Industrial Sampling Systems

Reliable Design & Maintenance for Process Analyzers

By Tony Waters

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Foreword

For more than 65 years, process instrumentation engineers and technicians have relied on Swagelok® products to connect and deliver stable samples to plant analyzers. Absolutely critical to process control, analyzers deliver a precise measure of process conditions quickly so that facility control systems can adjust parameters as needed to ensure the quality of a finished product.

Sampling technology has evolved steadily from early grab sampling to today's automated online systems. The fact remains, however, that analyzers can only be as accurate and responsive as the system of components that supplies them with a process sample.

The engineer in charge of designing these sampling systems and the technician managing them must be highly trained and experienced. Sampling system mistakes are always costly, are sometimes dangerous, and often go undetected. Incredibly, few colleges and universities offer sampling system design in their curricula. Perhaps it's because little has been written that could appropriately be used as a textbook. Until now.

Authored by Tony Waters, who is acknowledged by many as the leading expert in the design of sampling systems, *Industrial Sampling Systems* captures the experience and knowledge Tony has acquired during a career of more than 50 years. Its balance of theory and practical examples makes it the perfect reference for students as well as experienced sampling system engineers, designers, and technicians.

We're proud to be a part of the creation of this work and believe firmly that it will prove to be a valuable resource for those who are charged with the critical responsibility of designing, installing, and maintaining process analyzer systems. You, the reader, are the final judge of course, and we welcome your comments and feedback as you put this reference to work.

Arthur F. Anton
President and CEO
Swagelok Company

Preface

At first, it might not appear so. But this book is really about measurement, a peculiar kind of measurement that has given us all quite a lot of trouble since its inception in Germany, circa 1937, when the first process infrared analyzer débuted.

Process analyzers were a new breed of instrument. Instead of measuring the *quantity* of the stuff flowing through the pipes, they measured its *quality*—its clarity or purity, for instance.

I would not want to imply that this new kind of measurement has let us down: quite the opposite, in fact. Over the years, our ability to measure the quality of a process fluid has improved tremendously, and it continues to do so.

The trouble is not so much due to the measurement. It's due to the poor reliability of the process interface, the *Industrial Sampling System* that connects these delicate analytical instruments to harsh industrial processes.

Connecting a process analyzer to an industrial plant may seem to be a simple task; but really, it's quite complex. It demands a melding of instrumentation, analytical chemistry, and chemical engineering knowhow, and few people are skilled in all of those technical arts. I sincerely hope that those in colleges and training institutions will use this textbook to teach a new cadre of analyzer professionals the science and art—and yes, the fun—of sample system design.

Those of us now retiring learned all this the hard way. For 50 years, I've watched sampling systems fail in balmy places and icy places, and all places in between. Always for the same tired old reasons. And for more than half of those years, I've learned more about sampling from my students on six continents. Perhaps at last, I know how to do it.

Many friends and colleagues also learned the hard way. They built a body of knowledge and experience—what works and what doesn't—gleaned from oily jobsites, and from scattered talks and articles. Until now, that store of pragmatic insight and theory has not been conveniently accessible to the design engineer or maintenance technician.

Now, you have it.

We hope you enjoy the book. More so, we hope you act upon it to improve the performance of all your industrial sampling systems.

Tony Waters
Atascadero, California
April 2013

Acknowledgements

What an experience! Five years of oftentimes lonely but forever supported and uplifting work. I have so many to thank for their wise counsel, for their patience, and most of all for their valuable time. This book would not have left the starting gates without the enthusiasm of Swagelok executives, **Art Anton**, **Mike Butkovic**, and **Fran Dacek**; and would never have finished the course without their long patience and yes, their occasional scolding. In that long process, colleagues have become friends and friends have become mentors. A heartfelt high-five to **Doug Nordstrom** who from day one has been by my side as editor-in-chief, and to my mentors **Jimmy Converse**, **Bert Laan**, and **Zoli Hajdú** for sharing their real-world experience with sampling. And thanks to my technical review team who on their own time studied every word (really) and made so many good suggestions, and some not so good; particularly to **Ron Edmondson** and **Don Negrelli** who never missed a beat over four years of weekly meetings, and to **Sarah Liston**, **Chuck Hayes**, **Mike Gallagher**, **Jim Gotch**, **Andy Marshall**, **Brandon Fry**, and **Eric Kvarda**.

A book is so much more than the author and his technical team: it has to be produced. **Dave Waters** and **Jill Waters** set the tone with their delightful diagrams, while **Jim Peck** and **Jim Geshke** added the colorful page layouts and cover designs. Yet it wouldn't have happened at all without direction by **Fran Dacek**, coordination and proofreading by **Heather Gaynor**, editing by **Andy Evridge**, illustrations and permission by **Stephanie Hileman**, project management by **Gayle Poots**, brand reviews by **Jen Horn**, **Sunniva Collins**, **Rick Monreal**, **John Karkosiak**, and **Mark Rechner**, and some help with the Glossary from **Joe Patella**, **Mike Adkins**, **Joe Krance**, and **Mike LeRoy**.

And most of all, a big hug for my wife **Marilyn** who endured five years of solitude so I could get this out of my system. Perhaps we can go on vacation now?

My hearty thanks to you all.

Tony

How to Use This Book

Layout and Structure

The book responds to the needs of two different readers—the qualified practitioner who wants a quick answer to a pressing problem, and the newcomer studying the subject privately or in a formal learning course.

People working in industry will pick up the book to access information on a subject of particular interest at that time. They'll quickly look up a principle or an equation to assist them with a current need. These users are familiar with the subject and don't need multiple levels of explanation. They can go straight to the text and quickly find the information they need.

Newcomers and students working methodically through the text may need help with the basic science and technology used in sampling systems. We separate those explanations from the text. To describe the basic science of sampling, we use single-page *SCI-FILE*s located throughout the book.

As an example, the *SCI-FILE On Motion* included in Chapter 1 outlines Newton's Laws and defines the measurement units for the common variables of motion that we will need in subsequent chapters.

The table opposite lists the title and location of each *SCI-FILE*.

Section	Title	Page
01-1	On Motion	7
02-2	On Adsorption	47
03-2	On Ideal Gases	94
04-4	On Falling Bodies	167
05-2	On Real Gases	202
06-1	On Viscosity	248
06-2	On Critical Orifices	257
08-5	On Flammability	375
09-2	On Gas Solubility	407
09-3	On Raoult's Law	414
A-4	On Significance	641

To describe the underlying technology of sampling and analysis we use the Glossary in Appendix B. In each chapter, first occurrence of a technical term appears in colored text to indicate that more information about that term is included in the Glossary. As well as defining technical terms, the Glossary describes many process analyzers, defines measurement variables and their units, and gives useful information on selected chemical compounds. Separating all these descriptions from the text allows faster access for the experienced user.

In addition, readers who are unfamiliar with the principles of measurement will find that Appendix A gives an adequate primer on measurement science and its application to analytical instruments.

Quick Reference

A separate listing of numbered equations precedes the text in each chapter. As an aid to traceability, any equation used in another chapter retains its original reference number, and that number appears in parentheses alongside the equation.

A separate listing of the variables and symbols used in each chapter precedes the text in that chapter. An italic font distinguishes the symbols for variables, with vectors in bold. Symbols for measurement units appear in a roman (upright) font.

A convenient key to the graphical symbols used in illustrations is on the inside front cover, and there's a periodic table of the elements on the inside back cover.

As is common practice, a list of *References* at the end of each chapter provides sources for works cited in the text. In addition, the extensive bibliography in Appendix C catalogues selected books and articles that pertain to process sampling. This compilation may help those interested in the development of sampling to track the long history of the technology.

Use of SI Units

This book uses SI units for data and calculations. SI units are standard practice for international trade and commerce and almost universally used in science and technology. The big advantage of working in SI units is that calculations always work out perfectly, without ever needing a conversion factor. For more information on the SI system of units, read Appendix A-02 before getting started.

Table A01 in Appendix A-01 lists the names and symbols of the units we use and provides factors to convert US customary units to SI units.

In addition, the SI system of units allows the use of certain standard prefixes to increase or decrease the value of the standard unit. Table A10 in Appendix A-02 lists the prefixes commonly used in sample systems work.

Sampling techniques always involve pressure P, temperature T, and volume flow rate $\dot{V}$. Let's briefly review the units used for those key variables.

Units of Pressure

The SI unit of pressure is the pascal. The pascal is a small unit compared with the pressures common in sampling systems. To put it into perspective, it takes 101 325 pascals to make one standard atmosphere. So we need a larger unit for general measurement and discussion. Sometimes it is convenient to use kilopascal, but mostly we prefer to use bar.

The bar is a very convenient unit. By definition, it equals *exactly* 100 000 Pa or 100 kPa. That puts it very close to the standard atmosphere. In sampling, we often need to adjust gas volumes and gas flow rates to atmospheric pressure. Although atmospheric pressure varies from day to day, a reference pressure of 1.0 bar is close enough for those calculations, so we have adopted it for that purpose throughout this book.

Most pressure gauges and pressure transmitters measure process and sample pressures in gauge pressure. This is an additional complication. When your pressure gauge reads zero, the real or absolute pressure is not zero; it's about 1 bar! Because of this false zero, you can't use gauge pressure in calculations.

In this book, we use the unit symbols bara and barg for absolute and gauge pressure, respectively. We use kPa only for absolute pressure, never for gauge pressure. If you have a gauge pressure in kPa, just add 100 kPa to convert it to absolute pressure.

Since real atmospheric pressure is always close to one bar, it follows that:

$$x \text{ barg} = (x + 1) \text{ bara}$$

If the application data sheet gives pressures in barg, simply add 1 bar before doing any calculations. If you get data in psig, first convert it to psia:

$$x \text{ psig} = (x + 14.7\ ) \text{ psia}$$

Note that 14.7 psi used above is the American customary unit value for the standard atmosphere (equal to 101.325 kPa) rather than the 100 kPa (14.5 psi) standard atmosphere used throughout this book.

Then, to convert the absolute pressure to bara, divide the psia value by the conversion factor 14.5 psi/bar:

$$x \text{ psia} = x \text{ psia} \times \frac{1 \text{ bar}}{14.5 \text{ psi}} = \frac{x}{14.5} \text{ bara}$$

To avoid confusion or error, don't use gauge pressure in calculations; convert the gauge pressure to absolute pressure!

Don't use gauge pressure in calculations!

Units of Temperature

The SI unit of temperature is the kelvin *K*. It does not use the word *degree*, nor does it take the degree sign. One kelvin is conveniently equal to one Celsius degree.

The Celsius and Fahrenheit temperature scales have arbitrary zero points, so they don't work well in calculations. Instead, always convert temperatures to kelvins before entering the values in an equation.

Don't use °C or °F in calculations!

If your application data gives a temperature in degrees Fahrenheit, convert it to degrees Celsius:

$$x\ {}^{\circ}\mathrm{F} = \frac{x - 32}{1.8}\ {}^{\circ}\mathrm{C}$$

If your data is in degrees Celsius, the conversion to kelvins is easy. To get an exact conversion, you should add 273.15 to the Celsius value. But for the accuracy of calculation required in sampling systems, you can just add 273.

$$x\ {}^{\circ}\mathrm{C} = (x + 273)\ \mathrm{K}$$

$$x\ {}^{\circ}\mathrm{F} = \left(\frac{x - 32}{1.8} + 273\right)\mathrm{K}$$

One sometimes sees the measurement of differential temperature expressed in Celsius degrees $C°$, but those units don't work with SI units in calculations. Since one Celsius degree is exactly equal to one kelvin, we elected always to use kelvins for the measurement of temperature difference, *e.g.*,

$$\Delta T = 65\ {}^{\circ}\mathrm{C} - 32\ {}^{\circ}\mathrm{C} = 33\ \mathrm{K}$$

The kelvin units are compatible with other SI units in equations that employ differential temperature.

Units of Flow

The SI unit of volumetric flow rate is the *cubic meter per second*. It does not have a name. Unfortunately, a cubic meter is a large volume; it's equal to 1000 liters. The liter is a more convenient size (think of a four-inch cube), so we often measure volume in *liter* (L) and flow in *liter per minute* (L/min).

In sampling and analysis, it is very common to see volume or flow stated in cubic centimeter units, often abbreviated to cc or cc/min. Since one cubic centimeter is exactly equal to one milliliter, these statements are exact:

1 L = 1000 cm^3 (cc)
1 L/min = 1000 cm^3/min (cc/min)
1 mL/min = 1 cm^3/min (cc/min)

It's incorrect to use the abbreviations cc and cc/min in calculations because they are not real units.

Other Units

We use the abbreviations ppm and ppb without further explanation to refer to parts-per-million and parts-per-billion. When not otherwise stated, they refer to parts by volume.

Tubes and pipes in fractional inch sizes are still in common use, so we often use them in worked examples. To reduce monotony, we specify tube sizes without the obvious qualifier *outside diameter* or *o.d.* so "¼-inch tube" may be taken to be "¼-inch o.d. tube." Similarly, we omit *nominal bore* or *NB* when specifying pipe, so "½-inch SCH80 pipe" means "½-inch NB SCH80 pipe."

Calculations with Units

Sample system engineering involves a number of calculations, none of which is difficult to understand. We limit equations to those using simple algebra and give many worked examples to illustrate their use.

All numbered equations expect to receive input data in coherent SI units and return the calculated data in coherent SI units. Unnumbered equations and calculations in the text sometimes use other units. A prime after the symbol of a variable indicates that the calculated value is in noncoherent units.

Be careful when doing a calculation with prefixed units. Ideally, you should convert all data to the proper SI units, without the prefixes. Sometimes in the text, though, we take shortcuts. Consider the calculation of time delay in a liquid line for instance. Section 02-2 introduces this equation:

$$t = \frac{V}{\dot{V}} \tag{2-2}$$

The SI unit for volume V is m^3 and the SI unit for volume flow rate $\dot{V}$ is m^3/s. But our sampling data is likely to be in much smaller units; we might have a volume of 500 mL and a flow of 250 mL/min. Since it's obvious that the volume units will cancel out, it's not worth converting them to coherent SI units; we can enter the data directly in the equation.

To avoid mistakes, always enter the units into the equation alongside the data thereby confirming the units of the answer. In this example, the milliliters cancel out leaving the time t' in minutes:

$$t' = \frac{500\ \cancel{\text{mL}}}{1} \times \frac{\text{min}}{250\ \cancel{\text{mL}}}$$

$$t' = 2\ \text{min}$$

Notice the prime added to the symbol for time. This is an example of how we use a prime to indicate that the answer is not in SI units.

If these methods of including units in calculations are unclear to you, read Appendix A-03 before moving on.

Accuracy of Calculation

Because of uncertainty in the input data, calculations in sampling are always approximate. It's a mistake to imply that calculated data are more accurate than the input data. It's best to assume that all given data is accurate to two significant figures and then round calculated values to two significant figures. That's the approach used in the book.

When specifying a flowmeter setting, round up the calculated value to the next marked division on your flowmeter. Don't ask users to set a flow rate to a higher accuracy than the flowmeter can achieve.

The Scientific Notation

The scientific notation is a convenient way to express a wide range of values without using prefixed units. For instance, we prefer to measure a length in *meters*, whether that length is the microscopic distance between two atoms or the astronomic distance between two stars!

Using the scientific notation, the distance between atoms in a hydrogen molecule is about 7.4×10^{-11} m, and the distance from here to Alpha Centauri is about 4.1×10^{16} m. Another way to write or print these two values is 7.4E−11 m and 4.1E+16 m.

The scientific notation is now the standard way to present measurement values, particularly for tabulated data. If you would like to review how this notation works, refer to Appendix A-04.

Feedback Welcomed

In keeping with our core value of continuous improvement, Swagelok is interested in your feedback on the book. We've done our best to ensure the quality of the information found here, but there may be things we missed. If you find anything that you think should be changed in a future edition, you can send us your thoughts at www.industrial-sampling-systems.com. Here we will post any updates to content that will be included in future editions. We look forward to hearing from you.

A

Measures, Units, and Calculations

IN THIS APPENDIX:

614 **A-1 *About Measurement***
Introducing the science and practice of metrology and its application to analytical measurement.

621 **A-2 *Introducing SI Units***
Describing the SI system of units, the relationships between them, and their rules of usage.

629 **A-3 *Working with Units***
Converting between units or creating new ones and using the units to check calculations.

636 **A-4 *Presentation of Data***
Explaining the scientific notation and how to present data with an appropriate number of significant figures.

641 **A-5 *Measurement Uncertainty***
Understanding error and bias in measurement and monitoring their values with a control chart.

Tables & Figures in Appendix A

No.	Title
A01:	Selected Unit Conversion Factors
A02:	Precision, Bias and Accuracy
A03:	Zero Error
A04:	Span Error
A05:	Simple Nonlinearity
A06:	Typical Hysteresis
A07:	Fluoride Ion Electrode
A08:	The SI Base Units
A09:	Some SI Derived Units
A10:	Standard SI Prefixes
A11:	Various Concentration Units
A12:	Converting Weight and Mole Percent
A13:	The Scientific Notation
A14:	The Normal Curve of Error
A15:	The Normal Distribution
A16:	Confidence Levels
A17:	A Typical Control Chart
	SCI-FILE On Significance

SYMBOLS in Appendix A

Sym	Measure	SI Unit
a	acceleration	m/s^2
A	area	m^2
$\boldsymbol{d}$	displacement	m
E	work or energy	J
F	force	N
f	frequency	Hz
g	gravity acceleration	9.81 m/s^2
h	height or depth	m
M	molar mass (molecular wt.)	g/mol
L	length or distance	m
m	mass	Kg
$\boldsymbol{p}$	momentum	kg·m/s
n	amount of substance	mol
P	absolute pressure	Pa
P_w	power	W
G	specific gravity	none
t	time duration	s
T	absolute temperature	K
$\boldsymbol{u}$	average velocity	m/s
η	viscosity	Pa·s
V	volume	m^3
$\dot{V}$	volumetric flow rate	m^3/s
w	weight fraction	none
χ	mole fraction	none
φ	volume fraction	none
ρ	density	kg/m^3

SYMBOLS in Appendix A (*continued*)

	Statistics	
k	coverage limits	
$\bar{x}$	arithmetic mean	same as measure
s	standard deviation (estimated from sample set)	
σ	standard deviation (of population)	
u_c	combined standard uncertainty	
	Primes & Subscripts	
x'	Prime designates non-coherent units	
sub_1	Subscript 1 is the first or existing state	
sub_2	Subscript 2 is the new or converted state	
other	as defined in text	

EQUATIONS in Appendix A

No.	Equation	Usage
A-1	$\boldsymbol{F} = m \cdot \boldsymbol{a}$	force definition
A-2	$P = \frac{\boldsymbol{F}}{A}$	pressure definition
A-3	$\Delta P = h \cdot \rho \cdot \boldsymbol{g}$	liquid head
A-4	$\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^{n} x_i$	arithmetic mean
A-5	$s = \sqrt{\frac{1}{n-1} \cdot \sum_{i=1}^{n} (x_i - \bar{x})^2}$	standard deviation
A-6	$s_{\mathrm{M}} = \frac{s}{\sqrt{n}}$	standard error
A-7	$u_{\mathrm{c}} = \sqrt{s_1^2 + s_2^2 + s_3^2 + \ldots}$	standard uncertainty

"You, in this country, are subjected to the British insularity in weights and measures; you use the foot, inch and yard.

I am obliged to use that system, but must apologize to you for doing so, because it is so inconvenient, and I hope Americans will do everything in their power to introduce the French metrical system. . . . I look upon our English system as a wickedly, brain-destroying system of bondage under which we suffer. The reason why we continue to use it, is the imaginary difficulty of making a change, and nothing else; but I do not think in America that any such difficulty should stand in the way of adopting so splendidly useful a reform."

Baron Kelvin (1884)

Table A01 – Selected Unit Conversion Factors

Quantity Measured	*Convert from (incoherent unit)*		*Convert To:*	*Multiply By:*	
Acceleration	foot per second squared	ft/s^2	m/s^2	3.038	E–01
Area	square foot	ft^2	m^2	9.290	E–02
	square inch	in^2	m^2	6.452	E–04
Density	pound per cubic foot	lb/ft^3	kg/m^3	1.602	E+01
Energy, Work	British thermal unit	BTU	J	1.055	E+03
	calorie	cal	J	4.187	E+00
	kilowatt-hour	kW·h	J	3.600	E+06
	watt-second	W·s	J	1.000	E+00
Flow	cubic foot per hour (cfh)	ft^3/hr	m^3/s	7.866	E–06
	cubic foot per minute (cfm)	ft^3/min	m^3/s	4.719	E–04
	liter per minute	L/min	m^3/s	1.667	E–05
	US gallon per hour	gal/h	m^3/s	1.052	E–06
	UK gallon per hour	gal/h	m^3/s	1.263	E–06
Force	dyne	dyn	N	1.000	E–05
	kilogram-force	kgf	N	9.807	E+00
	pound-weight	lbf	N	4.448	E+00
Length	angstrom	Å	m	1.000	E–10
	foot	ft	m	3.048	E–01
	inch	in	m	2.540	E–02
	micron	µm	m	1.000	E–06
Mass	pound	lb	kg	4.536	E–01
Pressure	atmosphere	std	Pa	1.013	E+05
	bar	bar	Pa	1.000	E+05
	inch of water @ 60° F	in H_2O	Pa	2.488	E+02
	pound per square inch	psi	Pa	6.895	E+03
	torr	mm Hg	Pa	1.333	E+02
Viscosity	centipoise	cP	Pa·s	1.000	E–03
	centistokes	cSt	m^2/s	1.000	E–06
Volume	liter	L	m^3	1.000	E–03
	cubic centimeter (milliliter mL)	cm^3	m^3	1.000	E–06
	cubic millimeter (microliter µL)	mm^3	m^3	1.000	E–09
	cubic foot	ft^3	m^3	2.832	E–02
	gallon (imperial)	UK gal	m^3	4.546	E–03
	gallon (US)	US gal	m^3	3.785	E–03
	barrel (42 US gal)	bbl	m^3	1.233	E+03

Selected from NIST Guide to the SI (Thompson & Taylor 2008)

WHY STUDY THIS?

Appendix A is intended as an introduction to measurement that is adequate for those who are about to study sampling technology in an academic setting and illuminating for those who will just refer to an occasional description or explanation. Consigned to this appendage, the material becomes optional in a curriculum. But should you wish to include the subject in a formal study program, this appendix follows the format of the main sequence, complete with summaries and self-assessment questions.

While measurement is not the core subject of the book, sampling involves many measurements. You will use these values to select components, to control operating conditions, and to calculate performance criteria. This appendix introduces the SI units used in calculations throughout the book. It describes how to use those units in equations and shows some alternative ways to format the resulting data.

A-1 About Measurement

Definition

Measurement is a distinct branch of science known as metrology. Scientists who specialize in metrology strive for perfection in measurement but work under the dread certainty that they will never achieve it. They, more than most, know that all measurements are and always will be imperfect estimates of the elusive values we seek.

According to these metrologists, a measurement is an *estimate* of the quantity of a continuous variable such as a length, a weight, or a temperature. Thus, all measurements are quantities; they represent the amount of something.

Variables

A variable is a defined quantitative property of a physical entity or an energy phenomenon that can adopt different values. It's what we want to measure.

The length of a line and the internal volume of a vessel are typical physical variables, while the temperature and pressure of a sample gas are examples of energy variables.

A continuous variable is one that can have an infinite number of possible values. So it would take an infinite number of decimal digits to specify its current value exactly. That's why all measurements are estimates, rather than infallible determinations.

The measurand is the variable that you are trying to measure. It's a generic term that applies to any kind of measurement. When talking about analytical measurements, chemists often call it the analyte, especially when they are measuring a unique chemical species.

We represent a measured variable by an italic letter symbol that identifies that measurand and represents its current quantity. For instance, the symbol P represents absolute pressure. A list of the symbols used therein precedes each chapter of the book.

Unit of Measure

To measure anything, you need a unit of measure or *unit* for short. A unit of measure is a standard quantity of the measured variable agreed by those that make and need the measurement as a reasonable incremental quantity of the variable. It is important that we define the unit quantity without ambiguity and that we can reproduce it with high accuracy.

Each unit of measure has an agreed symbol that represents one measure of that variable. The symbol is not an abbreviation; it is a mathematical quantity and is subject to the laws of algebra. So when we place a numeral in front of the unit symbol, we are multiplying the unit quantity by that number. We can also multiply or divide a symbol by itself or by other symbols to create different unit quantities.

For example, acceleration is the rate of change of velocity with time. So the unit of acceleration ($\mathrm{m/s^2}$) comes from dividing the velocity unit (m/s) by the time unit (s):

$$\frac{\mathrm{m/s}}{\mathrm{s}} = \mathrm{m/s^2}$$

To distinguish variables from units of measure, it is customary to write the symbols of variables in *italic font* and the symbols for units in upright roman font. To cite an example, you should be able to recognize the symbol m (the mass of an object) as distinct from the symbol m (a meter of length).

How to Specify a Measurement

To document a measurement without ambiguity, you need to specify three properties of that measurement. The first two are already familiar; they are a numeric value and a unit of measure.

But since the value is an estimate, you should also give an indication of how accurate it is. For example, consider the measurement:

5.01 m ± 0.3 %

This value illustrates the three defining properties of any measurement:

- The numeric value (*e.g.*, 5.01) specifies the magnitude of the measured variable relative to the size of the specified unit of measure.
- The unit symbol (*e.g.*, m for meter) represents an agreed and accurately specified quantity of the measured variable that is a convenient size for measuring and calculation.
- The indication of accuracy (*e.g.*, ±0.3 % of value). We shall see that specifying upper and lower limits, as done here, is insufficient because it doesn't say how often the result will deviate beyond those limits—and it will!

Measurements and Counts

Not all variables are continuous. The cash in your pocket is variable, but it can't adopt an infinite number of possible values; the smallest coin value limits that. So you can't *measure* your pocket change; you have to count it—and hopefully get an exact number, not an estimate.

Thus, a count is not a measurement.

A count is not a measurement!

Sometimes it is not so easy to get an exact count; counting the votes in a political election comes to mind. Nevertheless, an exact count is feasible, given an effective procedure. A miscount is due to human mistakes that, in principle, you can eliminate. Then the count will have an exact value.

A measurement, by definition, can *never* have an exact value.

Putting items into categories is another kind of count. So is matching their color to certain hues on a color chart. There are a limited number of outcomes, so these determinations are not measurements.

Certain factors in mathematical equations, like the power of two in the expression πr^2, are exact counts. So are the numbers of atoms in a chemical formula and the number of molecules in a chemical equation.

Even a number having multiple decimal digits can be a count. For instance, the number 0.092 903 04 is, by definition, the exact area of one square foot expressed in square meters. An exact number cannot be a measurement, even when you round it to 0.093 m^2. It certainly *looks* like a measurement, but it's a count.

It's important to know the difference between a count and a measurement when using them in mathematical equations. A count is an exact number so its accuracy is never in question, but you should always worry about the accuracy of a measurement. We address that issue later in this appendix.

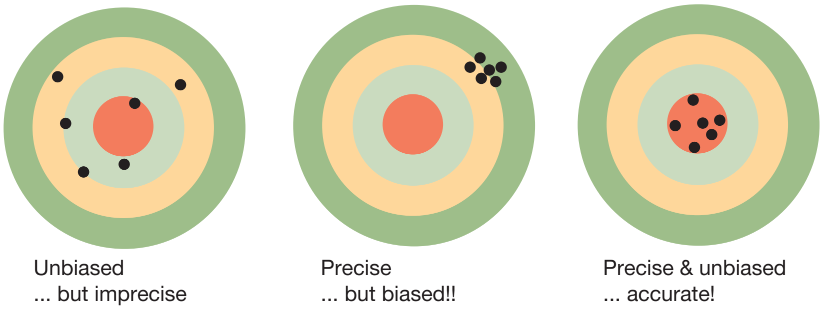
The distinction between measurements and counts fades at molecular levels. We shall see that the chemical unit of quantity, the mole, is actually a count. But molecules are small and far too numerous to count, so we resort to measuring them!

The Quality of a Measurement

Precision

A measurement is an *estimate* because the exact value cannot be determined. All measurements are subject to random error caused by countless minor variations in the measurement environment that you can reduce but not eliminate. Even a simple task exhibits this randomness. In one of my training classes, I ask trainees to measure the length of a line printed on the page. The results typically vary by more than one millimeter!

Figure A02 – Precision, Bias, and Accuracy



This ever-present random error limits our ability to measure, and that in turn limits our ability to understand our world or control our processes. Yet scientific discovery depends on improved measurement technology, as does enhanced process control.

To improve a measurement, you must reduce its random variation; but to improve anything you first have to measure it! Later in this appendix, you'll see how to measure the variation itself, thereby arriving at a statistical estimate of variability that scientists call the precision of the measurement procedure.

In the instrument business, we call it repeatability.

Becoming Accurate

Target shooting provides a visual illustration of the distinction between precision and accuracy. The first target in Figure A02 shows a familiar pattern that exhibits poor repeatability. The shooter is on target but inconsistent; his shooting isn't accurate because it lacks precision. To improve accuracy, he needs to practice better technique and reduce the scatter of his shots.

It's the same with measurements too: a measurement can't be more accurate than it is precise.

It is always good to improve precision. But even a precise measurement may not be accurate. Consider the second target in Figure A02. This shooter is quite precise, but she gets the wrong result every time! Her aim is biased.

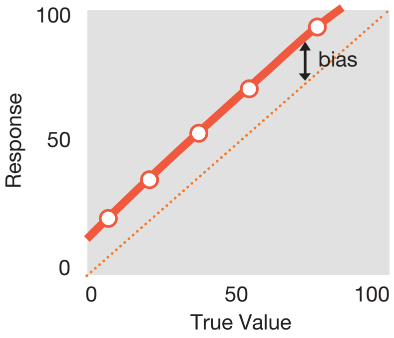
Yet those who evaluate her shooting would say that it's very good. That odd opinion comes from the sure knowledge that once a shooter achieves good precision it is easy for her to become very accurate indeed. All she has to do is calibrate her gun sights.

Measurement accuracy can't be better than its precision!

And so it is with measurement. Once you are getting precise results, you can eliminate a constant bias, sometimes called a systematic error, by calibrating the response. For the third target of Figure A02, our previous shooter has calibrated her sights, and she is now *accurate*—both precise and unbiased.

Accuracy is what we all seek to achieve, shooters and analysts alike.

Figure A03 – Zero Error



Three Forms of Bias

In target shooting, there is only one correct result, so a simple calibration of aim is enough to eliminate bias. A measurement is not so simple; the correct result can be anywhere in the measurement range, which allows three forms of bias called zero error, span error, and nonlinearity.

Figure A03 illustrates the linear response of a measuring device that has a simple zero error. When the measured value varies, the bias is always the same. Calibrating the zero response to read *zero* eliminates the bias at every point on the range. By adjusting the zero, you are effectively adding a constant positive or negative number to the sensor response.

Figure A04 shows a different kind of bias. This time, the zero response is correct and the error is proportional to the measurement value. This is a span error. To eliminate a span error you will need to calibrate the sensor response, usually by adjusting an electronic gain control. By changing the gain, you are effectively multiplying the sensor response by a constant correction factor.

Figure A04 – Span Error

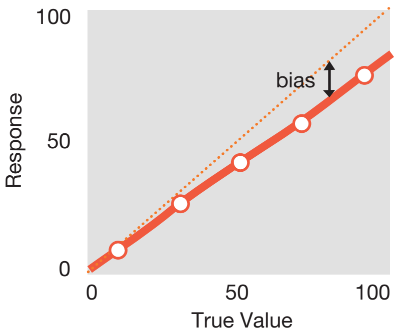
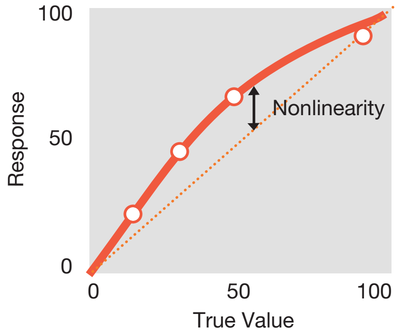


Figure A05 introduces another kind of error. The sensor response is nonlinear, so the bias is not constant at all; the amount of the error changes with the magnitude of the measurand. Relative to a straight line, the response might even be high at one amount of the measurand and low at another. If you calibrate this kind of response with only two points—one zero and one span—all other levels of the measurand will remain biased to different degrees, reducing the accuracy of the measurement.

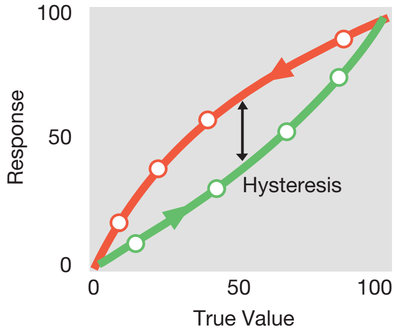
Figure A05 – Simple Nonlinearity



All measuring instruments are to some extent nonlinear. Some devices use multiple calibration points that apply different span corrections at different quantities of the measurand, thus adjusting the response to approximate a straight line. Unfortunately, even with sophisticated correction algorithms, it's impossible to remove all traces of nonlinearity. Some error remains.

Figure A06 indicates that the linearity error might be different depending upon whether the measurand is rising or falling. The response often lags the change in the variable. This is an example of hysteresis, which was a common error with the sticky mechanical pointer movements of the past. Hysteresis depends on measurement history and is difficult to remove by calibration. The adsorption of molecules on tubing and filter elements is an example of hysteresis in sampling systems. The instrument response lags the measurand whether the concentration is rising or falling.

Figure A06 – Typical Hysteresis



Calibrating the Response

Most of our instruments can't determine the absolute value of the measured variable—they simply respond to it. The amount of that response is typically an unknown function of the measurand.

To illustrate, consider a simple pressure gauge. It would be difficult to calculate the exact fluid pressure starting from the deflection of the pointer and invoking the internal contact area, the stiffness of the Bourdon tube, and the mechanical advantage of the movement. Perhaps engineers who design pressure gauges actually do such calculations, but they would never expect an exact response. They wouldn't even expect every gauge off the assembly line to give the same response. There are too many subtle influences for that! No, the design criterion is to get *enough* response.

Accuracy always comes from calibration against known reference values, which introduces two more sources of error: the accuracy of the reference values and the efficacy of the calibration procedure.

In summary, the quality of a measurement depends on four factors:

- The random error inherent in the measurement procedure
- The effectiveness of the calibration procedure
- The accuracy of the reference values
- The linearity of the response

Inevitable error in all four of these factors always limits the accuracy of any measurement.

Analytical Measurement

An analytical measurement is one that measures the *composition* of a sample. It measures the quantity of certain specified entities in a mixture with other entities. The entities are usually molecules, but they can be atoms, ions, or particles instead.

An analytical measurement is typically more complex than a physical one, as the sensor has to respond to the entities of interest while ignoring all other entities that might be present from time to time. Because of this increased complexity, an analytical method of measurement typically suffers more sources of error than a conventional measurement, and it is important to know its expected precision and accuracy.

Analytical Precision

We apply two measures of precision to laboratory methods of analysis:

- The repeatability of a method is its precision when performed by the same analyst in the same laboratory using the same equipment and within a short time period.
- The reproducibility of a method is its precision when performed by various people in different laboratories using different equipment over longer periods. Clearly, reproducibility admits to more sources of error than repeatability and thus has lower precision.

The definition of *repeatability* is a better fit to process analyzers, so we prefer that term to indicate the precision of our instruments.

Often, a laboratory will measure the repeatability of an analytical method by analyzing the same sample repetitively. While a useful statistic, this does not include the variability introduced by the sample collection procedure. A laboratory can measure only the samples delivered to it. The process of extracting those samples from an operating process and carrying them to the laboratory adds several additional components of variation that may end up being the largest ones.

The repeatability specification of a process analyzer also omits the variability inherent in sample extraction, transportation, and conditioning. Reducing that additional variability is a key goal of this book. Happily, we have one big advantage over our laboratory cousins; our sampling systems work without manual intervention—and an automated procedure is usually more precise than a manual one. So if we design our systems well, they will be less prone to random error than the manual procedures used by the laboratory.

Analytical Interference

All measurements are uncertain because they endure random error and bias, but analytical measurement has a unique way of deceiving you; it can suffer interference from other chemicals in the sample.

An analytical method is a set of procedures that selectively engages the analyte to generate a quantitative result. The analytical chemist strives to make the method *robust*, so it responds only to the concentration of the analyte and is unaffected by changes in the concentration of other materials present in the sample, or by changes in the measurement environment.

Inevitably, those who develop analytical methods are unable to fend off all interferences—there are limits to what they can do. Realizing this, the responsible chemist will document the residual interferences. Typically, a published chemical method of analysis will list the interfering chemical species and state the degree of interference you can expect from each.

Many process analyzers use physical sensors rather than chemical methods of analysis. These sensors are *selective*: they respond to the desired variable and try to ignore all others, but none of them is fully free from interference. Reputable manufacturers publish a list of interferences for their products, but not all do.

So you should remain alert. Interference is a peculiar analytical malady that can range from devastating to hardly noticeable. It can appear or disappear at any time without warning and may falsely increase or decrease the value of your measurement.

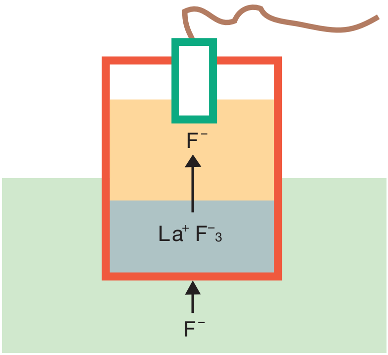
Positive Interference

Positive interference causes a falsely high result: something feigns the analyte and the analyzer responds to it. The response to the interferant is typically less than the response to the analyte. But it's not always so—the interference might even overwhelm your measurement!

An example of positive interference occurs in the measurement of fluoride ions in water, a measurand used to control the fluoride dosing of municipal water supplies.

The measuring instrument is an ion-selective electrode, employing a lanthanum fluoride crystal as its selective membrane; see Figure A07. The negative fluoride ions can attach to the outer surface of the crystal and detach from the inner surface, or vice versa, an ability that in theory is exclusively theirs. The movement of these ions develops an electrode potential proportional to the concentration difference of fluoride ions between the inner electrolyte and the sample solution. The instrument measures this electrode potential and outputs a calibrated signal indicating the fluoride concentration in parts-per-million.

Figure A07 – Fluoride Ion Electrode



Unfortunately, ion-selective electrodes all tend to suffer from interference, and the fluoride electrode is no exception.

Positive interference occurs in alkaline solution. Such solutions contain many hydroxyl ions that are similar in size to the fluoride ions and also carry unit negative charge. The hydroxyl ions can imitate fluoride ions by attaching to the crystal, thus generating an additional electrode response and a higher fluoride reading. The hydroxyl ions thereby create a positive interference.

Sample conditioning is often necessary to reduce interference. In this case, the remedy is to reduce the concentration of hydroxyl ions by neutralizing the sample with a buffer solution. The addition of a buffer solution eliminates most of the offending hydroxide ions, but it also dilutes the concentration of the analyte, so it is important to treat calibration samples in exactly the same way.

Negative Interference

Fluoride ions also provide an example of negative interference. It happens in acid solution. Some of the plentiful hydrogen ions react with free fluoride ions to make molecular hydrogen fluoride, also known as hydrofluoric acid:

$$H^+ + F^- = HF$$

The measuring electrode does not respond to hydrogen fluoride molecules in the solution. It measures only the remaining fluoride ions, thus giving a low value. The hydrogen ions thereby cause a negative interference.

Again, the remedy is to add buffer solution, this time to absorb the hydrogen ions and release the fluoride ions for measurement.

Another example of negative interference occurs with the popular zirconia cell used to measure oxygen in stack gases. The sensor cell runs at over 600 °C, so if a combustible gas like carbon monoxide is present, it burns at the cell using up some of the oxygen:

$$2CO + O_2 = 2CO_2$$

The zirconia cell then measures the residual oxygen, but the measurement is lower than it should be; the combustibles have caused a negative interference.

The easiest way to reduce this interference is to measure the combustibles and compensate for their effect. In practice, control engineers usually ignore the error, perhaps through ignorance of its existence. In most furnace stacks, the combustibles level is about 1 % of the measured oxygen concentration, so the effect is negligible. Yet it may suddenly become significant at times of process upset—just when the control system most needs the measurement!

Dealing with Interference

You can't eliminate interference by calibration!

Interference is not the same as bias, it comes and goes. You can't eliminate interference by calibration because it's rarely constant.

Analyzers try to eliminate known interferences by removing the interfering species or masking its effect. Either approach may require sample treatment inside the analyzer or as part of the sample conditioning system. Typical treatments are pH control by the addition of buffer solutions or the destruction of the interfering species by the addition of a chemical reactant.

Sample treatment to minimize interference might affect the design of your sampling system. You will need to know the special needs of each analyzer before designing or maintaining the sampling system for that analyzer. Each application is different, so be sure to understand yours!

Summary

Section A-1 introduced these concepts:

- A measurement is an estimate of the value of a continuous variable and can never be exact.
- A continuous variable is a measured quantity that can assume an infinite number of different values.
- A count is an exact number, not a measurement, but it might be incorrect due to a human mistake.
- The measurand is the measured variable; for analytical measurements, it is often called the analyte.
- Measurements are expressed as multiples of a unit of measure that is an agreed quantity of the measurand.
- Each unit of measure has a designated symbol that stands for one standard measure of that variable.
- To fully specify a measurement you need a numeric value, a unit of measure, and an indication of accuracy.
- All measurements suffer error from random fluctuations in the procedure and the measurement environment.
- The precision of a measurement is a measure of its variability; instrument people call it repeatability.
- To improve precision, you should minimize the random variations that affect the measuring procedure.
- Measurements are also to some extent biased; even the average of several readings may not be the true value.
- To improve accuracy, calibrate the measuring device to minimize the bias caused by zero and span errors.
- When the response isn't linear, multiple calibrations may be necessary at different points in the measurement range.
- Analytical measurements typically suffer more sources of error and lower precision than physical measurements do.
- The precision of a process analyzer is better stated as repeatability, rather than reproducibility.
- An automatic process analyzer is typically more precise than a manual laboratory method, but it might be less accurate!
- Most analytical methods are subject to interference by certain other substances that may be present in the sample.
- Interference can cause an increase or decrease in the measured value and cannot be corrected by calibration.
- Interference can often be masked by sample treatment, such as the controlled addition of a chemical reagent.

Q Self Assessment Questions – SAQ A-1

1. *What three properties of a measurement must you specify to define it completely?*

2. *Give two examples of quantities that are counts, not measurements.*

3. *True or false? Lack of repeatability is due to mistakes in the measurement procedure.*

4. *True or false? Measurement bias is the result of countless small variations in the measurement environment that you can't control.*

A-2 Introducing SI Units

The International System of Units

This book uses SI units in equations and data tables. SI is an abbreviation for the French *Système International d'Unités*, and by good fortune also represents the English translation: the International System of Units.

The definition of SI units is under the control of the International Bureau of Weights and Measures, whose French initials are BIPM. The BIPM from time to time publishes a document entitled *The International System of Units (SI)* to promulgate its decisions and recommendations concerning SI units (BIPM 2006, 94). The informal name of this document is the *SI Brochure*.

The National Institute of Standards and Technology (NIST) issues a slightly amended version of the SI Brochure for use within the United States of America (Taylor and Thompson 2008). The differences are mainly in spelling.

SI Base Units and Derived Units

The SI system of units relies on the seven clearly defined base units listed in Table A08. These seven base units have very precise definitions that are independent of each other. Seven base units are enough to measure every variable in the universe, as we can derive all other units from these seven.

The choice of the seven base units is somewhat arbitrary. In each case, the BIPM selected the unit that it could most precisely define and measure. Exact definition and measurement of the seven base units are crucial because the values of all other units depend on them.

The SI protocol derives other units by combining two or more base units. For instance, we measure velocity in *meter-per-second* (m/s). Acceleration, which is the rate of change of velocity, then becomes *meter-per-second-squared* (m/s^2). Units like these do not have separate names, they just combine the names of two base units—in these examples, the meter and the second.

Table A09 shows some SI derived units used in this text. The BIPM assigned names to some of them in honor of the scientist who did original work on that measurement.

A Coherent Set

The definition of an SI derived unit always follows the definition of the variable itself, according to the relevant equation of physics. You'll never need a numeric conversion factor. The technical term for this property is *coherence*; the SI base units and derived units form a coherent set.

Table A08 – The SI Base Units

Quantity Measured	*Symbol for Quantity*	*Unit Name*	*Unit Symbol*
Length	L, D, r, *etc*	meter	m
Mass	m	kilogram	kg
Time, duration	t	second	s
Temperature	T	kelvin	K
Electric current	I, i	ampere	A
Amount of substance	n	mole	mol
Luminous intensity	I_V	candela	cd

From the SI Brochure (BIPM 2006).

Table A09 – Some SI Derived Units

Quantity Measured	*Quantity Symbol*	*Unit Name*	*Unit Symbol*	*Derived From*	*Base Units*
Frequency	f	hertz	Hz	$1/t$	1/s
Area	A	*The SI has not assigned special names for these units*		L^2	$\mathrm{m^2}$
Volume	V			L^3	$\mathrm{m^3}$
Density	ρ			m/V	$\mathrm{kg/m^3}$
Velocity	$\mathbf{u}$			$\mathbf{d}/t$	m/s
Acceleration	$\mathbf{a}$			$\mathbf{u}/t$	$\mathrm{m/s^2}$
Momentum	$\mathbf{p}$			$m \cdot \mathbf{u}$	kg·m/s
Force	$\mathbf{F}$	newton	N	$m \cdot \mathbf{a}$	$\mathrm{kg \cdot m/s^2}$
Pressure	P	pascal	Pa	$\mathbf{F}/A$	$\mathrm{kg/(m \cdot s^2)}$
Viscosity	η	pascal second	Pa·s	$\mathbf{F} \cdot t/A$	kg/(m·s)
Energy or Work	E, W	joule	J	$\mathbf{F} \cdot L$	$\mathrm{kg \cdot m^2/s^2}$
Power	P_W	watt	W	E/t	$\mathrm{kg \cdot m^2/s^3}$

The BIPM has named 22 derived units; all are coherent.
The above selection lists some derived units used in this text. From BIPM (2006).

Take the unit of force as an example. Newton's Second Law defines force as:

$$\mathbf{F} = m \cdot \mathbf{a} \qquad \text{Eq. A-1}$$

So Newton's Law also *defines* the SI unit of force that, not coincidentally, we call the newton N. Inserting the units of mass and acceleration into Equation A-1 gives:

$$\mathrm{N} = \mathrm{kg} \cdot \frac{\mathrm{m}}{\mathrm{s}^2}$$

Thus, if you multiply the mass of the object in kilograms by the acceleration in *meter-per-second-squared*, you will get the force in newtons without need of numeric factors. Notice that all the units that make up the newton are SI base units. The new name given to the unit—*newton*—doesn't change the fact that it comprises kilograms, meters, and seconds.

As another example, consider the unit of pressure. Physics defines pressure P as the amount of force $\mathbf{F}$ acting on a unit surface area A:

$$P = \frac{\mathbf{F}}{A} \qquad \text{Eq. A-2}$$

From this definition, the derived unit of pressure is *newton-per-square-meter* $\mathrm{N/m^2}$. The BIPM named this unit the pascal Pa. Inserting the base units of force and area into Equation A-2 shows that the pascal is a function of base units—again without numeric multipliers:

$$\mathrm{Pa} = \frac{\mathrm{kg} \cdot \mathrm{m}}{\mathrm{s}^2} \cdot \frac{1}{\mathrm{m}^2} = \frac{\mathrm{kg}}{\mathrm{m} \cdot \mathrm{s}^2}$$

Coherence is a very useful property as it simplifies equations and eliminates error. It's true that coherence also results in some units being much larger or much smaller than we typically use in our industry, but that is a minor inconvenience and is easy to overcome by using either a unit prefix or the scientific notation. For a review of the latter, consult Section A-04.

Unit Prefixes

The SI system of units allows the use of certain standard prefixes to increase or decrease the value of the standard unit. Table A10 lists some selected prefixes.

Table A10 – Standard SI Prefixes

Prefix	*Example*	*Symbol*	*Size*
tera	terameter	Tm	10^{12} m
giga	gigameter	Gm	10^{9} m
mega	megameter	Mm	10^{6} m
kilo	kilometer	km	10^{3} m
	meter	m	
milli	millimeter	mm	10^{-3} m
micro	micrometer	µm	10^{-6} m
nano	nanometer	nm	10^{-9} m
pico	picometer	pm	10^{-12} m

The prefixes used here are all single characters. Prefixes are not hyphenated and never stand alone. In the table above, we applied the prefixes to the meter symbol m as an example of their use.

You can apply any standard prefix to any base unit or any derived unit. For instance, the prefix kilo makes a unit 1000 times larger. So a kilopascal is 1000 times the pressure of a pascal and a kilometer is 1000 times as long as a meter.

It's strictly one-on-one, though; you should not use two prefixes on one SI unit. For instance, the millimicron is not an acceptable unit—use nanometers instead. Also, a prefix cannot stand alone. For instance, the micron μ is also obsolete, replace it with the micrometer μm.

For historical reasons, the base unit of mass is an anomaly. The SI Brochure designates the kilogram as the base unit, but you can still replace the prefix *kilo* to make other mass units like milligram mg or megagram Mg.

Prefixed units are good for reporting and discussing practical measurements, but they can cause errors when incorrectly used in equations or when used to report scientific data. Those prefixes are just built-in factors, after all—easy ones, but factors nonetheless. Because all prefixed units contain factors, they are *incoherent* when used in equations.

As a visual example, imagine a highway engineer calculating the surface area of a road by multiplying the road width in meters by its length in kilometers! The answer would be meaningless. Our confused highway engineer should first multiply his kilometer length by 1000 to get the road length in meters. Then his calculation would give the road surface area correctly in square meters.

! If your data is in noncoherent units, you must convert it to coherent SI units before entering the values into the equations in this book. The occasional exceptions to this rule are clearly noted.

You can make an exception to this rule when the prefixed units cancel out. For instance, to calculate time delay in transport lines we divide the line volume V by the sample flow rate $\dot{V}$ using Equation 2-2:

$$t = \frac{V}{\dot{V}} \qquad \text{Eq. (2-2)}$$

While the purist would argue that the coherent SI unit of volume is the cubic meter and the unit of flow rate is cubic-meter-per-second, these units are inconveniently large for sampling work. So we often measure line volume in milliliter and flow rate in milliliter-per-minute. These units are fine for calculating time delay, since the milliliters cancel when entered in Equation 2-2, returning the time delay in minutes. For instance:

$$t' = \frac{500\ \cancel{\text{mL}}}{250\ \cancel{\text{mL}}/\text{min}} = 2\ \text{min}$$

This book uses the prime symbol (as in t' above) to indicate that the value of the variable works out in noncoherent units.

Formatting SI Units

The SI Brochure specifies the proper formatting of data and unit symbols to ensure clear communication of information and to avoid confusion between the many units. The instructions that follow are from the US version of the SI Brochure (Taylor and Thompson 2008), but they are not materially different from the official French version.

Formatting rules:

- Unit names are English words and accept the plural form just like other nouns.
- Be careful with the unit of conductance; the unit name siemens is both singular and plural!
- Never capitalize a unit name, even when it is a real person's name.
- Write unit symbols in lower case *except* when the unit name honors a real person.

- Print unit symbols in an upright font, not italic.
- *Never* write a unit symbol in plural form: kgs means kilogram-second, *not* kilograms!
- Don't hyphenate prefixed names: write a wavelength as twenty micrometers, not twenty micro-meters.
- Leave a space between the value and its unit symbol: write 75 m, not 75m.
  This rule even applies to the % and the degree signs: write 3.9 %, not 3.9% and write 23 °C, not 23°C.

Following these rules, we capitalize the symbols for hertz Hz, kelvin K, and ampere A, but not for kilogram kg, meter m, and candela cd. The liter L is an exception, granted to avoid confusion between the lowercase l and the numeral 1.

Use the correct case for a unit prefix: 10 MV is enough to kill you!

A unit symbol is not an abbreviation, so don't place a period after it unless it falls at the end of a sentence. And don't invent your own symbol—there is no such thing as 59 secs.

It's helpful to remember that unit symbols are algebraic entities and must have a *numeric* multiplier. So it's okay to write 10 kg, but not ten kg.

You can multiply and divide symbols using the laws of algebra. When multiplying *different* symbols, it's clearer to separate them with a middle dot: write the viscosity of your oil as 2.6 mPa·s rather than 2.6 mPas. When you are dividing symbols, use the solidus (/) or the negative exponent. For instance, it's equally acceptable to write the acceleration due to gravity as 9.81 $\mathrm{m/s^2}$ or 9.81 $\mathrm{m \cdot s^{-2}}$.

When more than four numerals sit before or after the decimal marker, SI practice is to use a narrow space to separate triads of digits, rather than the comma or period separator that is standard in different countries.

We follow that practice throughout the book, *e.g.,*

1 lb = 0.453 592 37 kg
1 psi = 6894.757 28 Pa
1 bar = 100 000 Pa

Amount of Substance

One of the seven SI base units is the mole, which the SI calls the *amount of substance*. Its unit symbol is mol. The mole is a convenient size for counting molecules, so it is useful in chemical analysis. You will need to understand it.

Strangely, the mole is actually a count. Scientists use it to count the number of entities present in a defined situation. The entities can be anything, really: electrons, protons, ions, atoms, or molecules for starters; so you always have to say what entities you are talking about. The entities don't have to be small; according to recent estimates, our universe contains about 0.1 mol of stars!

The mole is a very large count . . . nearly a trillion trillion!

One mole is a very large number of entities, about 6.022×10^{23}, give or take a few. We will never know the exact number.

The definition of the mole is the *number of atomic entities in exactly 12 g of carbon-12.* Carbon-12 is the most abundant isotope of carbon, having six protons and six neutrons in its atomic nucleus.

We can't *count* that many atoms, but we can *measure* them by their mass. We can dispense 12 g of carbon quite precisely on a laboratory balance, but not perfectly—it's now a measurement, not a count!

For any other element, the mass of one mole of its atoms is equal to its atomic mass (also known as atomic weight) expressed in grams. This is true because the atomic mass of each element is just its relative mass compared to carbon-12. Refer to the periodic table at the back of the book for the atomic mass of each element.

By definition, the atomic mass of carbon-12 is exactly 12 atomic mass units (amu). In comparison, the atomic mass of hydrogen is 1.008 amu. It follows that one mole of hydrogen atoms must have a mass of 1.008 g.

You can readily see that the atomic mass unit is equal to exactly one-twelfth of the mass of a carbon-12 atom. But did you realize that one mole of amu is exactly equal to 1 g?

Mostly, chemists use the mole to count molecules, rather than atoms. The chemical formula of methane, for example, is CH_4, indicating that one methane molecule contains one carbon atom (atomic mass: 12.01 amu) and four hydrogen atoms (atomic mass: 4×1.008 amu). Adding the atomic masses gives a molar mass (alias molecular weight) for methane of 16.04 amu. Therefore, 16.04 g of methane contains one mole of molecules.

Chemists *count* molecules because they enjoy reacting molecules together one by one. For instance, with the help of a catalyst, a chemist can make two molecules of ammonia gas (NH_3) by reacting three molecules of hydrogen with one molecule of nitrogen. The chemical equation shows what happens to the molecules:

$$3H_2 + N_2 = 2NH_3$$

Notice the number of each kind of atom doesn't change; you end up with the same number that you started with. That's rather important, since chemists do not have a permit to create or destroy atoms.

A chemical engineer designing an ammonia production plant will use the above equation too. But ammonia plants don't make two ammonia molecules at a time, they make quadrillions of them. In fact, they make *moles* of them. Even a mole is not big enough for chemical engineers; they prefer the kilomole (kmol) to measure the number of molecules flowing through their pipes.

Measures of Concentration

The mole fraction is the simplest and most effective unit of concentration and the one most used by chemical engineers to specify the composition of their streams. The mole fraction is just the numerical proportion of molecules in the fluid that conform to the definition of the measurand, which might be methane or C_4 paraffins, for example.

Being a fraction, it has no units. When calculated, its units are mol/mol, but these cancel out leaving a plain fraction. Ironically, engineers always write a mole fraction as a decimal number, often with far too many decimal places! Even so, it's an excellent unit that permits no ambiguity.

That's more than can be said for percentages. There are three ways to calculate a percentage, and they each have different values:

- Mole percent is the mole fraction multiplied by one hundred.
- Volume percent is the *volume fraction* multiplied by one hundred.
- Weight percent is the *weight fraction* multiplied by one hundred.

Arguably, we should measure in units of mass percent rather than weight percent. In practice, chemists often mix calibration samples by mass because that is what a chemical balance measures. But it doesn't matter. The pull of gravity is the same on each molecule, so mass percent and weight percent are always equal.

Percentages work well down to about 0.1 %. For lower concentrations, it is better to use smaller units. If you look at a percentage as a part-per-hundred, it might help you to see its relation to the smaller units of concentration:

$$0.1\ \% = 1000\ \text{ppm}$$

In American usage, the smaller units are:

part-per-hundred (%)	1 part in 10^2	the fraction 10^{-2}
part-per-million (ppm)	1 part in 10^6	the fraction 10^{-6}
part-per-billion (ppb)	1 part in 10^9	the fraction 10^{-9}
part-per-trillion (ppt)	1 part in 10^{12}	the fraction 10^{-12}

All of these units are ratios. Like percentages, they can be mole ratios, volume ratios, or mass ratios. Each is ambiguous unless you specify the basis of the ratio.

The symbol ppt usually designates a *part-per-trillion.* The ideal-sized unit *part-per-thousand* (also ppt!) never made it into general use because the familiar *percent* upstaged it. So ppt will probably mean parts-per-trillion whenever you see it. Check the context just to be sure.

A Problem with Ratios

Since measures of concentration like percent or parts-per-million are simple ratios of identical quantities—of two volumes or two weights, for instance—the quantity units cancel out leaving no units at all!

So we reluctantly conclude that the customary “units” of concentration, like %, ppm, and ppb, *are not real units of measure*, since they do not represent an amount of a measurand. Nonetheless, they are deeply entrenched in analytical parlance, and it is important that you understand them.

%, ppm, and ppb are not real units of measure!

In this text, we decided to use ppm, ppb, or ppt solely as descriptive abbreviations, not as the symbols of units. As such, they may appear without numeric multipliers. Moreover, we do not qualify them unless the distinction between a mole, volume, or weight ratio is pertinent to the issue at hand.

Table A11 shows the concentration units commonly encountered in process analysis and their preferred SI equivalents.

SI Units of Concentration

The most common measure of concentration is the percentage. The SI accepts its symbol % simply as a symbol for the number 0.01 and not as a unit of measure. Using this definition, an analytical measurement of 9.3 % reduces to 0.093 without units of any kind.

Yet the units chosen for the ratio profoundly affect the measured value. A percentage by weight is often quite different when calculated by volume. Any ratio is meaningless without a notation of the units being ratioed.

Ratios written in words such as parts-per-million, parts-per-billion, and the like are forbidden under the language-independence rules of the SI. So are their acronyms ppm, ppb, etc.

To avoid misinterpretation, there are other ways to express analytical data. For example, if you are measuring carbon monoxide CO, instead of writing 9.3 % *by weight*, 2.7 % *by volume*, or 6.4 % *by mole*, you can employ one of these display formats:

An equality:	$w_{\mathrm{CO}} = 9.3\ \%$	$\varphi_{\mathrm{CO}} = 2.7\ \%$	$\chi_{\mathrm{CO}} = 6.4\ \%$
Fractions:	$w_{\mathrm{CO}} = 0.093$	$\varphi_{\mathrm{CO}} = 0.027$	$\chi_{\mathrm{CO}} = 0.064$
The SI units:	93 g/kg	27 mL/L	64 mmol/mol
A variable:	9.3 % *m*	2.7 % *V*	6.4 % *M*

Table A11 – Various Concentration Units

Measured Quantity	*Example in Ratio Units**	*Value in SI Prefixed Units*		*Value in Scientific Notation*
Measurement by Mole Ratio				
Mole fraction	0.01	10 mmol/mol		$1 \times 10^{-2}\ M$
Percent	1 % *M*	10 mmol/mol		$1 \times 10^{-2}\ M$
Parts per million	1 ppm *M*	1 µmol/mol		$1 \times 10^{-6}\ M$
Parts per billion	1 ppb *M*	1 nmol/mol		$1 \times 10^{-9}\ M$
Parts per trillion	1 ppt *M*	1 pmol/mol		$1 \times 10^{-12}\ M$
Measurement By Volume Ratio				
Percent	1 % *V*	10 mL/L	10 L/m³	$1 \times 10^{-2}\ V$
Parts per million	1 ppm *V*	1 µL/L	1 mL/m³	$1 \times 10^{-6}\ V$
Parts per billion	1 ppb *V*	1 µL/m³	1 mm³/m³	$1 \times 10^{-9}\ V$
Parts per trillion	1 ppt *V*	1 nL/m³		$1 \times 10^{-12}\ V$
Measurement by Mass or Weight Ratio				
Percent	1 % *w*	10 g/kg		$1 \times 10^{-2}\ w$ or m
Parts per million	1 ppm *w*	1 mg/kg		$1 \times 10^{-6}\ w$ or m
Parts per billion	1 ppb *w*	1 µg/kg		$1 \times 10^{-9}\ w$ or m
Parts per trillion	1 ppt *w*	1 ng/kg		$1 \times 10^{-12}\ w$ or m
Measurement by Mass or Weight per Unit Volume				
Percent	1 % *w/V*	10 g/L	10 kg/m³	1×10 kg/m³
Parts per million	1 ppm *w/V*	1 mg/L	1 g/m³	1×10^{-3} kg/m³
Parts per billion	1 ppb *w/V*	1 µg/L	1 mg/m³	1×10^{-6} kg/m³
Parts per trillion	1 ppt *w/V*	1 ng/L	1 µg/m³	1×10^{-9} kg/m³

* These customary units are disallowed under the SI.

Because the % symbol is equal to the number 0.01, the first two formats are equivalent. These equality formats are preferred because the standard weight, volume, or mole fraction symbol (w_B, φ_B, or χ_B) indicates which quantity of *substance B* is ratioed.

The third format is clear as it shows the ratioed SI units explicitly. It might be the easiest for a reader to understand.

The fourth format uses the symbol of a variable to indicate what is being ratioed. The symbol of each variable should appear in an italic typeface and should have its meaning defined somewhere in your writing.

Frankly, it seems unlikely that ppm or ppb will vanish any time soon, so we continue to use them in this book. In formal writing, though, you may need to use or interpret a proper SI format. If so, an example may help: The following expressions are equivalent ways of reporting a carbon monoxide concentration by weight or by volume:

• Ratio units:	87 ppm *w*	133 ppm *V*
• An equality:	$w_{CO} = 8.7 \times 10^{-5}$	$\varphi_{CO} = 1.33 \times 10^{-4}$
• The SI units:	87 mg/kg	133 mL/m³
• A variable:	$8.7 \times 10^{-5}\ w$	$1.33 \times 10^{-4}\ V$

Again, the equality is preferred, but the explicit ratio of SI units might be the easiest format to understand.

Engineering Units of Concentration

When analyzing liquid solutions, analytical chemists often measure analyte concentration in mixed mass-volume units such as *milligram-per-liter* mg/L. In the laboratory, it's easier to measure solids by mass and liquids by volume, so chemists make standard solutions

Be careful when using ppm units for analyzing solutions!

by dissolving a known mass of the solute in pure water and topping off the solution to exactly one liter.

Since a liter of pure water is almost exactly one kilogram, a concentration of 1 mg/L is very close to 1 mg/kg. For this reason, an analyst may say *ppm* instead of mg/L, and *ppb* instead of μg/L. This language is acceptable during discussion, but it's better to use the proper engineering units (*e.g.,* g/m^3) in reports.

Many instruments classified as process analyzers do not make concentration measurements and always use engineering units. A flash point analyzer might report in degree Celsius, a conductivity analyzer in siemens per centimeter, and a viscosity analyzer in centipoise.

Summary

Section A-2 introduced these concepts:

- SI units of measure are the internationally recognized standard for science, technology, and commerce.
- The SI defines seven base units and derives other units using the laws of physics, thus forming a coherent set.
- Coherent units require no constants or conversion factors, which simplifies calculation.
- Unit symbols may be multiplied or divided by other unit symbols to create new units.
- Conveniently, some derived units have their own name, but they remain an algebraic combination of base units.
- Adding a standard prefix modifies the size of an SI unit, but the resulting prefixed unit is no longer coherent.
- There are rules for the written format of SI unit names and symbols, to avoid the misinterpretation of data.
- The mole is a count: the number of atomic entities in exactly 12 g of carbon-12—about 6.022×10^{23}.
- The mass of one mole of any substance is equal to its molar mass in grams.
- Analytical units of measure are usually simple fractions without units of any kind.
- The simplest analytical unit is the mole fraction—often used by chemical engineers.
- All ratio units depend on the quantities being ratioed, which must be stated.
- Analytical measures like % and ppm are not quantities of the measurand, so they are not real units.
- The % symbol has been accepted by SI just to mean the number 0.01, but ppm, ppb, etc., are not allowed.
- Analyses made in weight-per-volume ratio (like mg/L) are sometimes incorrectly stated as % or ppm.

Self Assessment Question – SAQ A-2

As written here, these measurements have format errors. Rewrite them in the proper SI format:

- *using appropriate prefixed units*
- *with the correct unit symbols*

a distance	*31 KM*
a mass	*3100 gms*
a temperature	*298 °K*
a pressure	*7 Mpas*
a flow rate	*30 lpm*
a viscosity	*0.003 pas*
a measurement signal	*20 MA*

Self Assessment Questions – SAQ A-5

Seven measurements of a constant quantity of a measurand yield these values: 103, 107, 104, 106, 102, 106, and 107 nm. In your answers to the following questions, include the correct units.

1. *What is the mean of these measurements?*
2. *What is the estimated standard deviation of the measuring technique, based on this set of results?*
3. *What is the estimated precision of a single measurement at the 95 % confidence level? Use data from Table A16.**
4. *If the measurand does not change, what percentage of future measurements would you expect to exceed 107 mm?*

* Note: A more advanced evaluation would slightly expand the confidence limits because the small number of results used here does not provide an accurate estimate of the standard deviation. The data in Table A16 uses 20 results, but here you only have seven. For details, refer to ASTM D 6299 (ASTM 2008).

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Answers to SAQ

SAQ A-1

1Q1. *The three properties are: a numerical quantity, a unit of measure, and an indication of accuracy.*

1Q2. *There are many examples of counts, for example: an amount of money, an exact conversion factor, the number of votes in an election, the value of an integer exponent like the 2 in* πr^2*, and the number of atoms in a chemical formula.*

1Q3. *False. Mistakes are human errors. Lack of repeatability is due to random changes in the measurement environment that may not be controllable.*

1Q4. *False. Measurement bias is due to calibration error, uncorrected nonlinearity, or interference from other chemicals in the sample.*

SAQ A-2

31 km, 3.1 kg, 298 K, 7 MPa, 30 L/min, 3 mPa · s, 20 mA

SAQ A-3

Number of moles in 100 g for hydrogen = 4/2 = 2 mol

Number of moles in 100 g for oxygen = 96/32 = 3 mol

5 moles of mixture contain 2 mol hydrogen = 40 % M

5 moles of mixture contain 3 mol oxygen = 60 % M

SAQ A-4

4Q1. 1.23×10^{-5} *m*

4Q2. *1.23E–5 m*

4Q3. *a) 4.0 s (two significant figures)*
b) 10 m^2 *(one significant figure)*
c) 3.3 L (because we assume that sample system data is valid to two significant figures)

SAQ A-5

5Q1. *105 nm*

5Q2. *2.0 nm*

5Q3. *±4.0 nm (95 % confidence)*

5Q4. *107 nm is one standard deviation above the mean. About 68 % of results will fall between 103 nm and 107 nm. The remaining 32 % will be equally likely to be less than 103 nm or more than 107 nm, so only 16 % of new results will be above 107 nm.*