

QUANTITATIVE CHEMICAL ANALYSIS

DESCRIPTION OF TECHNIQUES

Quantitative chemical analysis is performed to accurately determine the concentration of elements in the material comprising a given sample. A variety of analysis techniques are used for metals and alloys to determine the alloy composition of raw materials to verify conformance to a specification or to identify the alloy used to make a specific component. Quantitative analysis methods are also used occasionally for evaluation of foreign material contaminants in special cases for failure analysis or investigation of product manufacturing or handling problems.

Quantitative chemical analysis may be performed by one or more complimentary techniques, commonly including spark optical emission spectroscopy (Spark-OES), inductively-coupled plasma spectroscopy optical emission spectroscopy (ICP-OES), x-ray fluorescence spectroscopy (XRF), wet chemical analyses, combustion methods, and inert gas fusion (IG). The specific technique chosen will depend on the type of sample, quantity of material available for analysis, desired result, and cost constraints. In most cases, the applicable analysis techniques can detect parts-per-million concentrations or better.

Most of these techniques are destructive to the original sample. XRF can be performed nondestructively and Spark-OES can be performed with only minimal surface damage if the specimen size configuration allow the part to fit into the instrument without cutting. For the remaining methods discussed here, a small specimen is removed from the sample and is consumed in the analysis.

Prior to the widespread availability of analytical instruments, chemical analyses were performed by dissolving the sample and performing a specific chemical reaction with a standardized reagent for each element of interest. These 'wet chemistry' techniques are typically labor intensive and time consuming, and sometimes less accurate than the current instrumental methods.

Wet Chemistry - These methods include gravimetric and titrimetric techniques. An example of a gravimetric technique is the precipitation of chloride ion with silver to form a silver chloride precipitate which is dried and weighed to determine the chloride concentration in the original sample solution. Titrimetric procedures are typically based on acid-base reactions or complexing agents for metal ions. Since wet chemical analyses are now less common for the analysis of metals and similar inorganic materials, the remainder of this section will focus on the instrumental methods of analysis.

Spark-OES - Spark optical emission spectroscopy is a technique used for direct analysis of solid metal samples. The specimen is prepared by grinding to obtain a uniform, clean, flat area about 1 to 2 cm across. The prepared sample is placed in the spark-OES instrument and flooded with argon. A rapid series of high energy sparks are created across the argon-filled gap between an electrode (cathode) and the prepared sample's surface (acting as the anode). The sparks first ionize the argon, creating a conductive plasma. Secondly, the sparks melt, evaporate, and excite the sample elements at the spark point of impact. When the excited atoms in the plasma relax (de-excite) to a lower energy state, they emit light at characteristic wavelengths for each element. The intensities of these

emissions at the characteristic wavelengths are detected, measured, and compared to intensities for known standards to provide quantitative results. The total duration of the sparking is only a few milliseconds. Prior to actual measurements, the sample surface may be subjected to high power discharges to melt the surface and create a more homogeneous material.

XRF - X-ray fluorescence spectroscopy is a technique that can be used for direct analysis of solid metal samples, thin metal films, petroleum products, cement, coal, and various other materials. XRF is a fast technique and is non-destructive to the sample. It is frequently used for analyses performed in the field and for industrial quality control.

An x-ray tube is used to irradiate the sample with a primary beam of x-rays. Some of the impinging primary x-rays are absorbed by the sample elements in a process known as the photoelectric effect. The photoelectric effect occurs when all the energy of a primary x-ray is absorbed by an electron in an atom's innermost electron shell. This causes excitation and ejection of the absorbing electron (photoejection). The electron vacancies caused by the photoelectric effect are filled by electrons from higher energy states, and x-rays are emitted (fluorescence) to balance the energy difference between the electron states. The x-ray energy is characteristic of the element from which it was emitted.

The fluorescence x-rays are collimated and directed to an x-ray detector. The energy of each x-ray and number of x-rays at each energy are recorded. The x-ray intensities (counts) at each energy are compared to values for known standards for quantitative analysis of the unknown specimen.

ICP-OES - Inductively coupled plasma-optical emission spectroscopy is a technique for analyzing the concentration of metallic elements in solid and liquid samples. Like spark-OES, ICP-OES uses the optical emission principles of excited atoms to determine the elemental concentration. However, for ICP-OES, solid samples are dissolved (digested) in an appropriate solvent (typically acid) to produce a solution for analysis. The resulting sample solution (or an original liquid solution for analysis) is often diluted in water to obtain a final specimen suitable for analysis.

The ICP-OES instrument uses argon gas flowing through a torch consisting of three concentric quartz tubes. A copper coil circumscribing the top of the torch is connected to a radio frequency (RF) generator. The use of the copper coil with the RF power is called inductive coupling.

When the RF power is applied in the copper coil, an alternating current occurs within the coil. The oscillation of the alternating current causes electric and magnetic fields at the end of the torch. A spark applied to the argon gas causes some electrons to be stripped from the argon atoms. The electrons are caught and accelerated by the RF generated electric/magnetic field. The high energy free electrons collide with other atoms, stripping off more electrons in a chain reaction, resulting in a plasma of electrons, ions, and atoms. This is known as an inductively coupled plasma (ICP) discharge. This ICP discharge is maintained as the RF energy is continually transferred to the plasma by the copper coil.

The liquid samples are nebulized into an aerosol and introduced into the center of the plasma. The plasma excites the sample atoms, which subsequently relax to a lower energy state by emitting light at elementally characteristic wavelengths. The intensities of these characteristic wavelengths are detected, measured, and compared to intensities for known standards to provide quantitative results.

Combustion Methods - High temperature combustion is used to determine carbon and sulfur content in a variety of materials, both organic and inorganic. The sample is accurately weighed and placed in a ceramic crucible or combustion boat, often along with combustion accelerators. The crucible is placed in a high-temperature furnace which is then flooded with oxygen. The furnace is heated to 1370 - 1425°C, causing the combustion of the carbon and sulfur in the sample to form CO, CO₂, and SO₂. The gases are separated and analyzed by infrared absorption or thermal conductivity detectors. A heated catalyst is used to convert the CO to CO₂ prior to detection.

The infrared absorption detector measures the absorption of the infrared wavelengths characteristic to CO₂ and SO₂. The amount of infrared absorption at these wavelengths is correlated to a quantitative content based on standards and the weight of the original specimen.

The thermal conductivity detectors monitor the thermal conductivity of the carrier gas. As the evolved gases pass the detector, changes in the thermal conductivity correspond to a change in the gas (e.g. from the inert carrier gas to hydrogen) and the amount of evolved gas present. These changes correspond to the amount of CO₂ and SO₂ generated and indicate the amount of sulfur or carbon in the original specimen.

IG - Inert gas fusion is a quantitative analytical technique for determining the concentrations of nitrogen, oxygen, and hydrogen in ferrous and nonferrous materials. The sample is accurately weighed and placed in a pure graphite crucible in a fusion furnace with an inert gas atmosphere. The crucible is heated to 2000 - 3000°C, resulting in the sample fusing to a molten state. The hydrogen and nitrogen gases dissociate from the molten material and are carried away from the fusion chamber as H₂ and N₂. The oxygen released from the material bonds with carbon (from the graphite crucible) to form CO or CO₂ and is carried away.

An inert carrier gas flushes the gases evolved from the sample out of the fusion chamber. The fusion gases are separated and carried to the detector. The individual concentrations for the evolved gases are detected by infrared absorption (for CO and CO₂ only) or thermal conductive techniques (N₂, H₂, CO, and CO₂) as described for Combustion Methods above.

ANALYTICAL INFORMATION

Spark-OES - The intensities of the characteristic wavelengths of emitted photons are measured and compared to intensities for known standards to provide quantitative results. All metallic elements plus carbon, sulfur, and phosphorus can be detected, with analysis for most performed simultaneously. The minimum detection limits are in the parts-per-million range.

XRF - The energy of each x-ray and the number of x-rays for each energy are measured. Elements from beryllium to uranium can be detected. The minimum detection limits are typically in the parts-per-million range. Because the characteristic x-ray intensity will vary with the thickness of films on a dissimilar substrate, the thickness of thin films can also be measured by XRF.

ICP-OES - The intensities of the characteristic wavelengths are measured and compared to intensities for known standards to provide quantitative results. All metallic elements can be detected, with analysis for most performed simultaneously. The minimum detection limits are typically parts-per-million to parts-per-billion for the dissolved samples. Since specimens for this technique are solutions, standards suitable for most material types can be easily prepared.

Combustion methods - Quantitative results are obtained for carbon and sulfur contents in metals, inorganics, and organics. Lower detection limits for carbon range from 0.1 to 10 parts per-million with upper detection limits of 2.5 - 3.5 %. Lower detection limits for sulfur range from 0.1 to 50 parts per-million with upper detection limits of 0.2 - 2.5 %.

IG - Quantitative results for most metals and alloys can be obtained in the parts-per-million to parts-per-billion range for nitrogen, hydrogen, and oxygen.

TYPICAL APPLICATIONS

- Alloy identification for ferrous and non-ferrous materials
- Industrial alloy verification for quality control
- Mineral and Cement composition
- Sulfur, chlorine, lead, etc., determination in petroleum products
- Additives to polymers
- Trace metals in alloys, water, or solutions
- Contamination of water or solutions

SAMPLE REQUIREMENTS

Spark -OES - The sample must be a conductive metallic solid with a minimum diameter of 5 mm or larger, depending on the instrument.

XRF - The samples may be solids, liquids or powders. Samples often require little or no preparation prior to analysis. Qualitative analysis may use samples as small as 1 mm across. Quantitative analysis may require a larger sample, up to 30 mm in diameter.

ICP-OES - The samples may be solid or in a solution. A few grams of a solid sample are typically needed for digestion and dilution. For samples in solution, at least several milliliters may be required for dilution.

Combustion methods - One gram or less of a solid, chips, or powder sample is typically required. Samples should not be contaminated with sulfur or carbon prior to analysis.

IG - One gram of material is required for nitrogen or oxygen determination. Samples may be solids, chips, or powders. Hydrogen determination generally requires two grams of a solid sample.