Fundamentals of
ANALYTICAL CHEMISTRY

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> **Random, or indeterminate, errors are errors that affect the precision of measurement.**

Figures 2-1 and 2-3 suggest that chemical analyses are affected by at least two types of errors. One type, called *random* (or *indeterminate*) *error*, causes data to be scattered more or less symmetrically around a mean value. Refer again to Figure 2-3, and notice that the scatter in the data, and thus the random error, for analysts 1 and 3 is significantly less than that for analysts 2 and 4. In general, then, the random error in a measurement is reflected by its precision.

> **Systematic, or determinate, errors affect the accuracy of results.**

A second type of error, called *systematic* (or *determinate*) *error*, causes the mean of a set of data to differ from the accepted value. For example, the results of analysts 1 and 2 in Figure 2-3 have little systematic error, but the data of analysts 3 and 4 show determinate errors of about -0.7 and -1.2% nitrogen. In general, a systematic error causes the results in a series of replicate measurements to be all high or all low.

> **An *outlier* is an occasional result in replicate measurements that obviously differs significantly from the rest of the results.**

A third type of error is *gross error*. Gross errors differ from indeterminate and determinate errors. They usually occur only occasionally, are often large, and may cause a result to be either high or low. Gross errors lead to *outliers*—results that appear to differ markedly from all other data in a set of replicate measurements. There is no evidence of a gross error in Figures 2-1 and 2-3. Had one of the results shown in Figure 2-1 occurred at 22.5 ppm Fe, it might have been an outlier.

2B SYSTEMATIC ERRORS

Systematic errors have a definite value, an assignable cause, and are of the same magnitude for replicate measurements made in the same way. Systematic errors lead to *bias* in measurement technique. Note that bias affects all of the data in a set in the same way and that it bears a sign.

> **Bias measures the systematic error associated with an analysis. It has a negative sign if it causes the results to be low and a positive sign otherwise.**

2B-1 Sources of Systematic Errors

There are three types of systematic errors: (1) *Instrument errors* are caused by imperfections in measuring devices and instabilities in their power supplies. (2) *Method errors* arise from nonideal chemical or physical behavior of analytical systems. (3) *Personal errors* result from the carelessness, inattention, or personal limitations of the experimenter.

Instrument Errors

All measuring devices are sources of systematic errors. For example, pipets, burets, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations. These differences may arise from using glassware at a temperature that differs significantly from the calibration temperature, from distortions in container walls due to heating while drying, from errors in the original calibration, or from contaminants on the inner surfaces of the containers. Calibration eliminates most systematic errors of this type.

Electronic instruments are subject to instrumental systematic errors. These uncertainties have many sources. For example, errors emerge as the voltage of a battery-operated power supply decreases with use. Errors result from increased resistance in circuits because of dirty electrical contacts. Temperature changes

cause variations in resistors and standard potential sources. Currents induced from 110-V power lines affect electronic instruments. Errors from these and other sources are detectable and correctable.

Method Errors

The nonideal chemical or physical behavior of the reagents and reactions upon which an analysis is based often introduces systematic method errors. Such sources of nonideality include the slowness of some reactions, the incompleteness of others, the instability of some species, the nonspecificity of most reagents, and the possible occurrence of side reactions that interfere with the measurement process. For example, a common method error in volumetric methods results from the small excess of reagent required to cause an indicator to undergo the color change that signals completion of the reaction. The accuracy of such an analysis is thus limited by the very phenomenon that makes the titration possible.

Another example of method error is illustrated by the data in Figure 2-3, in which the results by analysts 3 and 4 show a negative bias that can be traced to the chemical nature of the sample, nicotinic acid. The analytical method used involves the decomposition of the organic samples in hot concentrated sulfuric acid, which converts the nitrogen in the samples to ammonium sulfate. The amount of ammonia in the ammonium sulfate is then determined in the measurement step. Experiments have shown that compounds containing a pyridine ring such as nicotinic acid (see page 15) are incompletely decomposed by the sulfuric acid unless special precautions are taken. Without these precautions, low results are obtained. It is highly likely that the negative errors, $(\bar{x}_3 - x_t)$ and $(\bar{x}_4 - x_t)$ in Figure 2-3 are systematic errors that can be blamed on incomplete decomposition of the samples.

Errors inherent in a method are often difficult to detect and are thus the most serious of the three types of systematic error.

Of the three types of systematic errors encountered in a chemical analysis, method errors are usually the most difficult to identify and correct.

Personal Errors

Many measurements require personal judgments. Examples include estimating the position of a pointer between two scale divisions, the color of a solution at the end point in a titration, or the level of a liquid with respect to a graduation in a pipet or buret (see Figure 3-5, page 41). Judgments of this type are often subject to systematic, unidirectional errors. For example, one person may read a pointer consistently high, another may be slightly slow in activating a timer, and a third may be less sensitive to color changes. An analyst who is insensitive to color changes tends to use excess reagent in a volumetric analysis. Physical handicaps are often sources of personal determinate errors.

A universal source of personal error is prejudice. Most of us, no matter how honest, have a natural tendency to estimate scale readings in a direction that improves the precision in a set of results, or we may have a preconceived notion of the true value for the measurement. We then subconsciously cause the results to fall close to this value. Number bias is another source of personal error that varies considerably from person to person. The most common number bias encountered in estimating the position of a needle on a scale involves a preference for the digits 0 and 5. Also prevalent is a prejudice favoring small digits over large and even numbers over odd.

Color blindness is a good example of a handicap that amplifies personal errors in a volumetric analysis. A famous color-blind analytical chemist enlisted his wife to come to the laboratory to help him detect color changes at end points of titrations.

Digital readouts on pH meters, laboratory balances, and other electronic instruments eliminate number bias because no judgment is involved in taking a reading.

Persons who make measurements must guard against personal bias to preserve the integrity of the collected data.

2B-2 The Effect of Systematic Errors upon Analytical Results

> **Constant errors are independent of the size of the sample being analyzed. Proportional errors decrease or increase in proportion to the size of the sample.**

Systematic errors may be either *constant* or *proportional*. The magnitude of a constant error does not depend on the size of the quantity measured. Proportional errors increase or decrease in proportion to the size of the sample taken for analysis.

Constant Errors

Constant errors become more serious as the size of the quantity measured decreases. The effect of solubility losses on the results of a gravimetric analysis illustrates this behavior.

EXAMPLE 2-2

Suppose that 0.50 mg of precipitate is lost as a result of being washed with 200 mL of wash liquid. If the precipitate weighs 500 mg, the relative error due to solubility loss is $-(0.50/500) \times 100\% = -0.1\%$. Loss of the same quantity from 50 mg of precipitate results in a relative error of -1.0%.

The excess of reagent required to bring about a color change during a titration is another example of constant error. This volume, usually small, remains the same regardless of the total volume of reagent required for the titration. Again, the relative error from this source becomes more serious as the total volume decreases. One way of minimizing the effect of constant error is to use as large a sample as possible.

Proportional Errors

A common cause of proportional errors is the presence of interfering contaminants in the sample. For example, a widely used method for the determination of copper is based upon the reaction of copper(II) ion with potassium iodide to give iodine. The quantity of iodine is then measured and is proportional to the amount of copper in the sample. Iron(III), if present, also liberates iodine from potassium iodide. Unless steps are taken to prevent this interference, high results are observed for the percentage of copper because the iodine produced will be a measure of the copper(II) *and* iron(III) in the sample. The size of this error is fixed by the *fraction* of iron contamination, which is independent of the size of sample taken. If the sample size is doubled, for example, the amount of iodine liberated by both the copper and the iron contaminant is also doubled. Thus, the magnitude of the reported percentage of copper is independent of sample size.

2B-3 Detection of Systematic Instrument and Personal Errors

> After entering a reading into the laboratory notebook, many scientists habitually make a second reading to assure the correctness of the entry.

Systematic instrument errors are usually found and corrected by calibration. Periodic calibration of equipment is always desirable because the response of most instruments changes with time as a result of wear, corrosion, or mistreatment.

Most personal errors can be minimized by care and self-discipline. It is a good habit to check instrument readings, notebook entries, and calculations systemati-

cally. Errors that result from a known physical handicap can usually be avoided by a careful choice of method.

2B-4 Detection of Systematic Method Errors

Bias in an analytical method is particularly difficult to detect. We may take one or more of the following steps to recognize and adjust for a systematic error in an analytical method.

Analysis of Standard Samples

The best way of estimating the bias of an analytical method is by the analysis of *standard reference materials*—materials that contain one or more analytes with exactly known concentration levels. Standard reference materials are obtained in several ways.

Standard materials can sometimes be prepared by synthesis. Here, carefully measured quantities of the pure components of a material are measured out and mixed so as to produce a homogeneous sample whose composition is known from the quantities taken. The overall composition of a synthetic standard material must approximate closely the composition of the samples to be analyzed. Great care must be taken to ensure that the concentration of analyte is known exactly. Unfortunately, the synthesis of such standard samples is often impossible or so difficult and time-consuming that this approach is not practical.

Standard reference materials can be purchased from a number of governmental and industrial sources. For example, the National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards) offers over 900 standard reference materials including rocks and minerals, gas mixtures, glasses, hydrocarbon mixtures, polymers, urban dusts, rainwaters, and river sediments.[2] The concentration of one or more of the components in these materials has been determined in one of three ways: (1) through analysis by a previously validated reference method, (2) through analysis by two or more independent, reliable measurement methods, or (3) through analysis by a network of cooperating laboratories, technically competent and thoroughly knowledgeable with the material being tested.

Several commercial supply houses also offer analyzed materials for method testing.[3]

One of the problems you will encounter in using standard reference materials to establish the presence or absence of bias is that the mean of your replicate analysis of the standard will ordinarily differ somewhat from the theoretical result. Then you are faced with the question whether this difference is due to random error of your measurements or to bias in the method. In Section 4B-1, we demonstrate a statistical test that can be applied to aid your judgment in answering this question.

Figure 2-4
Standard reference materials from NIST. (Photo courtesy of the National Institute of Standards and Technology.)

> A **standard reference material (SRM)** is a substance prepared and sold by the National Institute of Standards and Technology and certified to contain specified concentrations of one or more analytes.

> In using SRMs it is often difficult to separate bias from ordinary random error.

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[2]See U.S. Department of Commerce, *NIST Standard Reference Materials Catalog*, 1992–1993 ed., NIST Special Publication 260. Washington: Government Printing Office, 1992. For a description of the reference material programs of the NIST, see R. A. Alvarez, S. D. Rasberry, and G. A. Uriano, *Anal. Chem.*, **1982**, 54, 1226A; G. A. Uriano, *ASTM Standardization News*, **1979**, 7, 8.

[3]For sources of biological and environmental reference materials containing various elements, see C. Veillon, *Anal. Chem.*, **1986**, 58, 851A.