

Non Destructive and Destructive Analytical Techniques

Gamma Ray Spectroscopy: A variety of different types of detectors are used to determine the photon emission spectrum of radioactive materials. This spectrum is unique to each individual isotope, and with high enough detector resolution it can be used to identify the isotopes generating them. Gamma rays are emitted at discrete energies, sometimes they can be very clustered resembling a continuum, but usually distinct peaks can be seen in isotopic gamma spectrums. The better the resolution of the detector, the higher the confidence becomes in the identification of the emitting isotope. Resolution, in this case, refers to how wide the energy peak is for detected gamma-rays. As the peak gets wider the more difficult it becomes to make a determination of the true energy of the gamma-ray being detected. As the resolution improves the signals detected results in narrower peaks, and ultimately more precise identification of the parent isotope(s).

Coulometry: This refers to a broad range of techniques which utilize Faraday's laws in conjunction with some form electrolysis to determine one of the following: species concentration within a sample, sample mass, molecular mass, number of electrons present in the reaction, or the number of electrons passed during the experiment. Faraday's laws allow the relationship between sample mass, molecular mass, number of electrons present in the electrode, and the total number of electrons passed during the experiment be made such that if three of the four quantities are known, the fourth is calculated easily. The rate the species in question is consumed is not governed by concentration but rather by the mass transfer rate of the species to the electrode surface.

One major advantage of coulometry over some other methods of analysis is that the solution or products do not need to be dried and weighed. This is a crucial benefit for compounds that do not form solids easily. Also, this somewhat simplifies handling by not requiring additional equipment to perform drying, separation, and weighing. In most instances traditional wet chemistry must be performed, such as titration, to either prepare the sample for the coulometry process or to discern other data about the sample to account for drift in the Coulometric readings resultant from sample contamination. The two most widely used methods of coulometry are Potentiostatic and Coulometric Titration.

1. Potentiostatic coulometry works by keeping a working electrode at a constant potential, and measuring the current flowing through the circuit. The constant potential is maintained for sufficient time to completely oxidize or reduce all of the quantity being investigated. As the quantity is being consumed the current decreases accordingly. When the quantity is completely consumed the current drops to zero. Using specialized equipment the electrical parameters mentioned above are known, which allows the sample mass or molecular mass be determined.
2. Coulometric Titration is used to determine the concentration of a known species in solution. A constant current is applied to a solution until the species is completely oxidized or reduced. Upon reaching the endpoint of the reaction the voltage potential shifts dramatically. The amount and duration of the applied current it took to completely react the species are used to directly find the number of moles of the species in question. This process uses the current as a titrant in the same way wet chemistry uses reagents to chemically react with the analyte. If the volume of the solution is known then the concentration is easily found. Several specific methods have been developed for this technique. Two such methods are the Davies-Gray Uranium Titration (DG) and the NBL Modified DG. Using these techniques the concentrations of Uranium in things like spent fuel or raw ore can be found to within less than 0.015% uncertainty.

Gravimetry: Is a class of methods in analytic chemistry used for quantitative analysis. Gravimetry works, in general, by taking a known volume of solution and by using a variety of techniques, removing or acquiring the dissolved analyte, which can then be weighed. This methodology is only possible if the empirical formula is known. If the mass is found of the dissolved analyte in a known volume of solution then concentration is easily determined, but only if the empirical formula is known and diligence was taken to obtain exactly what is purported to be the empirical formula. The solid can be obtained by a variety of methods for example titration, desiccation, filtration, and evaporation. If performed carefully, gravimetry can yield extremely precise analysis.

Densitometry:

Overview

Densitometry utilizes the known relationship between atomic number and the mode of electromagnetic interaction to infer through excitation and preferential emission what the elemental composition of a known thickness of a target material is. Typically the energy of the incident radiation for this realm of discussion is X-rays or low energy gamma-rays. It follows that because the excitation sources are usually low energy that the dominant electromagnetic interaction is the photoelectric effect. The photoelectric effect is a strong function of atomic number (Z). Material identification is then accomplished by irradiating a known thickness of material with known discrete energy source(s) and the collection of the corresponding emission spectrum of the material. The gathered emission spectrum is analyzed and using known elemental or isotopic mass attenuation coefficients the material composition is found.

Three widely used densitometry methods are:

1. Single-line densitometry
2. Multiple-energy densitometry
3. Absorption-edge densitometry

The primary difference between the first two methods is implied by their names, whether a single discrete energy irradiation source is used or a multiple discrete energy source is used. The general approach is identical for both techniques. The most important difference between single and multiple-line densitometry is that single-line can only determine the concentration of one component of a mixture and it can only do that if the concentration of the other components in the mixture is held constant. In theory, the multiple-line method could be used to find X number of unknowns such that X numbers of discrete energies are used for irradiation. In practice this is not usually the case. More than two discrete irradiation energies results in a loss of fidelity of the measurement.

The third method, absorption edge densitometry, uses a specially tailored two-line energy irradiation source to exploit the difference in photon absorption relative to a specific electron shell. The transmission energies are selected such that they fall as close as possible on either side of an electron shell. Judiciously selecting the energies in this way allows the discontinuity of the photon mass attenuation coefficient between the last electron in a shell and the first electron in the following shell to be seen. Identification from this discontinuity is possible because the energies of the electrons within the shells are very well known published values. This technique is better suited to identifying the concentration of known solution components and not to the determination of unknown elements. This

technique is almost always applied to very homogenized solutions. If heterogeneity exists within the solution, the measurement will not be accurate for the bulk solution.

Inductively coupled plasma mass spectrometry (ICPMS): This is an extremely powerful DA technique that ionizes a sample, which is then separated based on its' mass to charge ratio where a detector receives a signal proportional to the concentration. These systems have a broad range of uses. They can be used to determine a metals' species, which means the valence state of the metal can be found e.g. Chromium(III) versus Chromium(VI). This system can typically determine atomic mass from 7 to 250 atomic mass units.* This technique is widely used in medicine for toxicology and proteomics, among several others. The sensitivity of ICPMS covers roughly 8 orders of magnitude. From nanograms per liter to upwards of 0.1 grams per liter. It also can detect all of the elements present in solution simultaneously, unlike some other photon absorption techniques. An alternate form of mass spectrometry is an isotopic dilution approach, which is covered below.

A derivative of ICPMS, Isotopic Dilution Mass Spectrometry (IDMS), has been developed for radioactive isotopic analysis that has an uncertainty typically better than 0.25%. This process involves adding a known amount of an additional radioactive isotope to the unknown solution and homogenizing it. The concentration of the unknown is found by the following equation:

$$B = A * (S_i - S_f) / S_f$$

Where B is the unknown concentration of the unknown substance, A is the mass of the known radioactive substance added to the solution, S_i and S_f are the initial and final activities of the sample, respectively. This methodology holds because activity is conserved, thereby adding a known amount of radioactivity allows the unknown amount of radioactivity to be inferred as the total is readily determined leaving only one unknown to solve for. The error is decreased with IDMS because knowing the amount of radioactivity added to the sample allows for more specific calibration.

The isotopic dilution method has its' applications, but ICPMS is a far more diverse in its' usability for mass spectrometry.

*There are some situations where elemental mass can't be determined in the amu range of 7-250 due to a mass relation to the quenching agent Argon. Any combination of elements that result in a mass equal to, or an integer multiple, of the atomic mass of Argon are misrepresented in the final tallies.