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Review

The Elements of Measurement

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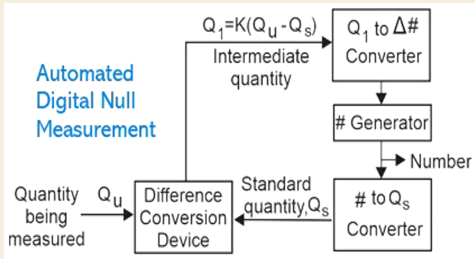
ABSTRACT: A fundamental structure for the measurement process is developed. Measurement is defined as the determination of the number of units of a particular quantity or property presented by the measured object or sample. Measurement is distinguished from qualitative observation and data interpretation. The limited sources of measurement numbers (scalar, digital, and counting readouts) reveal that all measurements except manual counting require a measurement device. Measurement systems consist of devices which convert one form of data encoding to another. They begin with the sensor and proceed through intermediate conversion devices until the readout device produces numbers. There are three classes of conversion devices: input (sensor), intermediate, and readout. The characteristics of the conversion devices in a system determine the overall system characteristics. Counting measurements have several unique characteristics. In automated counting, conversion devices are used in event detection, discrimination, and boundary setting. Variance in counting arises from event detection, boundary setting, and random event occurrence. Entire measurement systems or conversion device subsystems may operate by null comparison. Conversion devices in null comparison systems have a different arrangement. The time relationship of multiple or successive measurements affects the information content of data sets. Time-correlation of acquired data is critical in all stimulus-response measurement systems such as chromatography and time-of-flight mass spectrometry and in many subsystems such as lock-in amplifiers and box-car integrators.



KEYWORDS: *Measurements, Detection, Null-comparison, Null measurements, Conversion devices, Transfer function, Quantization, Stimulus-response measurements*

■ INTRODUCTION

A prerequisite for the development of the science of chemical measurement must be the development of a system by which the basic measurement process can be understood independently of the implementing technology. All of us have studied many specific measurement techniques in great depth. What we have may have missed, in these studies, is an overall structure of measurement systems and the devices they incorporate. This lack of measurement system structure impedes us in developing a general analysis of the measurement process and in imagining how elements used in one system could be used in another application. In this paper, I share with you the results of an inquiry into the elements of measurement that I began many years ago. In 1971, I categorized the ways in which data can be encoded and how measurements are performed by a series of devices that convert one form to another.[1] In this work, I show how complete measurement systems, from simple to complex, are combinations of data converters. This simplifies the description of their design and aids in the characterization of their performance. This paper builds on that work, extending it to the structure of complete measurement systems. There is probably little in this paper, taken point by point, that you do not already know. What this paper does is weave all these bits together into a systematic whole.

Measurements: Getting Numerical Data

Measurement is the determination of the number of standard units of a property inherent in an object or system. *The result of a measurement is always a number*. This distinguishes measurement from **observation**, which can be qualitative and subjective. Another important distinction is that between measurement and **interpretation**. Measurements produce the raw data. Interpreting those data gives us the **information** we want to gain from the measurements. These distinctions are important because the numbers we get do not, by themselves, tell us what they mean. A failure to differentiate between the measurement and interpretation processes blurs the factors that are critical to each of these steps. For example, we commonly refer to the measurement of optical absorbance, but we do not measure optical absorbance directly. We *measure* the intensities of light transmitted through the sample and blank solutions and then we *interpret* the data (by Beer's law calculation) to obtain the

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absorbance. That is just the first step of interpretation. The second is assigning the significance of that result. This paper will only deal with the means of producing the numerical data.

Since the result of a measurement is always a number, it is interesting to consider where measurement numbers come from. *Only three sources for measurement numbers have been devised*. They are **counting**, reading from a **scale**, and reading from a **digital display**. Of these, only manual counting does not require a mechanical or electronic device through which we obtain the number.

Measurement Qualities

An important aspect of measurement is an assessment of the quality of the measurement. Several parameters are available to assess measurement quality. They are accuracy, precision, resolution and range. These are, of course, the measures of the correctness, the variance, the minimum detectable difference in the output number and the range of input values over which the output number is valid. These qualities are interrelated, but in different ways depending on the measurement and the devices employed. For example, the range and resolution of a measurement employing an analog-to-digital converter are related through the range and the effective number of bits in the converter.[2] For a scalar readout, the resolution depends on the length of the scale, the change in value between adjacent marks and the skill of the observer in interpolation. The ability to assess the sources of inaccuracy, variance and resolution depends on an understanding of the measurement devices employed. For this, the characteristics of each conversion device employed must be considered.

Readout Conversion Devices

Those conversion devices that produce a number as their output **readout conversion devices**. Meter sticks convert the length of an object to a number of length units. Protractors convert the angle between two lines to a number of degrees. Analog-to-digital converters convert an input voltage to a number proportional to the input voltage. These are all examples of readout conversion devices. In fact, except for the digital display of a count value, these represent all the readout conversion devices that have been invented to date. In other words, there are **scalar readout devices** and **digital readout devices**. Of the scalar readout devices, there are two kinds: those with the scale on a line and those with the scale on an arc or circle.

The input quantity for a linear scale is necessarily *length*, and the input quantity for the partial or full circular scale must be *angle*. Thus, *all scalar readout devices are either length-to-number or angle-to-number converters*. From this it follows that all measurement devices that have a scalar readout, and measure something other than length or angle, must have a conversion device that converts the measured quantity to length or angle. There are many familiar examples. In a capillary thermometer, the liquid-filled bulb and stem convert temperature to the length of the liquid column in the stem. The scale next to the stem converts length to number (Figure 1). In a graduated cylinder, the glass cylinder converts the volume of a liquid to the length of the liquid column and the scale marked on the cylinder converts length to number. The motor or movement in an analog clock converts time to the angle of the hands and the scale marked on the clock face converts angle to number. The strip-chart recorder converts input voltage to a related position of the pen on the Y axis of the chart paper. The chart paper converts position to number. Finally, the movement in an analog panel meter

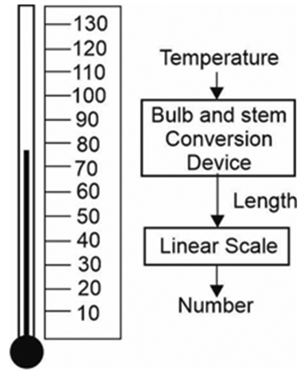

Figure 1. Liquid level in the bulb and stem convert temperature to length. The scale converts length to the temperature value.

converts electrical current to the angle of the pointer and the scale on the meter face converts angle to number.

Sometimes a scale is used to provide readout of a digital number. In such cases, the pointer cannot occupy positions between the scale markings but rather jumps from one to the next. Many quartz watches are like this. In this situation, the scale is not truly analog, no interpolation is possible, and the pointer and scale are operating as a digital readout device.

Input and Intermediate Conversion Devices

The device that converts the quantity to be measured to a different quantity is called an **input conversion device**. These are also called **sensors** or **input transducers**. Input conversion devices include the pH electrode that converts the pH of a solution to a related voltage and the photomultiplier tube that converts radiant power into a related electrical current. Additional conversion devices may be used between the input conversion device and the readout conversion device. These are often necessary to reconcile the data form from the sensor output to that required by the numerical readout device input. For example, a light sensor input conversion device converts light intensity to electrical current. The readout conversion device to be used is an analog-to-digital converter that converts voltage to a related number. An **intermediate conversion device** is thus required to convert the sensor output current to a related voltage (Figure 2). Intermediate conversion devices are also used for convenience or reduction in noise susceptibility in data transmission.

Conversion Device Transfer Function

Conversion devices convert the measurement data from one form to another. The units by which their output quantity is expressed are different from those of the input quantity. It is essential for the measurement function that there be a relationship between the input and output quantities for each conversion device. Mathematically, $Q_{out} = f(Q_{in})$ where f is some mathematical function. For many conversion devices, the output is a linear function of the input in the useful operating range. When this is the case, $Q_{out} = Q^{o}_{out} + KQ_{in}$, where Q^{o}_{out} is the output value when Q_{in} is zero and K is the proportionality constant between the input and output quantities. The units for K are output units/input units.

The mathematical expression of the input/output relationship is called the transfer function for the device. Sometimes it has been derived from the fundamentals of the device operation as in the pH/voltage relationship for a pH electrode (Figure 3). Often the first relationship is obtained empirically as a working curve. Sometimes the process defies a fundamental derivation of the

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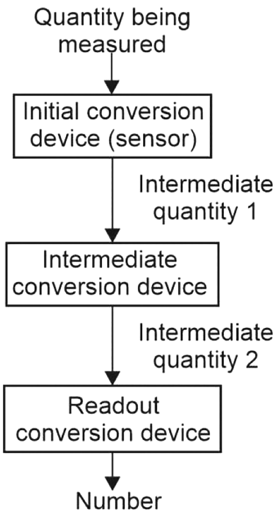

Figure 2. A sensor converts the measured quantity to some intermediate quantity. The intermediate conversion device converts that quantity to that which the numerical readout device requires at its input.

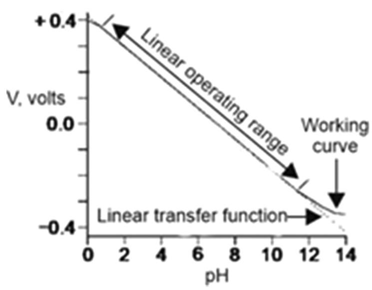

Figure 3. The working curve of a conversion device or measurement system is a plot of output as a function of the input quantity. It may be linear over a range of input values or not.

working curve, and an empirical transfer function equation is developed as for the voltage/temperature relationship for many thermocouples.

Accuracy, Sensitivity, Range, Resolution, and Precision

Each of the conversion devices used in a measurement has these qualities. The **accuracy** is the degree to which the relationship between the output quantity and the input quantity is known at the moment of the measurement. The difference between the predicted input value (based on the assumed relationship) and the actual input value is the inaccuracy of the conversion. The **sensitivity** of a conversion device is the slope of the working curve at the value of the input quantity being converted. If the working curve is linear, it is the value of K in the linear transfer function equation above. The useful **range** of a conversion device is the range of input values over which the input/output relationship is known and single-valued. This is usually bounded on the low end by the value of the input quantity below which the output quantity no longer decreases significantly. This can happen from noise or interference. The **detection limit** is usually given as 3−5 times this minimum in the useful range. At the upper end, the range is limited by the value of the input quantity beyond which the output quantity no longer increases significantly. This is often called the **saturation region**. In some devices, the value of the output quantity actually decreases after reaching a maximum giving a double-valued function.

The quality of **resolution** generally applies to readout conversion devices. It is the smallest change in the readout number that can be observed. A digital readout is constrained to unit changes in the least significant numeral, so the value of the least significant digit defines the resolution. For a scalar readout, the number can readily be read to 0.1−0.2 of the value of the distance between the two closest scale markings. If a buret has a mark every 0.1 mL, the volume can be read to 0.01−0.02 mL. The reading of a scale depends, in part, on the skill of the person taking the reading. The **precision** of a conversion device is the degree of reproducibility of the output quantity for repeated conversions of the same input quantity. For a readout conversion device, this can never be smaller than its resolution for a single measurement, though averaging multiple readings can sometimes provide a useful interpolation.

For all conversion devices, the precision is determined by the amount of change in the input/output relationship that occurs between measurements. These changes are called **noise** or **drift**, and all conversion devices are subject to them. This variance adds to any variance that may already be present in the quantity being measured. For example, in the determination of optical absorbance, we measure light intensities. Some of the variance in repeated measurements will come from the conversion devices in the light measurement system. Some of the variance can also arise from variations in light intensity that are not related to changes in absorbance. The amount of total noise or drift can be obtained by mathematical operations on repeated measurement values.[3] The statistical treatment of data is not included in this discussion because it is part of the interpretation process, not the measurement. Putting it another way, we do not measure the noise; we calculate the variance from multiple measurement values and define it as noise.

Glitches in the Working Curve

Two factors can interfere with a smooth and precise relationship between the input and output functions of conversion devices. They are hysteresis and quantization. When a device has **hysteresis**, there is a different relationship between the input and output functions depending on the direction of change in the input function. If the steering linkage of your car is loose, you experience hysteresis as the "play" or free movement in the steering wheel. Mechanical devices with gears and linkages often have some hysteresis, but some electronic and chemical systems also exhibit this behavior. When hysteresis is present, the device must be used consistently in one direction or there would be two different output values for a single input quantity.

Conversion devices that perform a digitization function introduce a stepwise irregularity in the transfer function called **quantization**. In digitization, the output can only change by integer numbers while the input may change infinitesimally. The transfer function of the digitizer can be written as $N = N^{o} + Kv$, where N is the output number and v is the input voltage. However, the value for N cannot be fractional so it is constrained to be rounded to the nearest integer value. The difference between the integer value of N and the actual value of $N^{o} + Kv$ is called quantization noise.[4] Quantization noise is reduced by increasing the number of quantization levels available in the digitizer. The number of quantization levels is equal to 2^{n}, where n is the number of bits in the converter. A 12-bit converter has 4096 quantization levels. Since the resolution of a measurement involving digitization is limited to one quantization level, increasing the number of bits in the converter also improves the resolution of the measurement.

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MEASUREMENT SYSTEMS

Except for counting or the measurement of length or angle, more than one conversion device is required in any measurement system. Thus, most measurement systems use combinations of conversion devices. As we saw in Figure 2, these are arranged serially with the output quantity of one conversion device serving as the input quantity of the next. The input conversion device converts the measured quantity to some other quantity. One or more intermediate conversion devices then convert this quantity to that required by the readout conversion device. The readout conversion device presents the number to the observer or data system.

At each stage in the measurement process, the quantity encoding the data is converted from one form to another. In my earlier work,[2] I called these data domains and showed how the various data domains were electrical quantities (voltage, current, power, or charge), digital quantities (time, number), or physical quantities (temperature, pH, light intensity, etc.). The important points here are that various quantities represent the measurement data at different points in the measurement system and that the output quantity of each conversion device must be the same as the input quantity of the next. Viewed in this way, a good understanding of the measurement process can be obtained from knowledge of the input/output relationship of each conversion device. It is not necessary to understand in detail the electronics or physical mechanisms used by the conversion devices.

System Characteristics

The characteristics of the individual conversion devices that make up a measurement system can be used to predict the characteristics of the overall system. The system transfer function will be the product of each of the conversion device transfer functions. The units of the output number are the reciprocal of the units for the measured quantity, i.e., number per volt or per pH unit, etc. This follows directly from the fact that the units for each conversion device output are output units/input units. The low limit of the range will be set by that conversion device that has the highest low limit (very often the input conversion device). Note that the low end of the range may be below the detection limit, in which case statistics determine the lowest useful end of the range. The high limit of the range is determined by the conversion device with the lowest saturation value. The expected overall variance can also be determined by combining the variances of the individual conversion devices in the appropriate way for the overall transfer function equation.[5]

The overall transfer function can be arranged so that the final number is the number of units of the input quantity. This process is illustrated for the analog thermometer made up of a bulb and stem and a linear scale (Figure 1). For the bulb and stem, the transfer function is $l = l^{o} + KT$, where l^{o} is the length of the liquid column when $T = 0$. For the linear scale, the transfer function is $\# = \#^{o} + K'l$ where $\#^{o}$ is the number marked on the scale where $l = 0$ and K' is the change in the number value per unit length of scale. The overall transfer function is the product of the two transfer functions so $\# = \#^{o} + K'l^{o} + K\,K'T$. If it is desired to have the output number equal the degrees of temperature, then $\# = T$. The conditions for which this will be true are seen by making this substitution into the overall transfer function. From this we see that if $\#^{o} = -K'l^{o}$ and $K' = 1/K$, the readout number will be the temperature. For systems with more conversion devices and nonlinear transfer functions, the process is more complex but the principle is the same. In computerized systems, no adjustment of the transfer function parameters is needed since the computer can be programmed to use the overall transfer function to obtain the number of input units from the number value produced by the measurement.

Not only is a linear transfer function no longer necessary, sometimes it is not even the most desirable. For wide dynamic range, a logarithmic transfer function offers many advantages. Such a response function was achieved for electroanalytical current measurements reaching into the picoamperes and providing useful cyclic voltammograms at the sub-nanoampere level.[6]

These days, most conversion measurement systems present the data in digital form. This means that the data are quantized at the quantization levels of the readout conversion device employed. Ideally, the quantization level is less than the variance of the measurement so that it is not the limiting factor. *From this, it follows that most digital measurement systems present more digits than are significant.*

COUNTING MEASUREMENT SYSTEMS

Counting proceeds in integer steps so is an inherently digital measurement. Either objects or events can be counted. We can assume that the counting device consistently advances one integer for each registered event or object. In this analysis, we see that counting measurements differ greatly from measurements based on conversion devices. The units of a counting measurement are the name of the objects or events that were counted. Examples are 52 cards or 79 lightning flashes. However, there is another aspect to counting measurements. All counting operations must occur within one or more boundaries. The name(s) of the boundaries becomes the denominator in the count units.[7] For example, 52 cards per deck, 79 lightning flashes between 7 and 10 per minute, and 5693 photons per second.

Variance in Counting Measurements

A major source of variance in counting measurements can come from imprecise applications of the definitions of the objects or events to be counted and the boundaries over which they will be counted (Figure 4). A binary decision must be made regarding each event or object to be counted. For example, the number of cards in a deck depend on whether the jokers "count" as cards, whether cards from another deck have gotten mixed in, and so on. In automated counting systems, this decision must be made by some recognition circuit. These recognition circuits are

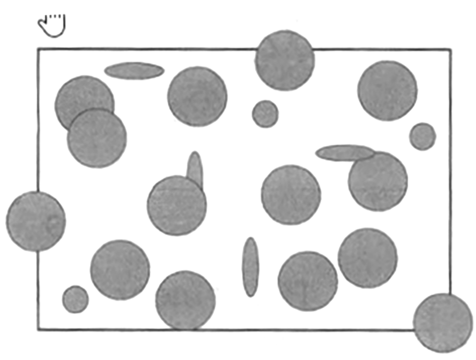

Figure 4. An accurate count depends on distinguishing the objects or events one wants to count from those that should not be included. This task is performed by a discriminator. In this case, exclusion would be by shape and/or location within the boundary.

themselves conversion devices. For example, a photomultiplier converts a photon hitting the photocathode into a pulse of current.

If the amplitude of the current pulse exceeds a preset threshold level, the pulse is assumed to have come from a photon and an increment command is sent to the counter. The degree of discrimination achieved by these conversion devices determines the extent to which false objects or events are counted and the fraction of true events and objects that are missed. Physicists often use the simultaneous detection of correlated phenomena in addition to a threshold value to improve the degree of discrimination. This is called coincidence counting.

Another source of variance in counting is in the application of the boundaries over which the count is taken. If the boundaries are imprecise or the position of an object or event with respect to the boundary is unclear, there is an uncertainty that can lead to variance in successive measurements. Examples are people standing in the doorway when counting the occupants in a room or people who come or go while the count is being taken. The boundaries for manual counting can take a variety of forms that we can sense. However, electronic counters have only start and stop inputs with which to impose the boundary. Therefore, the boundaries for automated counting systems must be converted to one or more time or condition intervals during which the count will be advanced.

Synchronized and Unsynchronized Boundaries

Two situations exist between the initiation of the count interval and the events to be counted. In one case, they are synchronized such that the beginning of the count interval is set by the occurrence of the first event to be counted. If the events occur at regular intervals during the count, the same number will be obtained for each repetition of the count measurement. In the other case, the initiation of the count is not synchronized with the event occurrence. In this case, repetitive measurements of regularly occurring events will result in two values that differ by one count (Figure 5). At first, it might seem as though synchronization is preferred because the result is more consistent. However, the average of the measured values without synchronization will give the average (now fractional) number of events that occur in the count interval. This increase in the number of significant figures through averaging (a data interpretation step) provides no new information if the count is synchronized.

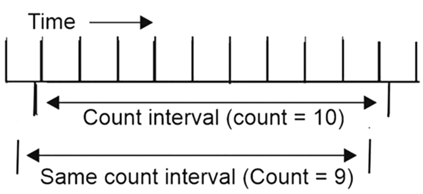

Figure 5. When counting regularly occurring events in a given time, the result will vary by one count depending on the time the count is started.

Counting Time

Digital time measurements are performed by counting time intervals. Therefore, time, for an electronic instrument, is considered a digital quantity. An electronic oscillator produces events (cycles) at regular intervals. The frequency of ordinary quartz crystal oscillators can be accurate to within one part in 10^5 and precise to within one part in 10^7. Even higher degrees of accuracy and precision are possible through frequent calibration and temperature control. In the atomic clock that sets the world standard, each second is divided into 9,192,631,770 parts. The stability of this oscillator is such that the clock it runs will not be off by more than 1 s in 100 million years. This makes the measurement of time or frequency one of the most accurate and precise measurements available to the scientist.[8] Digital frequency dividers are absolutely accurate and can create any desired frequency or time interval from the basic quartz oscillator. Timers count the number of time intervals between the start and stop commands to the counter. Frequency meters count the number of events that occur in a time interval generated by the quartz oscillator and the frequency divider.[9] These measurements are usually done without synchronization between the counted events and the start command so that a one-count variance is expected. Again, averaging repetitive measurements can provide additional significant figures.

Regular and Random Events

Random events occur at irregular intervals from zero to much greater than the average interval (Figure 6). Examples of randomly spaced events are nuclear disintegrations and the arrival of photons or ions at a detector. Counting randomly spaced events poses two difficulties for the experimenter. One is that two or more events can occur within the resolving power of the event detector (called the dead time). This results in an inaccurately low count. An estimate of the fraction of the events that were not counted can be obtained by considering how many counts (on average) would have occurred during the time the detector was busy with other counts.[10] This fraction is $1 - Nt_d$, where N is the observed count rate (in counts/second) and t_d is the dead time (in seconds). This approximation works only for values of Nt_d that are small compared to 1. Nevertheless, it is instructive to know that for the error to be less than 1%, the dead time must be less than 1% of the average count interval $(1/N)$. For values of Nt_d of 0.1 or larger, the simple approximation is no longer valid and methods based on binary or Poisson statistics must be used.

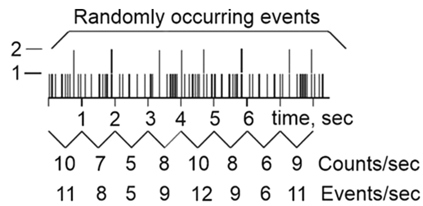

Figure 6. When counting randomly occurring events, multiple events can occur within the resolving power of the event detector and discriminator. This results in an undercount error, which, if small, can be corrected mathematically.

The other difficulty with the measurement of randomly spaced events is that the count results are not reproducible over repetitive time periods. The randomness of the event occurrence results in a variance in the number of events that occur over a given time period. The value of the standard deviation has been shown from Poisson statistics to be equal to the square root of the number of events counted.[11] The relative standard deviation is thus the reciprocal of the square root of the count. For example, if the count result is 100, the RSD is 1/10 or 10%. For the result of a single count measurement of randomly spaced events to be accurate to within 1%, 100^2 = 10,000 counts would have to be observed.

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Until recently, most counting measurements have been one-dimensional; that is, the objects or events to be counted occur serially in a single channel. Now, with the advent of digital images, objects in an image, or series of images, can be counted by pattern recognition. In this way, individual fluorescent molecules in a phospholipid membrane have been counted.[12]

NULL MEASUREMENT SYSTEMS

In a null measurement, a standard quantity is adjusted until it gives the same response as the quantity being measured. The numerical value is then obtained from the number of standard units that have been determined to be equal to the input quantity. An example is the two-pan balance upon which standard weights are used to offset the weight of the sample. Null measurement systems are composed of conversion devices, but they are organized differently from the linear systems discussed thus far. The block diagram of a null measurement system is shown in Figure 7. The goal of the system is to make Q_s, the standard quantity, as near equal to Q_u as possible. A differential conversion device converts the difference between the measured and standard quantities to another quantity. The value of this intermediate quantity relative to a preset value (generally zero) indicates whether the current value of Q_s is too large or too small. The Q_1-to-ΔQ_s converter operates to instruct the Q_s generator to reduce the difference to null. This process continues until null is achieved within the resolution of the adjustment in the value of Q_s. The measurement result is then the magnitude of Q_s. Sometimes this can be read directly from the Q_s adjustment mechanism. Occasionally, another conversion device is required to convert Q_s to a numerical value.

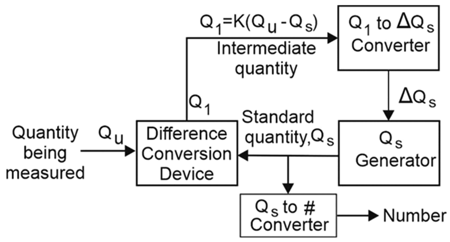

Figure 7. In a null measurement system, the quantity being measured is compared with the output of an adjustable generator of the same quantity. The output Q_1 of the comparator (too large or too small) is used to adjust the standard quantity generator to bring the difference to zero. Another conversion device or system converts the generated quantity to a number. This approach is often the case for manual null measurements such as the double-pan balance.

Null measurement systems that are inherently digital have a somewhat different configuration as shown in Figure 8. The Q_1-to-Δ# converter instructs the number to increase or decrease. This number is then passed on to the number-to-Q_s converter. When the difference is reduced to less than the change in Q_s caused by an integer change in the number, the process is complete, and the number generator output contains the measurement value.

Qualities of Null Measurements

Null measurements offer one great advantage over direct conversion measurements. The accuracy of the measurement is determined by the adjustable standard quantity and not by the transfer function of the conversion devices employed (assuming the Q_s-number conversion can be done completely accurately). It is like building the calibration step into the measurement process for each measurement value. Its greatest value is realized when the adjustable standard quantity is the same as the quantity being measured, that is, no conversion devices or data interpretation steps are required. This is the case in the two-pan analytical balance. In this system, many factors that could affect the downward force exerted by each pan cancel out leaving the difference indication due only to the difference between the sample and standard masses. In modern electronic balances, force is balanced, not mass, and calibrations are required.

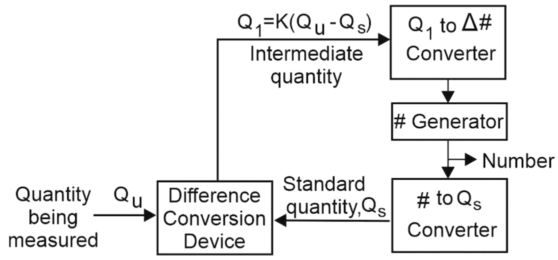

Figure 8. In null measurement with a direct digital output, the standard comparison quantity generator is set by the value of an input number. The output of the comparator instructs a number generator to increase or decrease as needed to bring the difference between the measured quantity and the standard quantity to zero.

To work effectively, the difference conversion device output for a null difference input must be known and stable. The sensitivity, resolution, and precision of the difference conversion device must be such that the smallest change in Q_s that can be made results in a readily detectable difference in its output. The smallest change in the standard quantity that can be made then determines the resolution of the measurement.

Relevance of Null Measurements Today

The disadvantage of the null measurement is that the system must be allowed to come to the null state before the measurement number is valid. If the null process is performed manually, this can be very tedious. Consequently, few manual null measurements are performed anymore. However, automated null measurements are still very common. The electronic balance employs null measurement as do the most common types of analog-to-digital converters (ADCs).[13]

If the input quantity is a voltage, the device is an ADC. The difference conversion device is a simple comparator which senses whether the input voltage is greater or less than the voltage generated by the # generator and number-to-voltage converter. The output of the difference conversion device (too large or too small) instructs the # generator to change accordingly. In a successive approximation converter, it tests first the most significant bit and works down from there. In a flash converter, there is a comparator for every number value and all are tested at once.

It is safe to say that advances in ADCs in resolution and speed have been among the most transformative developments in measurement systems. High-speed is now defined as greater than 10 megasamples per second with the fastest converters sampling in the low gigahertz range with 12−14 bits of resolution. As mentioned in Box 1, ADCs have replaced ion counting systems in time-of-flight mass spectrometers providing greater resolution and wider dynamic range. Resolutions are now up to 24 bits at megahertz speeds. That is 1 part in over 16 million.

The null principle is also fundamental to all operational amplifier circuits.[14] These automated null systems are now

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Box 1

An interesting problem involving pulse overlap exists in time-of-flight mass spectrometry. Ions of the same mass-to-charge ratio arrive at the detector at nearly the same time. Ion counting is desired for maximum sensitivity, but the number of ions arriving in this group must be low enough to avoid pulse overlap. This unfortunate trade-off limited the sensitivity, accuracy, and dynamic range of mass peak values until ion counting was replaced by fast analog-to-digital converters when their characteristics became favorable.

subsections (conversion devices) in most modern measurement systems.[15] Operational amplifier circuits are used for many intermediate conversion devices and the ADC is a common readout conversion device. The quantity nulled is hardly ever the quantity being measured; it is usually some intermediate quantity. Operational amplifier circuits often null the signal from the sensor. ADC's null a voltage that is derived from previous conversion devices.

CORRELATED DATA SETS

Each data point in a series is obtained at a particular instance in time. In many measurement applications, it is important to know the time for which the data point was valid. If there are delays in the measurement system, the computer time at the instant of acquisition might not be the true time of data validity. The time of digitization can be known precisely if a sample-and-hold circuit is used before the analog-to-digital converter. The time at which the circuit was turned from the sample state to hold can define the acquisition time to within nanoseconds.

Time is not the only parameter that may need to be correlated with the acquired data. Data sets for most instrumental measurements are actually data pairs. Examples are intensity/wavelength data pairs and intensity/mass-to-charge ratio data pairs. This situation exists whenever the acquired data will be plotted against some other parameter than time. When this is true, it is important that the paired data represent quantities that were both true at the same time.

Data Bandwidth

While the evaluation of sets of data in a determination is part of the interpretation process, there is an essential aspect of the measurement process that can affect the results obtained from correlating measurement values in a data set. This is the effective **bandwidth** of the data set as determined by the acquisition frequency. The bandwidth is the range of frequencies of variation of the measured quantity in the data set. This bandwidth is given by the Nyquist criteria as one-half the data acquisition rate. For example, if the data acquisition rate is set at 1000 data points per second, the data bandwidth is 500 Hz. This bandwidth could be from 0 to 500 Hz or from 2000 to 2500 Hz.

This same criterion applies to data taken with respect to any other variable. If photometric data are acquired using a scanning monochromator and an intensity measurement is made every nanometer, then the bandwidth of the data set is 2 nm; i.e., details on a scale of less than 2 nm will not be resolved. These examples assume that the response of the measurement system is fast compared to the rate of data acquisition.

Operation at a data acquisition rate greater than twice the bandwidth of the measurement system can improve the signal-to-noise ratio of the data, but it cannot increase the bandwidth of the data set. On the other hand, if the data acquisition rate is too slow to acquire all the bandwidth in the input signal, **aliasing** will occur causing distortion in the acquired signal set. (A familiar example of aliasing caused by under-sampling is the obviously wrong rate or direction of rotation of wheels and propellers in movies.) Thus, to avoid losing information and introducing distortion, the input signal should have the bandwidth required to contain all the measurement information, and the data acquisition rate should be greater than twice the entire bandwidth of the input signal.[16]

Stimulus-Response Measurements

Scientific measurements often take the form of the measurement of the response of a system to a stimulus of some sort. A pulsed laser may illuminate a sample and the photon or ion emission from the sample may be monitored as a function of time. The set of data representing the time course of the response is then correlated with the timing of the stimulus to provide the desired information. A block diagram of a general stimulus-response system is shown in Figure 9.

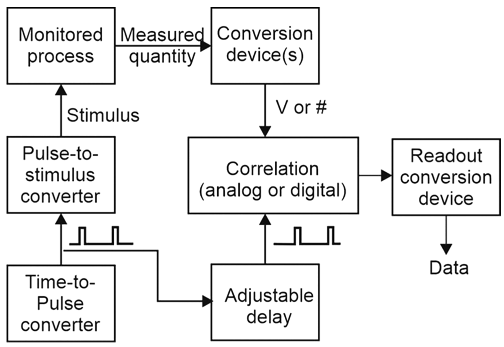

Figure 9. Stimulus-response measurement systems measure the change in the measured system caused by the application of the stimulus. A pulse generator triggers the application of the stimulus at a particular time and an input conversion device responds to the quantity expected to change. A delay generator determines the time (or times) between the application of the stimulus and the acquisition of the value of the response.

The process that is to be monitored is started by the pulse-to-stimulus converter in response to a pulsed trigger from the time-to-pulse converter. The measured quantity of the process is converted to another form by the input conversion device and this conversion is continuous or repetitive. The process-monitor data output and a time signal related to the stimulus time are both fed to the system performing the correlation. If the response data are still in analog form (usually a voltage amplitude), the correlation device is often an analog multiplier. If the response data have been digitized, the correlation can be performed by computation. In this case, knowledge of the time at which each data point was valid, relative to the stimulus event is essential.

This general block diagram and data collection approach is the basis for many common analytical instruments and subsystems. In chromatography, the monitored process is the presence of analyte molecules in the detector and the stimulus is the injection of the sample. The correlation of the detector output intensity with the injection time provides the chromatographic retention time information.

In time-of-flight mass spectrometry, the stimulus event is the extraction of ions from the ion source to begin their flight to the detector. The duration of an ion's flight between the source and detector is related to its mass-to-charge ratio. The number of ions arriving at a particular time is related to the relative abundance ions of in the sample with a particular mass-to-charge ratio. An input conversion device may convert the arrival time to a related voltage that is then converted to number by an intermediate conversion device. The data system then keeps a cumulative record of the number of ions detected at each value of arrival time. If the frequency of ion arrival is too great for arrival time detection (a pulse overlap problem), a current-to-voltage input conversion device followed by a fast ADC is used to produce an intensity-time data set. Again, the correlation of the data intensities with the time of ion extraction is required for the assignment of ion mass-to-charge ratio.

Two common time-correlated measurement subsystems are also based on the stimulus-response block diagram. They are the box-car integrator and the lock-in amplifier. The box-car integrator is often used when the response to the stimulus is more rapid than the measurement process can follow. In this case, the stimulus response is converted at just one brief time window after each stimulus. The integral of the response over this window is recorded as the response value corresponding to that time window. The delay time between the stimulus and the integrated time window is changed between application of the stimuli so that a complete curve of the stimulus response can be obtained.[17] The response to repeated stimuli is assumed to be the same. The lock-in-amplifier depends on a regular repetition of the stimulus event, which is usually in the form of a modulation of the process. The process can be modulated by supplying pulsed energy or chopping a steady-state output. The effect of the modulation on the process is extracted from the continuous or repetitive data stream by correlation with the modulation frequency. In this way, information at the repetition frequency can be recovered even though otherwise buried in noise. The delay adjustment is used to provide the maximum correlation or to measure the delay time between the modulation and response.[18]

Multidimensional Data Sets

As we move to more complex instrumentation and hyphenated techniques, there can be several levels of nested systems for measurement occurring simultaneously. An example is when a scanning spectrometer (or mass spectrometer) is used as the detector for chromatographic separation. The sample injection is the stimulus for the chromatographic process. To collect spectra repetitively, the spectrometer must be triggered at regular intervals and the time of the beginning of each spectral scan must be kept relative to chromatographic time. However, the intensity values at wavelengths or masses measured during the scan are acquired when the eluant composition may have changed from that at the beginning of the scan. The result is a skewing of the spectral data relative to that of a constant composition measurement. To avoid this, one must collect the whole spectrum simultaneously (array detection) or assign each spectral intensity to its correct chromatographic time.[19]

SUMMARY

The science of chemical measurements has been difficult to define and develop in a coherent way. It covers a huge variety of techniques, practices, chemical systems, and applications. Among its practitioners, there are instrumentalists, chemometricians, fundamental researchers, computer scientists, separations scientists, and methods developers. One thing that is common to all is making measurements and interpreting the data from them. This, then, is a place to start in the development of a science, i.e., a coherent framework, for collecting data. Without such a framework, all measurement processes will continue to be taught and understood as individual techniques. The fundamentals involved will all be “borrowed” from statistics, electronics, physics, and other disciplines. The development presented here is an attempt to put the measurement process on a sound fundamental basis that can aid the analysis and understanding of the data collection process. It is elementary in the simplicity of the building blocks (conversion devices) of measurement systems. Yet, it is comprehensive in its ability to describe the function of the most sophisticated instruments in terms that are readily understood. From this simple development come a set of rules and principles that can guide the developer and user of measurement tools. As mentioned in the Introduction, there is little in this development that is not obvious or that most of us did not already know. Its strengths lie in the new perspectives on measurements it offers and in the structures it provides for the measurement part of the science of chemical measurement.

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Notes

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REFERENCES

(1) Enke, C. G. Data Domains—An Analysis of Digital and Analog Instrumentation Systems and Components. *Anal. Chem.* **1971**, *43* (1), 69A−80A.
(2) Analog Devices Tutorial, MT-003, MT-003: Understand SINAD, ENOB, SNR, THD, THD + N, and SFDR so You Don't Get Lost in the Noise Floor. *Analog Devices*. Available at https://www.analog.com/en/search.html?q=MT-003 (accessed 2022-06-06).
(3) Coefficient of Variation. *Wikipedia*. https://en.wikipedia.org/wiki/Coefficient_of_variation (accessed 2022-06-05).
(4) Kelly, P. C.; Horlick, G. Practical Considerations for Digitizing Analog Signals. *Anal. Chem.* **1973**, *45*, 518−527.
(5) Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders Publishing, 1996; pp 33−39.
(6) Mészáros, G.; Li, C.; Pobelov, I.; Wandlowski, T.; et al. Current measurements in a wide dynamic range—applications in electrochemical nanotechnology. *Nanotechnology* **2007**, *18*, 424004−424008.
(7) Malmstadt, H. V.; Enke, C. G. *Digital Electronics for Scientists*; W.A. Benjamin, Inc.: New York, 1969; pp 2−5.
(8) How Do We Measure Time? *National Institute of Science and Technology (NIST)*. https://www.nist.gov/how-do-you-measure-it/

how-do-we-measure-time#:~:text=The%20short%20answer,one%20energy%20level%20to%20another (accessed 2022-06-08).
(9) Malmstadt, H. V.; Enke, C. G.; Crouch, S. R. *Microcomputers and Electronic Instrumentation, Making the Right Connections*; American Chemical Society, 1994; p 41.
(10) Price, W. J. *Nuclear Radiation Detection*; McGraw-Hill: New York, 1964; p 367.
(11) Price, W. J. *Nuclear Radiation Detection*; McGraw-Hill: New York, 1964; pp 57−61.
(12) Schmidt, T.; Schutz, G. J.; Gruber, H. J.; Schindler, H. Local Stoichiometries Determined by Counting Individual Molecules. *Anal. Chem.* **1996**, *68*, 4397−4401.
(13) Malmstadt, H. V.; Enke, C. G.; Crouch, S. R. *Microcomputers and Electronic Instrumentation, Making the Right Connections*; American Chemical Society, 1994; pp 299−308.
(14) Enke, C. G. The Analog Revolution and its On-Going Role in Modern Analytical Measurements. *Anal. Chem.* **2015**, *87*, 11935−11947.
(15) Kester, W., Ed., *Data Conversion Handbook, Analog Devices*; Elsevier-Newnes: Amsterdam, 2005.
(16) Sampling (signal processing). *Wikipedia*.https://en.wikipedia.org/wiki/Sampling_(signal_processing)#:~:text=The%20sampling%20frequency%20or%20sampling,is%2048%2C000%20samples%20per%20second (accessed 2022-06-08).
(17) Boxcar averager. *Wikipedia*. https://en.wikipedia.org/wiki/Boxcar_averager (accessed 2022-06-08).
(18) Northrup, R. B. *Introduction to Instrumentation and Measurements*, 2nd ed.; CRC Press: Boca Raton, FL, 2005.
(19) Holland, J. F.; Enke, C. G.; Allison, J.; Stults, J. T.; Pinkston, J. D.; Newcome, B.; Watson, J. T. Mass Spectrometry on the Chromatographic Time Scale: Realistic Expectations. *Anal. Chem.* **1983**, *55*, 997A.

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