big differences in the way the uncertainties were computed. The original data had more than twice the value of uncertainty ($11,000 compared to $4,000).

21.(a)

Film diffusion coefficient D_f ($cm^2 s^{-1}$)		Pore diffusion coefficient D_p ($cm^2 s^{-1}$)	
Scientific Notation	Engineering Notation	Scientific Notation	Engineering Notation
1.98×10^{-9}	1.98×10^{-9}	1.692×10^{-8}	16.92×10^{-9}
3.09×10^{-9}	3.09×10^{-9}	2.09×10^{-8}	20.9×10^{-9}

(b)

Initial conc. (C_0) in ppm	Equilibrium conc. (C_e) in ppm	First order rate constant, K_1 (S^{-1})	Time to reach half conc. $t_{1/2}$ (S)	Mean geometric radius r (cm)	Film diffusion coefficient D_f ($cm^2 s^{-1}$)	Pore diffusion coefficient D_p ($cm^2 s^{-1}$)
0.2	0.053	6.51×10^{-6}	1.06×10^{5}	0.245	0.198×10^{-8}	1.692×10^{-8}
0.5	0.106	8.05×10^{-6}	0.860×10^{5}	0.245	0.309×10^{-8}	2.09×10^{-8}

The D_p and D_f values were calculated for different initial concentrations assuming $\delta = 0.001$.

The data presented in the table showed that film diffusion is the rate-limiting step for the present study.