People are curious about the substances contained in material with which they come in contact. Precious metals may make them rich, medications may cure diseases and toxins and poisons may make them ill or worse. Analytical chemistry is the science which helps to satisfy such curiosity. Qualitative Analysis tries to answer the question "What's in this stuff?" and Quantitative Analysis tries to answer "How much?"

In 1894 the renowned chemist Wilhelm Ostwald summed up the matter when he wrote

"Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of science, since the questions which it enables us to answer arise wherever chemical processes are employed for scientific or technical purposes. Its supreme importance has caused it to be assiduously cultivated from a very early period in the history of chemistry, and its records comprise a large part of the quantitative work which is spread over the whole domain of science."

Today in routine medical examinations a single sample of blood can yield quantitative information on several dozen constituents. Quantitative analyses are used in one form or another in the processing of all raw materials, from the determination of carbon, nickel and chromium to determine the hardness of steel to the analysis of sugar content of grapes hour by hour near the time of harvest so as to give the vintner the best quality grape for fermentation into wine.

This class will offer you some experiences with four methods of quantitative analysis: gravimetric, acid-base volumetric, iodometric volumetric and spectroscopic. Some other methods, certainly equally as important as the ones with which you will come in contact ought at least to be mentioned: mass spectrometry for the determination of the masses of molecular fragments and their quantities, radioactivity for the determination of the abundance of certain isotopes, heat and rate of reaction, thermal conductivity, optical activity and refractive index.

---

**Steps in an Analysis**

The process of doing an analysis involves a number of steps which might not be done in the sequence shown, but are important points to consider and usually to execute in any analysis:

1. Deciding on an analytical method
2. Collecting and preparing the bulk sample(s)
3. Preparing the lab sample
4. Defining samples to be analyzed (replicate samples)
5. Preparing solutions of a sample
6. Paying attention to properties of the sample matrix so as to be able to eliminate interferences
7. Calibration, measurement and calculating results
8. Evaluation of results and estimation of reliability

1. The field of analytical chemistry is so very important in commerce that money is often involved and cost and profits are routinely considered. The cost of an analysis usually goes up with the level of accuracy demanded so it is not surprising that the method may be a compromise between accuracy and economics. The method to be used also is a function of the number of components in the sample which may interfere with a certain analysis.
2. The decision of how to collect and to prepare your bulk samples depends sometimes on what it is that one wants to demonstrate. *Pfiesteria piscicida*, a single-celled microorganism which lives in the Chesapeake Bay and other bodies of water near the Virginia and North Carolina coasts, is known to thrive where there is an overabundance of nutrients such as nitrogen and phosphorus in the water. These include nutrient-rich human sewage, fertilizers, certain industrial by-products and animal wastes from swine and poultry. Such an environment allows algae to proliferate and the algae provide a rich food source for *Pfiesteria*. In 1991 a billion fish died in the Neuse Estuary of North Carolina as the result of succumbing to an agent or an effect connected with an organism in the food chain of which *Pfiesteria* is one. Some say *Pfiesteria* produces a powerful toxin which kill the fish. Others suggest that the fish become part of the food chain and are eaten by the microorganisms. The matter is further complicated by evidence which suggests that some but not all varieties of a species of algae produce toxins and studies of the life cycle of *Pfiesteria* have produced ambiguous results. Proponents of one hypothesis will more likely than not defend their position vigorously in the face of evidence which other investigators find to be less than convincing. Periods of "red tide" along much of the coastline of the U.S. in which shellfish cannot be eaten because of their toxin content further complicate finding the source of natural products which are toxic to humans; moreover, one researcher claims that agricultural and industrial wastes are not the cause of algal blooms but the fault lies in red sand blown across the Atlantic Ocean from the Sahara Desert which triggers the algal blooms in the mid-Atlantic. As for the *Pfiesteria* controversy, more than a decade has passed and the matter seems to be nowhere near resolution. One would want to choose carefully how samples are to be taken based on whatever hypothesis it was to be tested. If the nutrient-algae-*Pfiesteria* link was a hypothesis to be supported, then water samples would have to be tied to a program of culture growth of the microorganism. If the link was felt to be well-established and the analysis was a part of an ongoing monitoring program then one might concentrate on regions where high nutrients might be expected to be found throughout the year. If the purpose of the analysis was a part of a program to protect the fish population then the samples might be taken during only certain months.

If a large quantity of precious metal ore is to be analyzed for the metal before a price can be agreed upon, one would definitely want to take samples from locations within the shipment at points of some wide separation so as to be able better to determine the variability of the metal within the shipment. Ores, which are commonly heterogeneous, require prudent choices to obtain representative samples.

3. **Preparing the lab sample.** Homogeneity of each sample taken from the larger bulk sample must be achieved at this point. Grinding and drying may be involved at this step. The determination of the amount of \(H_2O\) may be required as a part of the overall analysis. The grinding process not only achieves homogeneity but gives the technician a sample with finely divided particles for later work in producing a solution.

4. **Defining the samples to be analyzed (replicate samples).** Replication improves reliability because the variance between individual samples of the determined quantity of analyte establishes a level of reliability of the method used. Often individual quantities are weighed and those quantities become the laboratory samples; the process of analysis starts after this weighing. Sometimes the grinding operation is found not to produce a bulk sample sufficiently homogeneous to use this method. In this case then a larger sample may be weighed and that sample then dissolved in a measured volume of appropriate liquid. This process assures homogeneity of the analyte and measured volumes of the solution are then taken as the lab samples.

5. **Preparing solutions of a sample.** Most analyses are done on solutions because the analytical reactions go at greatest speed when the analyte is divided down to the atomic, ionic or molecular level. All of the sample must be dissolved so as to assure that none of the analyte has occluded onto the surface or within the crystal lattice of any
insoluble residue. Unfortunately, this step may be time-consuming but must be followed so as to exceed any reasonable doubt about the state of the analyte.

6. Paying attention to the properties of the sample matrix so as to be able to eliminate interferences. The families of elements found in the Periodic Table attest to there being few elements with unique properties. Thus, in practically all analyses there can be many interferences. Lead precipitates as the sulfide, but so does copper, mercury, nickel and silver. The oxidized forms of manganese (permanganate) and chromium (dichromate) have useful absorption spectra in the visible region. Both of these may be present in small amounts in steel. But iron which is present in the largest amount in steel oxidizes to Fe$^{3+}$ and has an absorption spectrum in the same region. Citrus fruits contain a large number of natural acids which would preclude the analysis for any one of them using simple acid-base titrimetry. It is often necessary that subtle differences in the chemistry of elements within families be exploited so as to eliminate all interferences from any analysis.

7. Calibration, measurement and calculating results. The measurement which leads to the final result is usually directly proportional to that result. In the gravimetric determination of sulfate, all of the sulfate in the sample precipitates as barium sulfate, \(\text{BaSO}_4\). The sulfate, the \(\text{SO}_4^{2-}\), is the amount one wishes to calculate, but the weight of \(\text{BaSO}_4\) is the measured quantity. In many cases for quantitative analyses, the calculation takes on the simple form

\[
c_A = k \times X
\]

where \(c_A\) is the desired quantity, the mass of \(\text{SO}_4^{2-}\) in 100 g of sample, but \(X\), the weight of \(\text{BaSO}_4\) is that which is measured. \(k\) is the proportionality constant which relates one to the other, in this case the ratio of the atomic weight sum for \(\text{SO}_4^{2-}\) divided by the atomic weight sum for \(\text{BaSO}_4\). Often one cannot so easily calculate \(k\); in the case of the colorimetric determination of manganese in steel, the absorbance of a known concentration of manganese must be measured. One then has

\[
[C_{A_{\text{known}}} = k \times X_{\text{measure}}]
\]

and \(k\) can be calculated from the absorbance of the known concentration by the quotient of \(c_A\) and \(X\). The assumption is that the proportionality holds for all solutions of Mn prepared in the same way, both known and unknown. A value of \(X\) for an unknown sample will yield a calculated value for the concentration of Mn in that sample.

8. Evaluating results and estimating reliability. The announcement of an experimentally determined value alone without some indication of its reliability has no scientific worth. In experimental science we have a means for implying some level of reliability: significant figures. As imperfect as is the use of significant figures the method does at least set some rather broad boundaries of reliability. Reporting a value of 2.50% Cr in a sample of stainless steel might suggest a maximum experimental deviation anywhere between ±0.01% and ±0.09%. If the experimental deviation were found to be between ±0.06% and ±0.09%, then one might consider reporting the value as 2.5 ±0.1% Cr. If nothing were known about the reliability of a quantity determined experimentally there would be no justification for reporting any value of that quantity to any number of significant figures. Any report of the measurement would be worthless. It is fortunate that rarely is nothing known about the reliability of any experimental measurement. More often than not the problem is one of data being taken poorly with bad estimates of their reliability, leading to results the validity of which is open to withering criticism.
Contributors and Attributions

Oliver Seely (Professor of Chemistry, Emeritus; California State University Dominguez Hills). This content are in the public domain and may be copied without restriction.