

Composition Sensors

Introduction

There are many useful analytical tools, such as photometric analysis, electrometric analysis, chromatography, mass spectrometry, thermal conductivity, and various physical property measurements (density and specific gravity), which can be used to determine the composition of mixtures. A wide array of methods to measure composition are available, so it is important to choose the best method given a set of conditions. The first step is to decide between measuring physical or chemical properties to determine the composition. If you choose to measure a physical property, make sure that it is unique to the desired component of the mixture and will accurately allow you to determine the composition. The goal of this article is to explain the various analytical methods and tools used to determine the composition of a given sample. After reading this, you should be able to determine which method of composition measurement is most appropriate for a given circumstance.

Types of Testing: On-line v. Off-line

On-line analysis is the continuous monitoring of the composition of a sample, which is under the influence of a control system and directed by an actuator which can respond and regulate the operating conditions in real time such that the desired set points are maintained. On-line testing can either be performed in-line or by slip stream testing. In on-line testing, the sensor is attached directly to the line and provides feedback via a transmitter. On the other hand, in slip stream testing, a side stream of the process runs alongside the main line. Such an apparatus closely resembles the set up of a bypass. The slip stream process conditions can be continuously manipulated to make the measurements easier to obtain. Similar to in-line testing, the sensor is directly attached to the slip stream and provides feedback through a transmitter. Advantages of on-line analysis include an immediate and continuous feedback responding to changes in process conditions. The main disadvantage of on-line testing is that it is usually much more complicated and more expensive than off-line testing. Also, off-line testing is more robust and has more varied applications, while on-line testing may not work in every situation. On-line testing prevents the continued production of undesired product, with an immediate response and correction of the flawed material.

Off-line analysis involves the extraction of a sample from the process or reaction, and its subsequent testing in a machine that may be situated at a location far away from the process line in a lab. In this case, a sample is manually removed which is later sent to the composition analyzer. The results of the analysis are examined and then they are sent to the control system or actuator to make the appropriate adjustments. On-line analysis is comparable to off-line testing, the primary difference being that in on-line testing, the samples are analyzed on a machine that is next to the process line. This greatly reduces time lost in transporting the sample, though it still permits the prospect of introducing contaminants into the sample. In off-line analysis, some of the disadvantages include sample dead-time, which is the time lost during transportation, variability of sample testing locations, and lag time for adjustments to be made to the process. In off-line analysis, the lag time between removing the sample from the system and receiving the results of the test could cause significant losses to the company, since the defective product is produced and the process is not corrected until the results are received. This prolonged defective

processing could result in the accumulation of losses worth thousands of dollars, which could have been avoided if an on-line analysis system was set up in place.

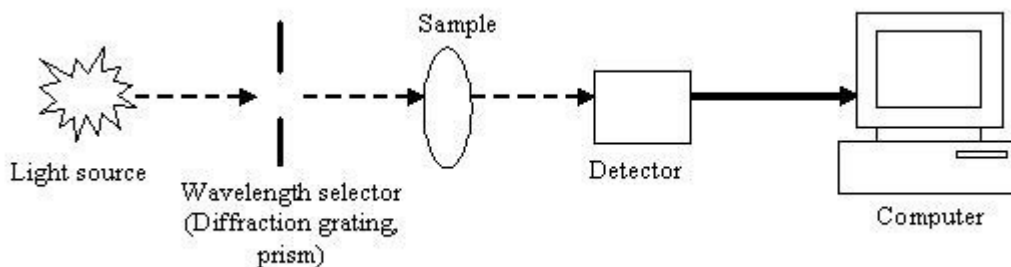
While both methods are widely used in industry, there is a push towards more on-line testing. A paper published in 2003 urging drug companies to adopt more in-process analytical testing such as on-line testing, endorsed by the Food and Drug Administration reflects this trend. This has been a part of a broader effort by the FDA to encourage companies to move towards better manufacturing practices. While on-line testing maybe comparatively expensive to install at first, the savings from the process would not only recoup the costs associated with installation, but also prevent significant losses. Many companies have adopted lean manufacturing techniques, and one of its hallmarks is to correct a defect as early in the production process as possible, not allowing defective products to move on to the next processing step. Allowing defective products to perpetuate through the system may even contaminate other non-defective materials in the production process.

Standards and Calibration Curves

Before discussing the different ways to measure the composition of a sample, one needs to understand that composition sensors use standards or calibration curves to measure an unknown composition against a known one(s). The standard can either be an internal standard against which all other measurements are compared, such as a reference cell or a series of standards used to create a calibration curve. With a calibration curve, a series of known standards are measured with the sensor and the signal produced by the sensor is graphed on the y-axis of a plot; the known information about each sample is graphed on the x-axis. From this information, a relationship can be developed between the signal output from the sensor and the known quantity that you are trying to measure. The data measured for the unknown sample can then be compared to the calibration curve graphically or using the equation written to describe the curve. Using this information, the measurement made by the sensor can be interpreted as a useful composition measurement of weight percent, volume percent, mole percent, etc.

Photometric Analysis

Photometric analysis is the measurement of the intensity of visible light and other electromagnetic (EM) waves. Through the measurement of these values, the composition of samples or flows can be determined in various different ways. A wide range of photometric devices based on many differing principles are used in the chemical engineering industry for this purpose. A few of the most common instruments are covered in this article.



Types of Photometers

A photometer is any type of instrument used to measure characteristics of light. There are two broad categories of photometers: dispersive and non-dispersive.

Dispersive Photometers

In dispersive photometers, the light from the source is dispersed and a narrow spectral band is selectively directed to the sample and detector. A monochromator is usually the tool that performs this function. The dispersing element of the monochromator can be a diffraction grating, prism, and interference filters. Diffraction gratings are the most common; for each position of the grating a narrow band of dispersed light passes through an exit slit. Dispersive devices can scan across a spectrum and make measurements at several wavelengths. This capability allows them to be used for the analysis of multiple components.

Non-dispersive Photometers

Non-dispersive photometers use a narrow-band-pass filter to block out a large amount of undesired radiation. They make measurements at selected discrete wavelengths. The filter passes radiation at the selected reference and measurement wavelengths. The reference wavelength filter selects a band where none of the components present in a process stream absorb radiation; the measurement wavelength filter is selected to match the absorption band of the component being analyzed. The ratio of the transmitted light at the reference and measurement wavelengths is measured by the photometer. Non-dispersive photometers are usually used to measure a single component in the process stream.

An example of such a device is the Non-Dispersive Infrared (NDIR) analyzer that is frequently used to measure the concentrations of certain gases in a mixed gas flow. The NDIR analyzer uses a reference non-absorbent gas such as O_2 , Cl_2 and N_2 and compares that to a sample gas like CO, CO_2 , SO_2 , CH_4 , etc. Two beams of infrared radiation are used: a reference beam for the non-absorbent gas and an analyzing beam for the sample.

Spectrophotometers

Spectrophotometers are widely used as composition sensors. Spectrophotometers are photometers that measure the intensity of light at specific wavelengths. Many different types of spectrophotometers exist, and they are typically categorized based on the ranges of wavelengths they monitor: ultraviolet (280-380 nm), visible light (400-700nm), infrared (0.7-1000 μ m), or microwave (1-300mm). Other important distinctions are the measurement technique, the method of obtaining the spectrum, and the source of intensity variation.

The emission spectrum recorded by the spectrophotometer typically consists of a series of narrow peaks of varying heights, also known as spectral lines. The height or amplitude of those lines can be related to the concentration or abundance of the specific material through a calibration curve and their position on the spectrum distinguishes the components of the material. While there are numerous methods for obtaining a spectrum, the most common application of a spectrophotometer is for the measurement of light absorption.

Absorption

The degree of absorption of electromagnetic waves exhibited by the components in the sample is a distinctive feature that can be used to reveal the composition of the sample. Absorption is related to the inverse of transmittance by:

$$A = \log\left(\frac{1}{T}\right)$$

A = Absorbance (Absorbance unit, AU)

T = Transmittance (as percentage)

Spectrophotometers based on absorption have a radiation source that will emit a specified range of EM waves to be absorbed by the sample by measuring the intensity of light that passes through the sample. A useful relationship used to quantitatively determine the concentration of an absorbing species in solution is the *Beer-Lambert Law*:

$$A = -\log\left(\frac{I}{I_0}\right) = \epsilon * c * L$$

I = Intensity of incident light at a particular wavelength

I₀ = Intensity of transmitted light

epsilon = molar absorptivity or extinction coefficient (1 / M * cm)

c = concentration of the absorbing species

L = path length through the sample

According to the *Beer-Lambert Law*, the absorbance of a solution is directly proportional to its concentration. The constant *epsilon* is a fundamental molecular property for a given solvent. It can be found from references tables or determined through the construction of a calibration curve. The *Beer-Lambert Law* is useful for characterizing many compounds, but does not hold for all species. For example, very large, complex molecules such as organic dyes often exhibit a 2nd order polynomial relationship between absorbance and concentration.

Two widely-used devices that measure the absorbance of samples are *Ultraviolet* and *Infrared* spectrophotometers.

Ultraviolet (UV) Spectrophotometers

UV spectrophotometry is a useful method for detecting and quantifying substances in solution. Certain compounds in the gaseous or liquid state absorb ultraviolet radiation, resulting in absorption peaks that can be correlated with specific functional groups. These species include aromatic and carbonyl compounds in organic substances and transition metal ions in solution. This property is useful for categorizing and measuring the composition of these types of samples, however this property cannot be used as a specific test for a given compound. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectra of compounds, as can variations in slit width in the spectrophotometer. Many organic

solvents have significant UV absorption and therefore will add peaks to the species dissolved in them. Solvent polarity, high electrolyte concentration, and pH can effect the absorption spectrum of an organic compound by causing protonation or deprotonation of the compound. Temperature can also cause complex molecules to change in conformation and can also alter the properties of the solvent used. Variations in the slit width will alter the effective bandwidth, distorting wavelength measurements.

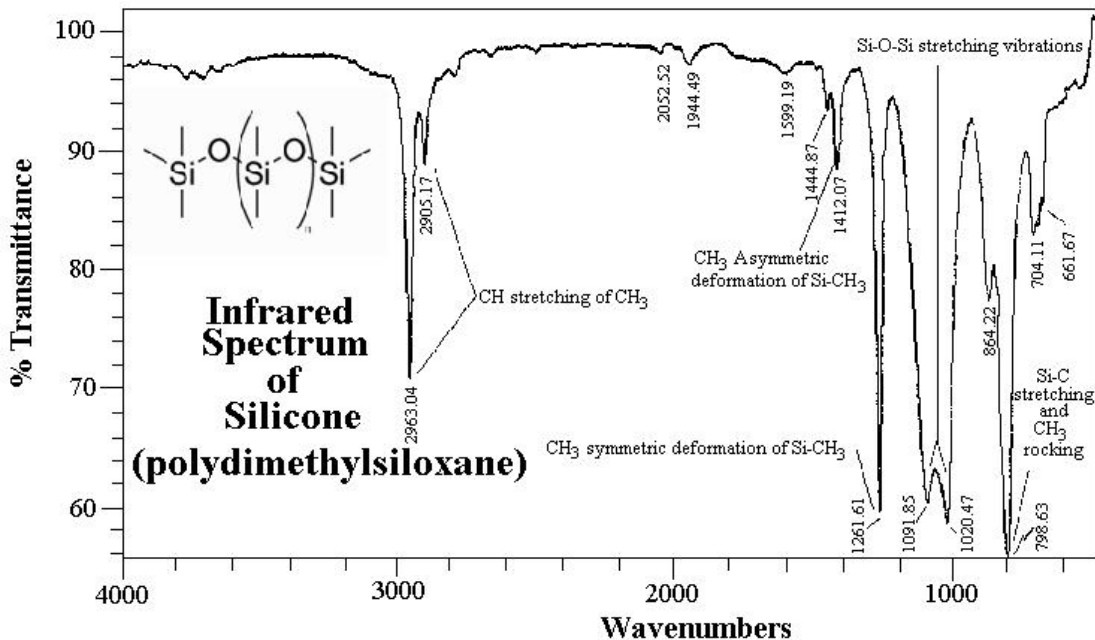
The basic components of the overall analyzer are the UV light source, sample holder, optical filters, and detector (typically a phototube). Optical filters (typically a monochromator or diffraction grating) separate the wavelengths of light going through the sample and ensure that only the desired wavelengths reach the detector.

Most UV analyzers are dispersive photometers that also function in the visible light spectrum and are called UV-Vis spectrophotometers. Since these instruments are generally found in laboratories, they are generally used for offline analysis. However, there are inline UV machines and sensors available for real-time inline measurements of process flow streams. UV spectrophotometers used throughout many industries for various applications.

Infrared (IR) Spectrophotometers

Infrared spectroscopy is based on the fact that there are specific frequencies at which molecular bonds rotate or vibrate when exposed to discrete energy levels of radiation. A beam of infrared light is passed through the sample, either one wavelength at a time with a monochromatic beam or using a Fourier transform instrument that measures all wavelengths at once. Inspection of the transmitted light reveals how much energy was absorbed at each wavelength, this data is then plotted (see example below). This plot allows the frequency of the vibrations to be associated with a particular bond type. The characteristic IR absorption spectra obtained for a sample can be used to identify the compound, while the amplitude of absorbance is proportional to the analyte concentration. IR analyzers are used to analyze gaseous or liquid compounds that can absorb IR waves. The system components are generally similar to those of an UV spectrophotometer, with the exception of the IR light source.

IR instruments have been used regularly in a fixed laboratory setting for decades now. Both dispersive and non-dispersive IR techniques exist. More recently, manufacturers of instruments have significantly reduced their size and power requirements. In addition to inline IR sensors for process streams, portable instrumentation is available for field analysis such as the monitoring of stack gases. Another relatively modern technology, the Fourier Transform Infrared (FTIR) Spectrometer, is widely used in industry today because of its high sensitivity and broad range of application. For example, FTIR analysis is used in the quantification of harmful organic peroxides in lubricants and fuels.



Radiation

Instead of measuring the absorption of light, many spectrophotometers measure the radiation of EM waves. Samples may radiate EM waves in many forms such as heat, luminescence, fluorescence, and phosphorescence. The measurement of such radiation is often employed in biological and pharmaceutical areas because of its high sensitivity and specificity. For example, fluorescence spectrophotometers are used to assay the presence and concentration of target biological compounds. Fluorescent probe molecules are introduced to the sample that will attach selectively to the biological molecule of interest and the device will then detect and measure the amount of fluorescent radiation. In these experiments, the appropriate standards must be measured to properly calibrate the radiation measured with sample concentration. Additionally, contamination of the sample can affect the radiation patterns.

Examples of other techniques utilizing the radiation EM waves include flame emission spectroscopy, particle-induced X-ray emission, and X-ray fluorescence. These methods are strictly used for laboratory analysis.

Photometry Using Visible Light

The manner in which certain materials interact with visible light can be used to analyze the composition of the sample material. Refractometers, turbidimeters, and opacity meters are all analyzers which utilize this principle.

Refractometry

The theory behind refractometry is that visible light bends (or refracts) when it passes two opaque media of differing densities. Snell's Law relates the angle of incidence α to the refractive index n by:

$$\frac{n_1}{n_2} = \frac{\alpha_2}{\alpha_1}$$

α_1, α_2 = angles of incidence

η_1, η_2 = refractive indices of the two media (unitless)

Alternatively, the critical angle may be used to analyze the composition. The critical angle is defined as the angle of incidence that produces a 90° refraction with respect to normal of the interface i.e. $\alpha_2 = 0^\circ$.

Thus, Snell's Law becomes:

$$\frac{n_1}{n_2} = \frac{1}{\sin \alpha_c}$$

α_c = critical angle

Please refer to the diagram below.

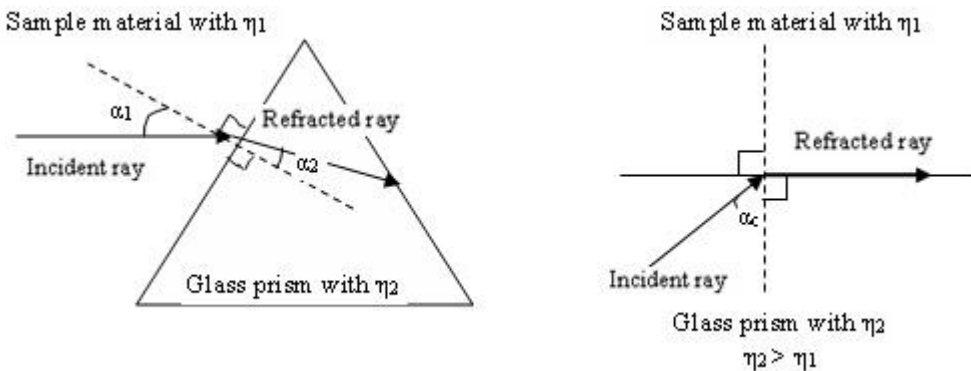


Figure 1: Light refraction at a glass-medium interface

Different materials will have different refractive indices; the experimental refractive index measured can be compared to a list of refractive index values at a data bank. Continuous process or online refractometers generally measure the changes in the critical angle at a glass-sample interface caused by the variations in composition concentrations. Refractometers are used in numerous industries such as food, chemical, metalworking industry because of its high accuracy and repeatability, low maintenance and easy installation. An example is the use of a refractometer to monitor the amount of juice concentrate in juice.

Turbidimeters

Turbidimeters measure the turbidity, or sample clarity, of fluids. A light beam passes through the analyzer and if the water, or other chemical that is to be tested, is "pure," then the light would travel undisturbed. However if the sample contains suspended solids or particles, the light would interact with the particles causing the particles to absorb the light and reflect it into different directions. An example is smoke in air that gives the air a hazy look.

Most modern turbidimeters are nephelometers. Nephelometers or nephelometric turbidimeters measure the *scattered* light reflected off the suspended particles in the sample. This instrument contains a light source, some sort of container to hold the sample, and photodetectors to sense the scattered light. A tungsten filament lamp is most commonly used as a light source. If the suspended particles, typically measured in nanometers, are smaller than the wavelength than the incident light, the reflected light is scattered equally in all directions. If the particles are larger than the wavelength of the incident light, the pattern of scattering will be focused away from the incident light.

Nephelometers are usually used when solids are present in the sample in small concentrations. When there is high turbidity in a sample, multiple scattering occurs and the turbidimeter may no longer be able to analyze the fluid. Disadvantages of nephelometers include being prone to fouling and incapability of analyzing fluids that have high concentrations of solid particles.

Turbidimeters are important to industry, specifically for chemical plants, oil refineries, and waste water treatment plants. For example, nephelometers are used in detecting the pollutants in water in water quality monitoring.

Opacity Monitors

Opacity monitors measure the *attenuation* of light due to *scattering and absorption* by the sample. Attenuation is defined as the decrease in intensity and amplitude of the measured light beam when compared to the emitted light beam. Opacity monitors differ from turbidimeters in that they analyze samples by measuring the percentage of transmission of the light source that passes through the sample and NOT the scattering of the light source. A common application is the measurement of smoke density in chimney stacks. The density of the pollutant or particle is expressed as percent opacity, percent transmittance, or optical density.

$$\% \text{ opacity} = 100 \times \text{opacity} = 100 - \% \text{ transmittance}$$

Electrometric Analysis

Electrometric analysis uses the principles of electrochemistry to analyze the composition of different samples.

Conductivity Cells

Conductivity cells measure a liquid's ability to conduct an electric current. Since liquids conduct current due to the presence of ions, the composition can be determined by measuring the concentration of the ions present. Conductivity cells determine concentration from the definition of molar conductivity (Λ). Molar conductivity is a property that can be influenced by temperature. It also varies with concentration if the chemical being measured is a weak electrolyte. It is defined by the following equation:

$$\Lambda = \frac{\kappa}{C}$$

Λ = molar conductivity [$\text{S}m^2/\text{kmol}$]

κ = conductivity [S]

C = concentration [kmol/m^3]

Since it is difficult to directly measure conductivity, conductivity cells measure the resistance (R) of a sample liquid between two electrodes when a small current is applied. Resistance is related to conductivity by the following equation:

$$\kappa = \left(\frac{A}{x}\right) \left(\frac{1}{R}\right)$$

κ = conductivity [S]

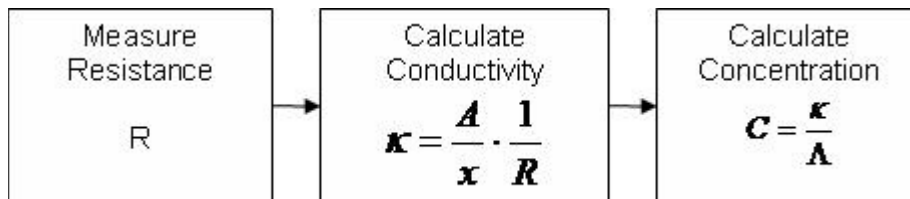
A = area of electrode [m^2]

x = distance between electrodes [m]

R = resistance [ohm, Ω]

Note that the electrode area, A, and distance between the two electrodes, x, are fixed for a particular sensor and are often expressed as a cell constant (k_c).

The following flow chart shows how composition is determined in terms of concentration:



Conductivity cells can be used in flow system and installed directly into the system of pipelines.

Conductivity cells can come in three types: two electrode probe, multiple electrode probe, or a non-contact, electrode-less probe (toroidal). The two electrode probe is one of the most common types and typically uses carbon or stainless steel as the electrodes. The multiple electrode probed has either two, four, or six electrodes. This probe has the advantage of reducing errors due to polarization (electrochemical reaction on the electrode surface) and fouling. Finally, the toroidal probe has no electrodes and instead measures the AC current in a closed loop of solution using two embedded toroids (a magnetic core with wire wrapped around it to make an inductor). The electrode-less probe is good for solutions that tend to have problems with polarization or oily fouling. In-line conductivity cells are suitable for temperatures up to 480K and pressures up to 1700 kN/ m_2 .

Since concentration is found from molar conductivity, which is a property of the fluid that is strongly dependent on temperature, a temperature sensor is often paired with a conductivity cell so temperature effects can be accounted for in concentration calculations.

Conductance cells are best used in applications where a single type of ion is present in a dilute solution. Higher concentrations lead to complications that cannot be described by the simplistic linear relation between concentration and conductivity, since molar conductivity starts to vary with higher concentrations of weak electrolytes.

Ion Selective Electrodes

pH Electrode

The pH electrode is commonly used in both the lab and industrial setting. This electrode is sensitive to the concentration of the H^+ ions. The pH electrode basically measures the potential difference between a reference solution and the sample. Please refer to [the pH sensor section](#) for examples and more information on relevant theory.

Other Ion Selective Electrodes

Electrodes can also be specific to other ions such as: Na^+ , K^+ , Ag^+ , ClO_4 , BF_4 , SO_2 , and CO_2 . An electrode's ion sensitivity depends mainly on the method of separating ions in the solution. The biggest problem with ion selective electrodes is the problem of not enough selectivity for the desired ion, and subsequent interference by other ions with similar chemical properties to the desired ion. Most electrodes use a membrane to separate a specific ion, though other techniques exist. Selective ion electrodes can be divided into the following three categories based on the mode of separation: solid membrane (glass or crystalline), liquid membrane (classical ion exchanger with a neutral or charged carrier), and membrane in a special electrode (gas sensing or enzyme electrode). Examples of ion selective electrodes used in industry include nitrate sensors for sewage treatment or river quality monitoring, hydrazine and sodium sensors for in boiler water, and chloride and fluoride sensors for in water treatment plants.

Oxidation-Reduction Potential (ORP) Sensors

ORP sensors, or also called Redox sensors, can determine concentration of ions that exist in two different oxidation states in solution. For example, this type of electrode can be used to analyze the composition of a solution with Fe^{2+} and Fe^{3+} ions. This type of electrode measures the potential caused by a solution's reduction or oxidation ability.

This type of sensor directly measures electric potential which indicates the reducing or oxidizing strength of a solution. The reducing or oxidizing power of a solution depends on whether the higher or lower oxidation state is preferred by the ion.

When an ion favors the higher oxidation state (or has reducing properties), the ions tend to give up electrons and the electrode becomes more negatively charged.

When an ion favors the lower oxidation state (or has oxidizing properties), the ions tend to gain electrons and the electrode becomes more positively charged.

When purchasing an ORP sensor from a vendor, many models come already packaged with a pH sensor, since these two measurements are often both monitored to keep a process running at the right conditions. For instance, in the pool and spa industry, its important to monitor both the concentration of sanitizers in the water with an ORP sensor, as well as measure the pH of the water.

Polarographic Sensors

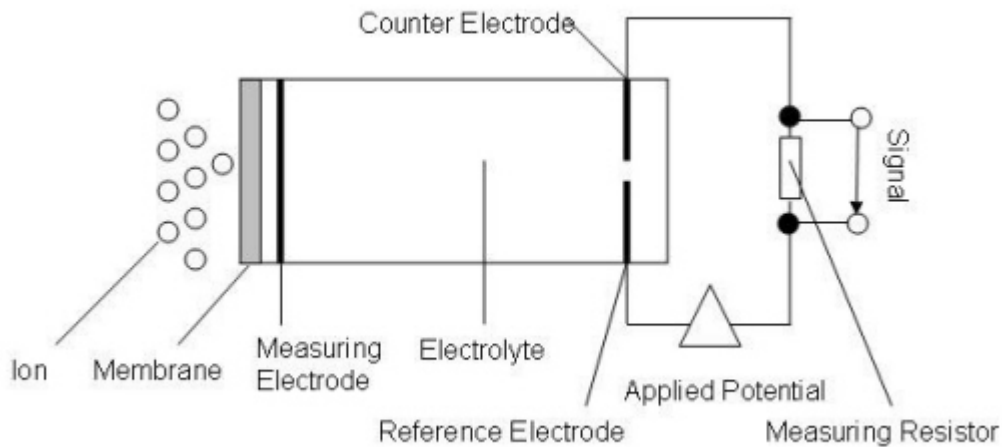
Polarographic sensors work by performing electrolysis with two types of electrodes: one which is polarizable and one which is not. They operate very similarly to voltameters, but with voltameters the potential is changed in a controlled manner and the voltage measured. The oldest system of polarographic measurement used dropping mercury electrodes. Here the principle is that that the surface tension of

mercury changes with how much charge is applied between the top and bottom of the electrode, and this surface tension change can be seen in how the weight of the mercury drops varies with time.

More modern types of polarography use two different types of metals which are connected in a solution with electrolytes, and electrons will move towards the more positively charged metal. This movement of electrons induces a current, which eventually stops once the charges are balanced (polarized). If all the charges are balanced within the system, no current will flow. Therefore a small potential is applied to a polarographic sensor so that a current exists for the sensor to measure.

The sample being analyzed needs to have the ability to depolarize the system, or tip the balance of charges. The ion of interest crosses a selective membrane and reacts by an oxidation/reduction reaction with a metal surface (often called the measuring electrode). The reaction between the ion and electrode causes an uneven distribution of charges. Once a system is depolarized, the potential of the system increases since a more positive and a more negative region exists separately. The increase in potential causes current to flow which is the signal measured by the sensor. This creates a graph showing the relationship between applied current versus measured potential. A disadvantage to this type of measurement tool is that this graph requires a calibration curve in order to interpret the data, and so analysis of composition using polarography can't be done in-line. The advantage of this type of method is that it is highly accurate and very reproducible.

Below is a basic schematic of a polarographic sensor.



Polarographic sensors are most commonly used assessing pollutants in air such as Cl_2 , HCl , HBr and HF . It can also be used to measure O_2 and other inert gases in flue.

High Temperature Ceramic Sensors

These types of sensors have a heated section of zirconium oxide (ZrO_2), also known as zirconia, that is slightly doped with yttria (Y_2O_3). This stable lattice structure is able to measure oxygen ion conduction at high temperatures. This sensor is exclusively used for measuring O_2 and is often used to measure O_2 composition in flue gases.

Chromatography

Chromatography is a set of physical methods used to separate and thus analyze complex mixtures. Chromatography consists of a mobile phase, usually a gas or a liquid, and a stationary phase, typically a solid or a liquid. These two phases are combined in a column of the stationary phase based on the type of chromatography one wishes to complete (i.e. Gas-liquid, Gas-solid, Liquid) in order to separate the mixture. The retention time of a component is the time before the component elutes from the column. The retention time and elution order are both based on the relative interaction between each solute and each phase. The stronger the solute's interaction with the mobile phase, relative to the stationary phase, the sooner the solute will elute from the column. Solute-phase interaction is a function of the charges of the molecules, the absorption of the stationary phase, and the relative solubility.

Chromatography by itself does not detect substances, but it is routinely coupled with a detection unit. Each substance is detected as it leaves the chromatograph. The retention time for each substance can then be compared to a standard to determine what substances were in the mixture. For unknown substances, the elution order can determine some properties of the substance. For example, a substance that initially elutes after ethanol in a nonpolar column is less polar than ethanol. However, other composition detectors are far better suited for analysis of unknown substances.

Chromatography is the most widely used composition detecting process for on-line analysis of samples within a complex mixture. Due to its precision, chromatography is commonly used to separate or purify samples within the chemical or biochemical industries. Depending on the type of chromatography used, even delicate mixtures like proteins can be analyzed. However, chromatography is primarily useful when there are some expectations for the components in a mixture; chromatography is not best for a completely unknown sample, but it is useful for detecting the composition of a process stream where most components are known and a suitable standard exists.

Types of Chromatography

Gas-Liquid Chromatography (GLC)

GLC is one of the more common types of chromatography. It is commonly referred to as GC (gas chromatography). In a typical run, the liquid mixture to be analyzed is added to the system and vaporized before entering the column. A carrier gas, often Helium, carries the vaporized sample through a column. The column can either be packed with stationary phase, or the column can have a very small diameter in which case it is lined with stationary phase (capillary tube). The gas mobile phase runs through the stationary phase within the column at various rates determined by relative volatility and affinity to the stationary phase. The longer a sample molecule spends in the gas phase, the faster it will elute from the column. For this reason, temperature and the chemical identity of the coating on the stationary phase are two important variables which may need to be manipulated to receive clear separation of the components in the mixture. In general, lower temperature will result in better separation but longer elution times and sample spreading due to flow effects. Efficient use of this apparatus requires a balance between these competing effects.

GC is relatively simple for a technician to use; a calibrated gas chromatograph can run several samples without a large amount of sample preparation. Gas chromatography works well on substances that

vaporize below 300°C and are free of ions; however, it does not work well on substances that decompose below 300°C.

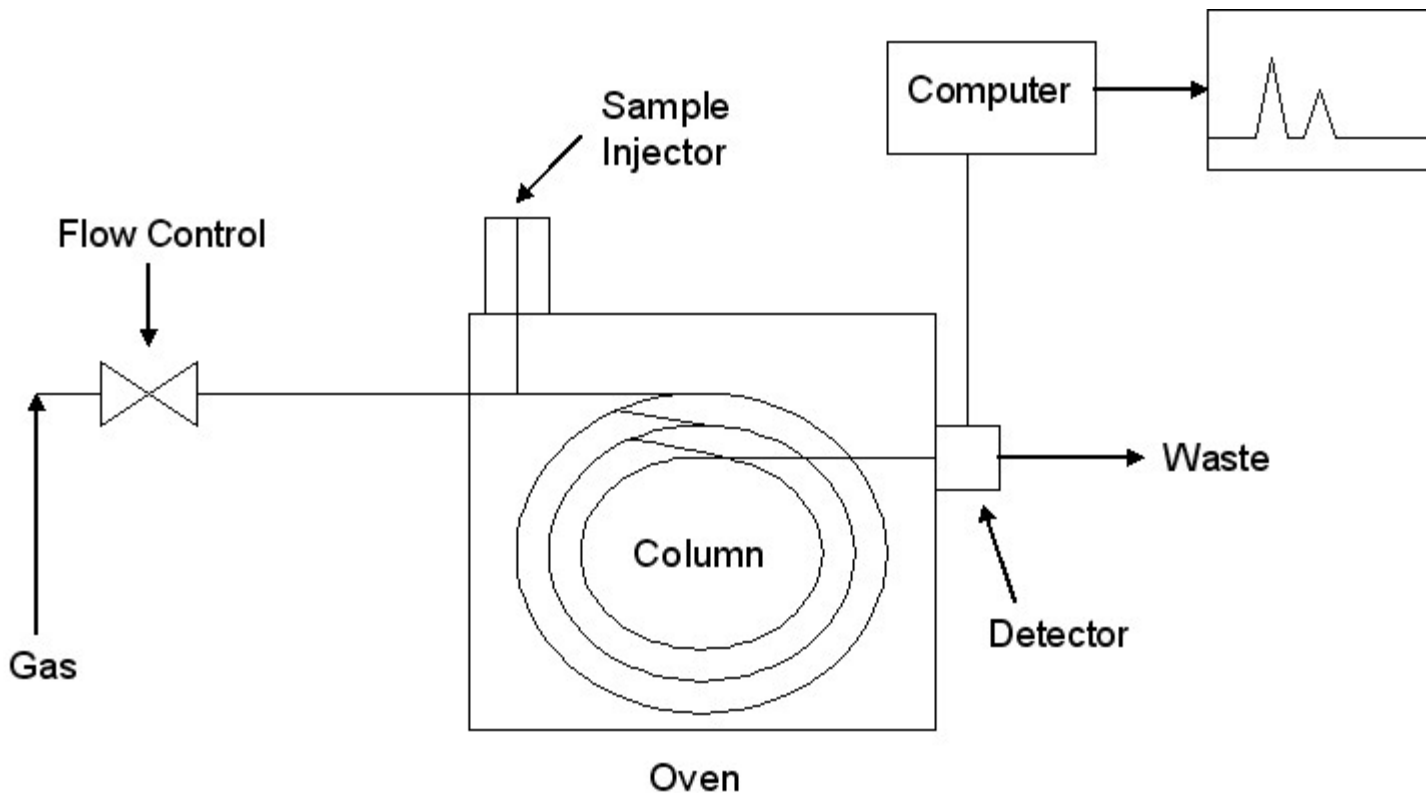


Figure: Diagram of Gas Chromatography

Gas-solid Chromatography (GSC)

GSC uses a gas mobile phase which runs through an absorbent solid (e.g. silica gel or alumina) stationary phase within the glass column as determined by absorption. This method operates along the same principles as gas-liquid chromatography. It is most commonly used with gases (as opposed to a vaporized substance) and with low molecular weight hydrocarbons.

Liquid-Chromatography (LC)

LC analyzes low volatility liquids within a solid stationary phase. Separation occurs from adsorption/desorption due to the solutes having different degrees of attraction to the stationary phase, typically due to the stationary phase having different polarity than the mobile phase. It is common to use a mixture of solvents to accurately separate mixtures. Liquid chromatography is used in several industries, including the pharmaceutical and petrochemical industries.

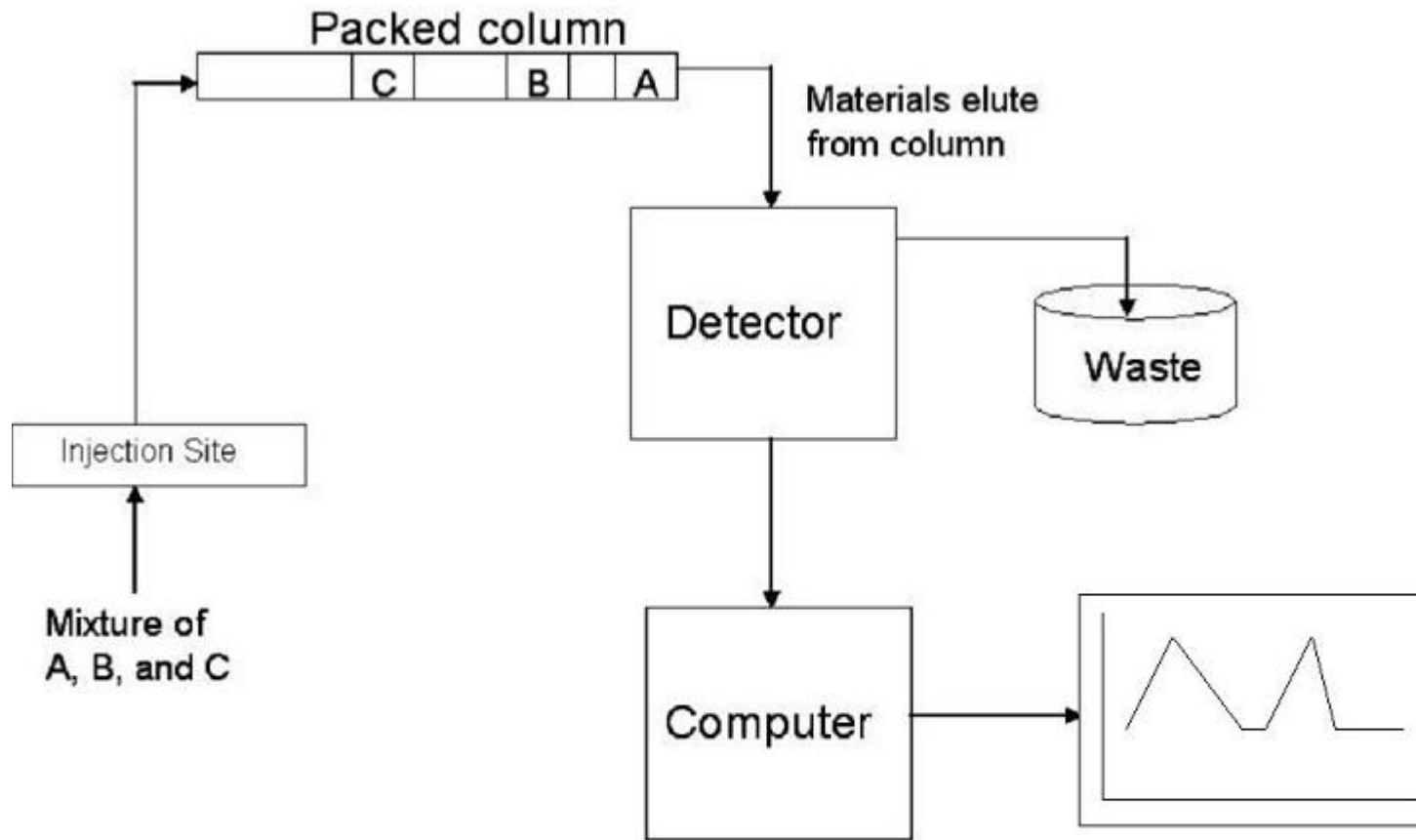
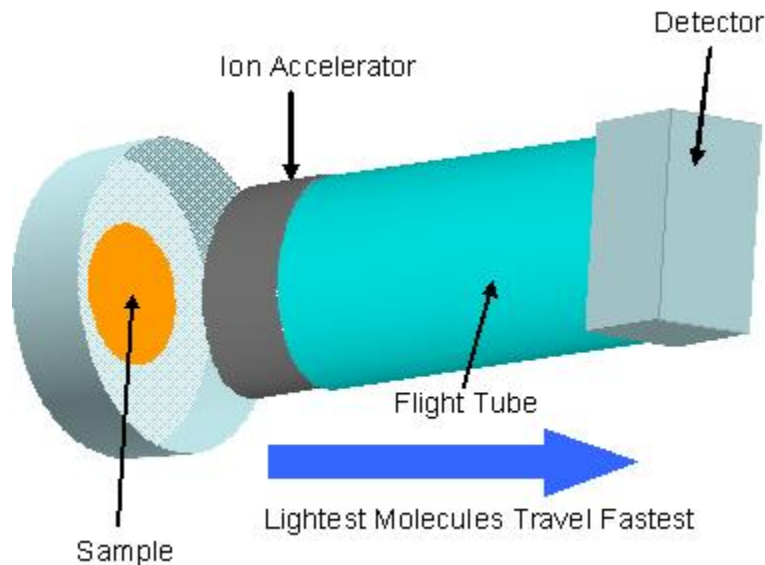


Figure: Example of Liquid Chromatography

Mass Spectrometry

Mass spectrometry is among the most precise compositional sensing tools, and, accordingly, one of the most expensive. The basic idea is illustrated below:



A sample is ionized—this may be performed by a number of techniques—the ions are subjected to an electrical force and accelerated through a tube. Because the electrical force applied to each molecule is the same, a molecule's acceleration through the tube depends on its mass ($F=ma$). The acceleration is also dependent on any charge on the molecule due to magnetic attractive or repulsive forces. At the end of the tube, a detector calculates the time of flight for each of the molecules.

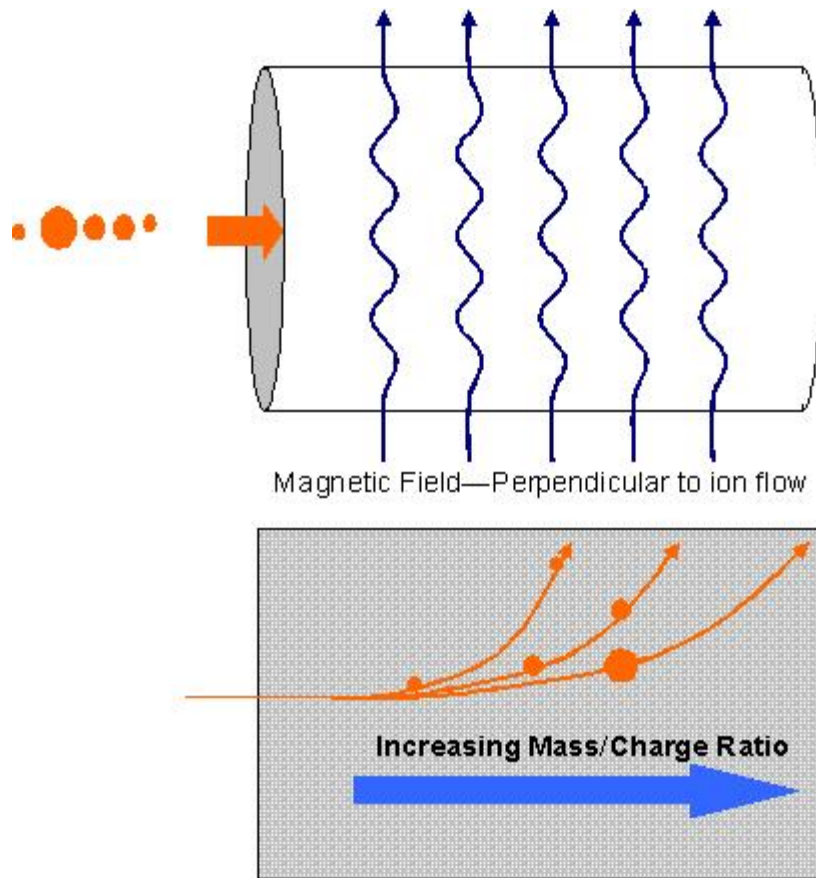
Mass spectrometry is essentially a tool to create a spectrum of distinct mass/charge ratios. It is very often used after chromatography separation techniques to serve as a molecule identification technique.

MS Components

There are 3 fundamental components for mass spectrometry—an ion source, a mass analyzer, and a detector.

The ion source is the component responsible for ionizing the sample. There are many different methods including chemical, electrical, or laser ionization. Selection of the proper ion source depends on the characteristics of the sample (phase, biologically active, etc.).

The mass analyzer is the technique and tool used to differentiate the ions in a spectrum based on the mass/charge ratio. The technique described earlier is the Time-of-Flight technique. Another common method is a sector field mass analyzer where the molecules are accelerated through a tube and a magnetic force is applied perpendicular to the direction of flight of the molecules. The molecules will deflect at different magnitudes depending on their size.

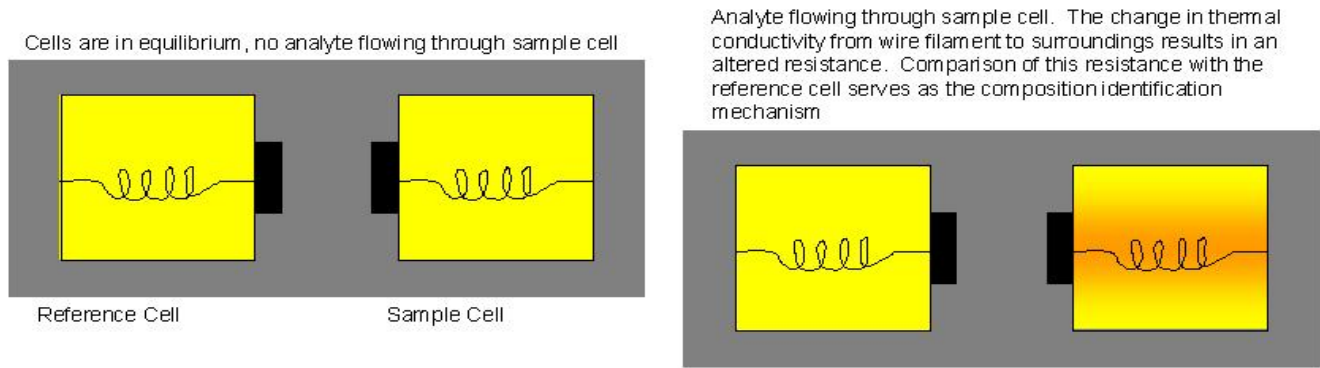


The detector generally amplifies changes in an electrical current that occur when molecules hit the detector.

Thermal Conductivity for Gases

Changes in thermal conductivity may be used to detect variations in a mixture of gases. When a heat source is present, gases and vapor will conduct heat. The change in heat between the source and gases will stabilize to a common temperature. The temperature is mainly dependent on the thermal conductivity and therefore the composition of the gas.

Typical equipment for thermal conductivity analyzers includes: a reference cell, a sample cell, a combined heat source (wire filaments or thermistors), and detector. The sample cell and reference cell are usually placed in a holder where the detector may be mounted. The reference is an identical cell of the sample cell, through which a known gas will flow. The reference-detector resistance will be constant and the sample-detector resistance will vary depending on the composition. Resistance is a function of temperature and the output from the detector bridge will be a function of sample composition.



Thermal conductivity, like mass spectrometry, is often used in combination with gas chromatography

Physical Property Measurements

Physical properties can be used to indirectly measure the composition, but this technique is not as versatile as those described above, since it only applies to a limited number of circumstances. The advantage to using physical properties to indirectly measure composition is that these types of measures are often cheaper than the types of sensors described above.

Density and Specific Gravity

Density and specific gravity measurements require a binary mixture with at least one fluid phase to make accurate measurements. Given the temperature and pressure, the density of a gas can be found using the ideal gas law or some other relationship, and since density is a function of composition, the composition can be measured indirectly. See [Thermodynamics](#) for more information. Specific gravity is simply the ratio of density of water over the density of the non-compressible component at the same physical conditions, which means that it is simply a dimensionless measurement of density.

Four different measuring devices for finding density are described below.

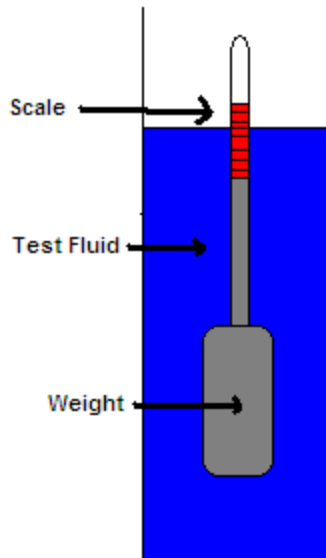
Liquid Column

In a liquid column, the pressure measurements in a column are used to determine the density. The column may be open to the atmosphere, where the gauge pressure at the bottom of the fixed-height column is measured. Or, the column may be closed, in which case the differential pressure measurement is made between the bottom of the fixed-height column and at the top of the column immediately below the liquid surface.

Displacement – Hydrometer

A hydrometer is usually made of glass and consists of a cylindrical stem and a bulb weighted with mercury or lead shot to make it float upright. The liquid to be tested is poured into a tall jar, and the hydrometer is gently lowered into the liquid until it floats freely. The point at which the surface of the liquid touches the stem of the hydrometer is noted. Hydrometers usually contain a paper scale inside the stem, so that the specific gravity can be read directly.

The operation of the hydrometer is based on the Archimedes principle that a solid suspended in a liquid will be buoyed up by a force equal to the weight of the liquid displaced. Thus, the lower the density of the substance, the lower the hydrometer will sink.

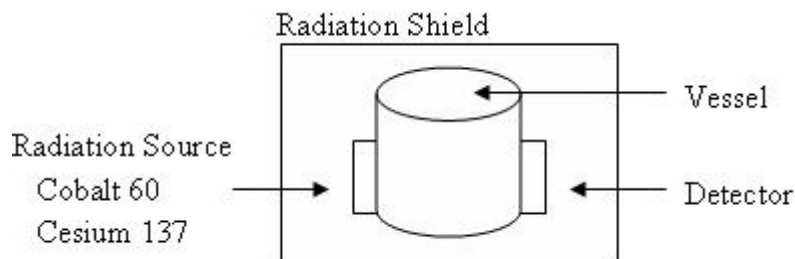


Direct Mass Measurement

With this technique, fluid is continuously passing through a U-shaped tube, where the tube is oscillating at its natural frequency. An electrochemical device strikes the tube periodically at the curved portion of the tube. The change in frequency between the electrochemical strike and the natural frequency is proportional to the changes in density which correlates to the composition of the substance.

Radiation-Density Gauges

Gamma radiation inside a pipe/vessel is used to determine the density of the liquid. Below is a diagram of the setup.



If the path-length for the radiation source is under 610 mm then cesium 137 is used. Above 610mm, cobalt 60 is used. The detector is usually an ionization gauge. The density is a function of the absorption of the radiation being detected. Decay of the vessel must be taken into consideration when calibrating temperatures.