CHAPTER 1.2

Analytical Testing

Meg Dietrich LeVier

Sampling and analytical testing are the basis of decision making in exploration, mineral evaluations, and/or environmental dispositions. Even before the 16th century, comprehensive schemes of assaying ores were known, using procedures that do not differ materially from some of those employed today. Most conventional methods of chemical analyses used today have evolved using sophisticated analytical instrumentation to detect and estimate quantities of elements in ores and minerals, particularly at low concentrations, to develop a detailed understanding of the ore characteristics and the corresponding response in mining and processing operations. This allows financial decisions to be made regarding treatments to optimize each ore type for extraction, increase production, or reduce costs.

The primary objectives of analytical testing are generally for one of the following reasons:

- For evaluating a mining property
- To develop a detailed understanding of the physical properties of the ores examined
- For plant quality control (QC)
- To provide comprehensive recommendations for process performance improvements
- For metallurgical accounting and inventory requirements
- For environmental considerations

ANALYTICAL TESTING STRATEGY

Selecting appropriate analytical tests can be a confusing process. Balancing cost and risk with quality fit for purpose is the goal of every test program. Costs for analysis can range from a few dollars per sample for "ballpark" exploration methods to hundreds of dollars per element when high accuracy and precision are required for contract settlements. The purpose and expected quality requirements need to be communicated to the laboratory when a program is initiated so that a suitable quality assurance and QC program can be included. Some examples of different assay programs and the associated QC procedures are as follows:

- **Exploration geochemistry.** This analysis is intended for exploration program rock samples with low metal contents. The frequency of inserted QC materials is low and the assay methods have low upper-measurement limits.
- **Ore-grade assaying.** This assay level is used when exploration geochemistry has identified higher-grade mineralized rock or core samples. The data from these analyses are often used for resource/reserve estimation. The frequency of inserted QC materials is more frequent, generally about 10%, and methods are designed to measure a wider range of elements.
- **Process control.** This level of analytical testing is used for metallurgical support and/or accounting, or the data are used to monitor a metallurgical process. The frequency of inserted QC materials is about 10%–20%. Methods are designed to analyze samples that contain up to 100% of the target element in some cases. High precision and accuracy is necessary and fewer samples are assayed at a time, but a large number of analytes per sample are measured.
- **Commercial settlement.** This grade of analysis is used when extremely high precision and accuracy data are required for high dollar value of concentrate and bullion shipments for commercial transactions and contract settlements, and to settle disputes between buyers and sellers of traded commodities (umpire analysis). The splitting limits (the accepted spread of analytical results agreed upon by concentrate or bullion seller and buyer) are determined by negotiation. The frequency of inserted QC materials is at least 100% and multiple replicates are analyzed.

Communication with a laboratory is vitally important for a successful analytical project. Once the expected quality of work is established, the detail must follow. Analytical laboratory managers need as much information as possible to prepare quotations to meet budget costs and project schedules, as well as for minimization of mistakes and unreal expectations. A laboratory visit or audit is prudent and one must be prepared to discuss numerous questions.

Meg Dietrich LeVier, Consulting Analytical Chemist, K. Marc LeVier & Associates Inc., Highlands Ranch, Colorado, USA

The following questions can be used as a checklist of analytical requirements to be communicated to the laboratory manager:

- What sample preparation protocols should be used?
- How many samples/day/week?
- What are the sample types? (Rocks, effluents, soils, concentrates, metals?)
- What are the approximate concentration ranges for each sample type and expected reporting limits?
- What are the accuracy and precision requirements? This may determine the analytical procedure required.
- What is the required turnaround time?
- For methods requiring sample dissolution, what method of dissolution will be employed?
- How many and what elements need to be determined per sample type?
- Are there specific QC reporting requirements?
- Are the analytical requirements likely to change on a regular basis?
- Are there regulatory or legal issues to take into consideration (e.g., environmental permit requirement or ISO/IEC 17025 [2005] specific protocol requirements)?
- Will there be liquid samples needing preservation, refrigeration, or that have short hold times?
- What sample volume is typically available?
- How are the data being used?
- What will the budget allow?
- May a subcontracted commercial laboratory be used?
- What is the reporting format? Spreadsheet or are data to be imported?
- Should completed samples be returned, stored, or disposed after 90 days?
- How will samples be transported to the laboratory?

SAMPLING AND SAMPLE PREPARATION FOR ANALYTICAL TESTING

The importance of sampling and sample preparation cannot be overemphasized. Typically, the focus of laboratory results is on the analytical method, and sampling is pretty much taken for granted. However, sampling is perhaps the major source of error in the measurement process and, potentially, is an overwhelming source of error for any metallurgical project. The selection of the actual sample preparation procedures depends on the type and size of the sample, the mineralogy, and the analytical and budgetary constraints. Discussion with the laboratory manager is required to determine the most suitable options to achieve the best outcomes in terms of precision, accuracy, and meaningful analytical data.

Common sense suggests that the larger the mass of the sample, the closer it should resemble the composition of the material it came from. However, preparing large masses by grinding entire lots of material is not practical. Understanding the Gy sampling theory, often presented in a short course by Francis Pitard (1993), will provide guidance for what may seem like an overwhelming amount of work. The simple task of taking a small amount of material out of a laboratory sample bag could possibly be the largest source of error in the whole measurement process, leading to meaningless results and incorrect and costly decisions.

Laboratories recognize that the quality of all analyses is dependent on the quality of sample preparation. Whether a blasthole is being collected, copper concentrate is shoveled from a stockpile, or a scoop is taken from a sample bag, analytical results from these samplings have financial significance. Some are more impactful than others. Fire assaying of gold is typically performed on 30 g of material and may represent thousands of tons of material. How can one know that the sampling is an accurate representation of that material? Biased sampling protocols can have negative consequences such as poor ore/waste selection decisions, deficient profit/loss decisions, inadequate reconciliations, or unbalanced metal accounting. To have confidence in the integrity of a sample and the sampling procedure, one must be sure all samplings and subsequent preparation are entirely random. Preparing a bulk sample, such as a 1,000 kg of HQ drill core, might include sawing the core into quarters, crushing, subdividing, pulverizing, subdividing again, and taking a split for assay. To understand how much mass should be used, one must refer to a *sampling nomogram*, which is a graphical representation that summarizes the relationship between the fragment size, the mass of the sample relative to the mass of the lot, and the relative variance that can be anticipated. Details of creating sampling nomograms and proper sampling procedures are found in Pitard (1993) and other chapters of this handbook.

During mineral sample preparation, geological or process material is broken down into a fine, dry pulp, ideally <75 µm particle size, that can be subsampled to provide a representative sample of the original material. Well-blended small particles are the key to ensuring that the target elements are effectively released from the rock for decomposition and further analysis. Quality protocols must be followed during all stages of sample preparation, including proper handling, safety, and sample tracking. Utilizing a laboratory information management system, or LIMS, for tracking allows each sample to be given a unique identification number. This maintains organization and allows samples to be tracked throughout all stages of analysis and enables easy monitoring of progress.

A few tips on the basic steps for preparing samples for optimal analytical testing, minimization of contamination, and longevity of grinding equipment are discussed in the following paragraphs.

Safe sample preparation procedures must be followed. A very small silica dust particle could easily be aspirated, which then becomes a health hazard that could lead to serious lung disease. An exposure control plan must be in place before work begins. Additionally, fibrous or asbestiform samples and samples of naturally occurring radioactive material require special handling during sample preparation and may result in higher preparation costs. Material must be clearly identified with the hazard on the sample submission and sample packaging. An isolated preparation and storage area is required. Additional personal protective equipment and awareness training must be given to employees (Horak et al. 2016).

Sample drying of all free moisture in mineral samples is important to ensure that particles do not adhere to the preparation equipment and that data are represented on a dry basis. Drying time and temperature depend on the type of sample with respect to mass, moisture, and matrix but is typically dried at 105°C to remove free moisture without compromising the sample. Clays containing crystalline water require much higher temperatures to dissociate the water. Removing this type of water is not usually necessary for analytical test samples. Samples containing volatile analytes, particularly mercury, can be lost during drying and are best dried at 60°C for a longer period. A sample is considered dry when it no longer has a weight change over a given drying period, generally 1 hour or more.

Crushing of rocks and core samples is required when particle sizes are too large for pulverizing equipment. The most common primary crushing tool in mineralogical laboratories is the jaw crusher. Jaw crushers handle rock material up to about 15 cm and can reduce most material down to about 85% passing 2 mm (10 mesh). Jaw crushers have an adjustable crushing diameter. The rocks are loaded, crushed to a target size of 2 mm, and fall to the bottom of the crusher, and, consequently, the crusher can be effectively cleaned between samples. Care must be taken to capture all dust fines. If the material is still damp or contains clay, samples can coat the jaws and the target particle size is not achieved. This can also cause cross contamination if the equipment is not cleaned between samples. A secondary roll crusher may be needed if the jaw crusher fails to crush to 85% passing 2 mm. Roll crushers are often difficult to clean, which can result in serious cross contamination. The contamination risk of using a roll crusher must be weighed against the benefits. If a roll crusher is being used, one must ensure that the crushing procedure specifies a cleaning step between samples to prevent cross contamination.

Splitting (subdividing) is a method of reducing sample volume by dividing the sample into representative subsamples. It is critical that methods used to reduce the ore to those few grams be as accurate as possible, and equipment is available that will assist in doing this. For instance, cone and quartering is the "old" method for splitting a large sample. Cone and quartering induces a margin of error of 19.2% (Allen and Khan 1970), which is not the best way to obtain accurate assays. To ensure that a proper representative sample is obtained, careful consideration is given when choosing the size and type of the splitter and its contact with the sample to split the material without bias. The rotary sample splitter has a relatively low margin of error of 0.125% (Table 1) and is capable of splitting large bulk samples of 6 mm ore. The use of a rotary splitter for large samples can eliminate significant error in obtaining a representative sample. A precision rotary splitter has a margin of error much lower than that of a typical Jones riffle splitter. Utilizing the most appropriate and accurate equipment will make the difference in achieving an unbiased sample. If a sample splitting method with a high margin of error must be used, then the overall error can be reduced by repeating the mixing and subsampling procedure several times.

Table 1 Standard deviations of samples produced from a 60%/40% mixture of fine and coarse sand

Sampling Method	Standard Deviation of Samples, %
Cone and quarter	6.81
Grab sampling	5.14
Chute-type sample splitter	1.01
Rotary riffle	0.125
Random variation for a theoretically perfect sampler	0.076

Adapted from Allen and Khan 1970

Milling is altering the material to a smaller particle size by grinding in a container typically made of hardened steel to create a fine homogeneous powder. A particle size of 85% passing 50 µm is ideal, although 85% passing 74 µm (200 mesh) is acceptable in most cases. This allows for a representative subsample to be taken for analysis and is a requirement for chemical analysis. One should not be able to feel any grit when rubbing ground material between two pieces of paper. Contamination from pulverizing bowls, such as Fe in mild steel bowls, may be a concern if Fe is a target analyte. For high-precision whole-rock analysis, tungsten carbide pulverizing is recommended. Very hard material may need to be pulverized in tungsten carbide grinding pots; however, this is not appropriate if tungsten, carbon, or cobalt are target elements. An appropriate grinding bowl needs to be selected for material hardness and potential contaminants (Table 2). Careful

Table 2 Properties of grinding container materials

Material	Major Elements	Minor Elements	Hardness	Resistance to Abrasion	Durability	Comparative Efficiency
Hardened steel	Fe	Cr, Si, Mn, C	Mohs: 5.5–6 Rockwell: C 60–65	Moderate	High	High
Stainless steel	Fe, Cr	Ni, Mn, S, Si*	Mohs: 5–5.5 Rockwell: C 55–60	Moderate	High	High
Cr-free steel	Fe	C, Mn, Si, Mo	Mohs: 5–5.5 Rockwell: C 55–60	Moderate	High	High
Tungsten carbide	W, C, Co	Ta, Ti, Nb	Mohs: 8.5+ Knoop: 1,400–1, 800	High	Long-wearing, subject to breakage	Very high
Alumina ceramic	Al	Si, Ca, Mg	Mohs: 9 Rockwell: R45N 74–79 Knoop: 1,160	Very high	Long-wearing, brittle	Moderate
Agate	Si	Al, Na, Fe, K, Ca, Mg*	Mohs: 6-7 Knoop: 550–800	Extremely high	Very long-wearing	Moderate
Zirconia	Zr	Y, Mg, Hf	Mohs: 8.5 Rockwell: R45N 74–79 Knoop: 1,160	Extremely high	Very long-wearing	Moderate
Silicon nitride	Si	Y, Al, Fe, Ca	Mohs: 8.5+ Knoop: 1,600	Extremely high	Very long-wearing	Moderate
Plastic	C	—	Mohs: 1.5	Low	Low, disposable	Low for grinding; high for blending

Source: SPEX SamplePrep 2016.
*All reported <0.02%

protocols must be followed when grinding. Overloading the grinding bowl is a common sample preparation error resulting in poor grind. Larger grinding pots are available in cases where larger samples need pulverizing, such as in the case of material with heterogeneity problems like particulate Au. Also, contamination may occur when particulate Au or other metallic smears inside the grinding bowl and must be cleaned out between samples using sand, sometimes multiple times. The laboratory seldom needs more than 150 g to complete several tests.

INSTRUMENTATION FOR ELEMENTAL ANALYSIS

To keep up with advancements in material processing, analytical methods require continuous improvement to be faster, more rugged, provide more information, and be more cost-effective. Qualitative wet chemical methods used during the 19th and early 20th centuries were replaced with more efficient quantitative techniques. The invention of the transistor, microprocessor, and other computer technologies brought electronic instrumentation into the laboratories. Classic wet chemical methods for elemental analysis, considered old-fashioned science, have mostly been replaced by instrumentation in analytical laboratories but are still used in certain applications.

There is considerable overlap of analytical methods, making selection of the appropriate instrument or tool confusing. In fact, all of the techniques may be able to perform a particular analysis at an acceptable level of accuracy and precision, depending on the requirements of a metallurgical project.

Samples may arrive to the laboratory in liquid or solid form. Most instrumental techniques are designed for either solids or liquids with some capable of measuring in either form with modifications. To establish a rational basis for decision making, one must understand the relative strengths and weaknesses of each of the techniques as they may apply to the requirements of a project. The complex technological details of each of the various techniques are not covered in this chapter, but it is helpful to have a general understanding of basic principles. The project requirements must first be determined and discussed with the laboratory manager. The laboratory manager will select methods based on requirements for turnaround time, degree of accuracy, budget, and so forth.

Instrumentation Commonly Used for Solid Material

Spark Optical Emission Spectroscopy

Spark optical emission spectroscopy (arc spark OES or spark OES) is typically used where metallic samples are produced, such as foundries. Sample material is vaporized with a testing probe by an arc spark discharge. The atoms and ions contained in the atomic vapor are excited into emission of radiation. The radiation emitted is passed to the spectrometer (arc spark OES) optics via an optical fiber, where it is dispersed into its spectral components. From the range of wavelengths emitted by each element, the most suitable line for the application is measured by means of a charge-coupled device. The radiation intensity, which is proportional to the concentration of the element in the sample, is compared to calibration curves. This is usually used for measuring concentrations of metals\alloys and impurity analysis in metals such as

- Steel, cast-iron, and high-alloyed steels;
- Nonferrous metals and their alloys;
- Al: wrought alloys, casting alloys, etc.;
- Cu: bronze, brass, cupronickel, etc.;
- Mg, Zn alloys, solders;
- Nitrogen in steel;
- Phosphorus in aluminum; and
- Ultra-low carbon analysis for elements such as Se, La, Te, and so on.

X-Ray Fluorescence

XRF is used on both solid and liquid material. It is fast and known for high precision. It is a useful tool for the elemental analysis of ores, concentrates, tails, metals, glass, and ceramics. When XRF is configured with purge gas, liquids may also be analyzed. X-rays form part of the electromagnetic spectrum. They are on the high-energy side of ultraviolet and are expressed in terms of their energy in kiloelectron volts (keV) or wavelength in nanometers (nm). XRF can be considered in a three-step process occurring at the atomic level:

1. An incoming X-ray knocks out an electron from one of the orbitals surrounding the nucleus within an atom of the material.
2. A hole is produced in the orbital, resulting in a high-energy and unstable configuration for the atom.
3. To restore equilibrium, an electron from a higher-energy, outer orbital falls into the hole. Since this is a lower-energy position, the excess energy is emitted in the form of a fluorescent X-ray.

The energy difference between the expelled and replacement electrons is characteristic of the element atom in which the fluorescence process is occurring; thus, the energy of the emitted fluorescent X-ray is directly linked to a specific element being analyzed.

The elements and concentrations that XRF analyzers can determine depend on the material being tested and the configuration of the instrument used. The two main XRF methodologies are energy-dispersive X-ray fluorescence (EDXRF) and wavelength-dispersive X-ray fluorescence (WDXRF). Each method has its own advantages and disadvantages. The range of detectable elements varies according to instrument configuration and setup, but typically EDXRF covers all elements from sodium (Na) to uranium (U), while WDXRF can extend this down to beryllium (Be). WDXRF systems can routinely provide much better working resolutions (between 5 and 20 eV), depending on their setup, whereas EDXRF systems typically provide less resolution (ranging from 150 to 300 eV or more), depending on the type of detector used. Limits of detection depend on the specific element and the sample matrix, but as a general rule, heavier elements will have better detection limits.

Comprehensive software algorithms using fundamental parameters, characteristics based on theoretical X-ray beam intensity, detector solid angle, matrix effects (element–element interactions), band overlap, and spectral backgrounds are used to calculate element concentrations based on the observed peak intensities. This provides a very fast, standardless quantification method, which will work well for various matrices. However, matrix-matched calibration standards are best for accuracy.

Advantages of XRF over other techniques are that it is a fast analytical tool for elemental composition. XRF can measure concentrations ranging from parts per million to 100% and can be used on solids, liquids, and powders. It can also be non-destructive to the sample, and the technique has high precision.

Whole rock analysis is the determination of major elements of a rock sample. This will total approximately 100% in nonmineralized samples with elements calculated as oxides—Al_2O_3 (aluminum oxide), CaO (calcium oxide), Cr_2O_3 (chromium oxide), K_2O (potassium oxide), MgO (magnesium oxide), MnO (manganous oxide), Na_2O (sodium oxide), P_2O_5 (phophorous pentoxide), Fe_2O_3 (iron oxide), SiO_2 (silicon dioxide), and TiO_2 (titanium dioxide)—and loss on ignition (LOI), which includes moisture and carbonaceous material, to sum to 100%. Where the analytes of concern in many industrial products (i.e., iron ore, cement, ilmenites, rutile, limestone) are the major elements, XRF is the first choice for instrumentation.

Disadvantages of EDXRF and WDXRF are that they suffer from matrix and inter-element interference due to signal enhancement or suppression. Also, the standard and sample must be matrix matched with respect to both the matrix and the particle size. Finding calibration standards with an exact match of sample type is difficult and time-consuming; consequently, sample preparation to match standards on hand becomes a simpler plan.

In general, the energy of the emitted X-ray for a particular element is independent of the chemistry of the material. For example, a calcium peak obtained from EDXRF for $CaCO_3$ (calcium carbonate), CaO, and $CaCl_2$ (calcium chloride) will be in exactly the same spectral position for all three materials. However, the wavelength shifts a bit for Cu when it occurs as CuS (covellite) compared to $CuSO_4$ (copper sulfate), and will require sample preparation by fusion for accurate total Cu measurement.

Sample preparation for semiquantitative analysis is minimal with direct analysis of loose powder. However, preparation for quantitative analysis is more rigorous by either of two methods. Both require the particle size to be <50 µm to minimize grain-size effects. Adding a binder and pressing into a pellet with a hydraulic press is one method. This technique is useful if very low detection is necessary and mineralogical effects are not expected to be a problem. Another preparation method involves mixing the finely ground sample with a flux of lithium tetraborate, metaborate, or a combination of the two, and a small amount of wetting agent in a platinum crucible. The crucible is fused at about 1,000°C and the melt is poured into a platinum mold, forming an amorphous glass disk. (Graphite crucibles may be substituted for platinum if needed for only a few fusions.) Fusion eliminates the physical and mineralogical interferences and allows the analyst to make corrections on only the inter-element effects. Alternatively, the melt may be poured into a solution of weak hydrochloric or nitric acid for analysis on other instrumentation. The level of skill required for routine analysis is low. However, skill level for accurate results of frequently changing ores can be high. The instrument cost for EDXRF is moderate (US$35,000–US$85,000), while the cost of a WDXRF can be quite high (US$150,000–US$275,000).

Other spectroscopic methods use the same principle as XRF but use incident radiation. These include laser-induced breakdown spectroscopy, electron microprobe analyzer, particle-induced X-ray emission, X-ray photoelectron spectroscopy, and auger. Although these techniques are extremely useful for mineral characterization, they are found exclusively in research or university laboratories and are reserved for specific applications. Details of these instruments are outside the scope of this chapter.

Instrumental Neutron Activation Analysis

Neutron activation analysis (NAA) is an analytical technique that measures gamma rays emitted from a sample that was irradiated by neutrons. The rate the gamma rays are emitted from an element in a sample is directly proportional to the concentration of that element. Multiple samples are placed in polyethylene vessels and simultaneously irradiated. Following irradiation, a high-resolution germanium detector coupled to a multichannel analyzing system measures sample decay. Sample data are compared to standard data.

Advantages of NAA over other analytical techniques are numerous and include ease of sample preparation, high precision, simultaneous measurement of multiple elements, high reproducibility, excellent interlaboratory comparability to other methods, large dynamic range from parts per billion to high percentages, and relatively low cost of analysis at approximately US$23 per sample.

The major disadvantage is the requirement to have access to a licensed nuclear reactor.

Combustion Infrared Analyzers

Elemental *combustion infrared analyzers* is a generic term for sulfur and carbon analysis. These types of analyzers are often referred to as Leco analysis although other manufacturers (e.g., Eltra, Horiba) produce similar instruments. Analytes of interest in metallurgical products may include light elements that are difficult to analyze in other ways and include C, S, O, H, and N. Final and intermediate metal and alloy products have tight limits on S, O, C, H, and N because each may be detrimental to the properties of the metal.

Total carbon and sulfur and phases of carbon and sulfur are of particular interest in characterizing ores and metallurgical products for process development, process control, and for estimating acid rock drainage. Carbon and sulfur are usually measured simultaneously on one of two types of carbon/sulfur (C/S) combustion infrared analyzers, resistance furnace or induction furnace. A common error is made when measuring geological and metallurgical process material on a combustion analyzer designed for metallic samples. Sulfur results are often erroneously low if samples contain crystalline water or hydroxide, such as clays and hydrated process material when measured on a combustion instrument with an induction furnace. Also, most induction styles were designed for very low concentrations of carbon and sulfur in metallic samples and are incapable of accurately measuring sulfur concentrations above 10%. Sulfur in geological or metallurgical process samples are best determined using a combustion analyzer with a resistance furnace and a dual concentration detector to accommodate a wide range of sulfur concentrations.

Combustion analyzers are simple to operate. In the case of a C/S instrument, a sample is weighed into a ceramic crucible and an accelerator (such as iron or tungsten oxide) is added to the sample and placed in the furnace. It is melted in a stream of pure oxygen in a high-temperature atmosphere, causing all sulfur forms to oxidize to sulfur dioxide (SO_2) and carbon forms to carbon dioxide (CO_2). The combustion gases pass through a halogen trap and moisture absorber for purification. The SO_2 and CO_2 are detected in infrared cells. Using Leco combustion analysis for estimating carbon and sulfur phases is detailed later in this document.

Instrumentation Used for Liquids

Metallurgical solid samples (e.g., pulps, sludges, concentrates, tailings) requiring elemental analysis are usually digested in acid or fused with salts and dissolved into a solution to be measured using one of the following liquid spectrometric techniques.

Flame Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS), commonly called atomic absorption (AA), is an invention that has since been labeled as one of the most significant achievements in chemical analysis in the last century. Measurement of metals went from hours to minutes. AAS remains a workhorse in most laboratories with little training required to operate the equipment.

A solution is first digested and aspirated into a flame and a ground-state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light absorbed and the concentration of analyte present in known standards is used to determine unknown sample concentrations by measuring the amount of light they absorb. This is a relatively low-cost and simple instrument to operate but is designed to measure one element at a time. Some newer models are programmed to measure other elements sequentially to increase productivity.

Accessories are used to expand the capabilities of AAS. Hydride generation and flow injection atomic spectroscopy are accessories for AAS to allow hydride generation of hydride-forming elements (As, Bi, Sb, Se, Sn, Te) using sodium borohydride to convert these elements into hydride gases. This technique works well for low detection in water samples. Other techniques must be used when significant amounts of base metals are present, such as those in sulfide concentrates.

AAS for mercury poses special analytical challenges because mercury may be partially or completely volatilized by high-temperature drying or acid digestions. It also amalgamates with gold resulting in low instrument response using the cold vapor method. Two AAS methods are used for Hg analysis:

1. **Cold vapor atomic absorption** is an AAS atomization method limited to only the determination of mercury, due to it being the only metallic element to have a large enough vapor pressure at ambient temperature. A sample is oxidized with nitric and sulfuric acid to Hg^{+2} and then reduced with stannous chloride to Hg^0. An inert gas carries the mercury gas through the reaction mixture. The concentration is determined by measuring the absorbance of this gas at 253.65 nm. Detection limits for this technique are in the parts-per-billion range, making it an excellent trace-level mercury detection AAS method. However, in the presence of Au, Hg is amalgamated and the signal is suppressed by an amount equivalent to the Au concentration, and a low reading results.
2. **Direct thermal combustion analysis** is the preferred method for higher concentrations of mercury typically found in gold processing plants because of gold–mercury amalgamation. A solid or liquid sample is weighed into a quartz or metal boat and dried. It is then thermally decomposed in an oxygen-rich furnace. Mercury and other combustibles are released from the sample and carried to a catalyst section of the furnace, where nitrogen and sulfur oxides, as well as halogens and other interfering compounds, are eliminated. Mercury is selectively trapped, in a separate furnace, through gold amalgamation. The amalgamation furnace is heated and mercury is rapidly released. Mercury vapor flows via a carrier gas through an optical path of the spectrophotometer, where it is quantitatively measured by AAS at 253.65 nm.

Graphite Furnace Atomic Absorption Spectroscopy

Graphite furnace atomic absorption spectroscopy is used when much lower detection limits than AAS can produce are required. A small volume (microliters) of digested sample is pipetted into a small graphite tube (the furnace). Then a series of three electrical heating steps are usually applied to the sample contained in the graphite furnace. The first of these is the drying stage, followed by the ashing stage where the temperature of the furnace is increased in the range of 400° to 800°C. The final stage is atomization where the temperature of the furnace is very rapidly raised to temperatures often as high as 2,700°C, effectively volatilizing the remaining metallic components on the furnace wall. Many of the volatilized metals will come off the walls in the atomic form, creating an atomic vapor. The absorbance measurement that occurs during this stage, using a hollow cathode lamp shone through the furnace, creates transmittance measurement that is common to all forms of spectrophotometry. An integrated signal of absorbance versus time is directly proportional to the actual mass of the element. This technique is relatively slow and most labs have abandoned it for other instrumentation.

Microwave Plasma–Atomic Emission Spectrometry

MP-AES is a relatively new technology, and, although it is not an acceptable technique where a laboratory must use a regulated environmental method for a particular analysis, it offers some advantages over other techniques. Remote mine-site laboratories often have difficulty receiving instrument gases, such as acetylene or argon. MP-AES uses nitrogen from a nitrogen generator as a plasma gas. The nitrogen MP is considerably hotter than the acetylene flame used in AAS, reaching temperatures nearing 5,000 K. At these temperatures, atomic emission is very strong for most elements, leading to improved detection and linear dynamic ranges over flame AAS for most elements. Operating costs can be significantly reduced compared to flame AAS by using a nitrogen generator. Using inert nitrogen is a safer choice over flammable acetylene. MP-AES can be a productive tool compared to flame AAS because it uses a scanning monochromator and a solid-state detector for multi-element analysis instead of individual lamps as used in AAS. A disadvantage of MP-AES is that it is limited in the amount of total dissolved solids (TDS) it can tolerate in a solution.

Inductively Coupled Plasma–Optical Emission Spectrometry

ICP-OES has become another laboratory staple. A solution in which elements are dissolved is pumped into a nebulizer, mixed with gas to produce a fine mist, and injected into an argon plasma that has been induced by means of high-frequency waves. The plasma electron temperature can range between ~6,000 K and ~10,000 K (~6 eV and ~100 eV; Shun'ko et al. 2014), comparable to the sun's surface. Charged elements become thermally excited and each element emits radiation in the form of light at a characteristic wavelength.

The intensity of the emission has a proportional relationship to the concentration of that element. In more modern units, the light is focused through a series of optics and separated energies fall upon an array of detectors, allowing for simultaneous measurement of approximately 1 to 60 elements per minute. The orientation of the torch may be aligned in a radial position or end-on axial position. Axial position is used to achieve 3–10 times lower detection of an analyte. Radial alignment is useful for major elements of interest.

Inductively Coupled Plasma–Mass Spectrometry

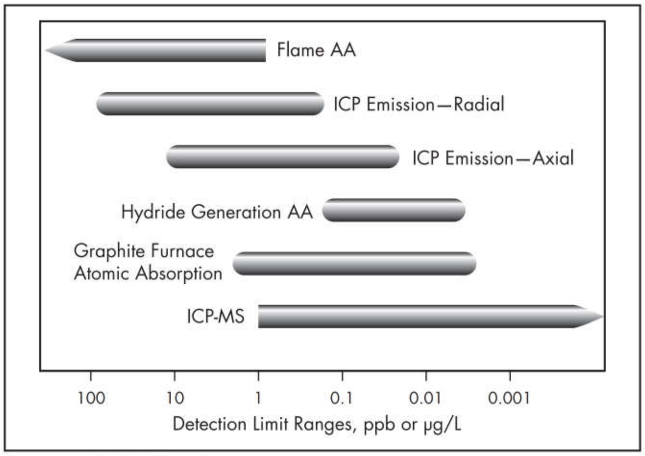
ICP-MS follows a sample introduction system through a high-temperature argon plasma similar to ICP-OES. A pair of cones, which allow only a fraction of the sample to enter the chamber, reduces the number of excited ions. The positively charged ion stream is focused through an electrostatic lens, which also has a positive charge, and collimates the ion beam, focusing it through a quadrupole where the ions are filtered by their mass-to-charge ratio. This ability to filter ions on their mass-to-charge ratio allows ICP-MS to take advantage of isotopic information, since different isotopes of the same element have different masses. A detector receives an ion signal proportional to the concentration. As ions hit the surface of the detector and are converted to electrons, the active film coating is consumed and detectors must be replaced if bombarded with high concentrations of ions. Care must be taken to protect the costly detector by diluting samples or choosing a less abundant isotope.

Interferences may be caused by chlorides from hydrochloric acid used in sample digestion or plasma gas combining with ions and forming masses that overlap with analytes of interest. High-resolution power is required to separate interferences from masses close to the analytes of interest. A skilled ICP-MS operator is required to understand how to overcome such interferences. High-resolution or magnetic sector mass spectrometers have become more common in ICP-MS, allowing the user to eliminate or reduce the effect of interferences due to mass overlap. Reaction or collision gases remove interfering ions through ion–neutral reactions (Tanner et al. 2002). Ammonia, methane, oxygen, and hydrogen have been used as reaction gases to eliminate interferences.

Analytical Interferences and Detection Limits

Interferences—matrix effects in particular—are the changes in the sample composition (non-analyte constituents) of the test material and are inherent in most chemical analyses. Often the bulk of the analyst's time is directed toward eliminating matrix effects, either by separation of the analyte from the matrix, chemical treatment measures, or by calibration procedures to minimize the effects. Steps taken to minimize interferences can compromise the expected detection limits of a particular method or instrumental response. If budget constraints require choosing to purchase only one instrument, ICP-OES is usually chosen over ICP-MS and XRF because the systematic errors are much easier to eliminate and the random measurement error can be as low as 0.5% (Gaines 2012). Addressing specific interferences for each instrument or analytical method is out of the scope of this chapter. Thompson (2005) describes strategies for minimizing interferences and calculating uncertainties.

Published detection limits for analytical instrumentation are useful when comparing relative responses between analytical instruments but seldom represent actual reporting limits. A relative comparison of detection ranges for instruments measuring elements in solution are shown in Figure 1. However, matrix effects and other factors contribute to the overall uncertainty and method reporting limits. Most acid solutions of ores and metallurgical samples contain high amounts of TDS, causing unstable or suppressed instrument response. Accessories are necessary to improve detection, stability, and uncertainty. Specialized nebulizers for high TDS and gas humidifiers aid in analysis.



Courtesy of PerkinElmer, Inc.

Figure 1 Typical detection limit ranges for the major atomic spectroscopy techniques

SAMPLE DECOMPOSITION

Before solution analysis is possible, the samples must first undergo dissolution, a process to convert solids to a solution ready for instrumental measurement. Total dissolution is the goal; however, it is not always possible to liberate all elements of interest in a single procedure. Losses occur from volatilization, precipitation, and adsorption onto the vessel walls or incomplete digestion. This may lead to underestimation of elements of interest. Contamination is nearly impossible to avoid, as no single digestion vessel is perfect for all analytes. One must understand the limitations and advantages of each approach.

Acid digestion and salt fusion are the typical approaches, with acid digestion as the preferred method of dissolution of mineralogical matrices into a solution containing metals. Acids are reagents of choice because of low sample contamination with other metals compared to fluxing salts. Larger sample sizes may be used in acid digestions, and final solutions are low in dissolved solids.

The metals below hydrogen in the electromotive series only need to displace hydrogen and will dissolve in nonoxidizing acids with the evolution of hydrogen, but some are too slow to react, such as with hydrochloric acid on lead, cobalt, nickel, cadmium, and chromium.

Oxidizing acids must be used to dissolve the metals above hydrogen in the electromotive series. The most common of the oxidizing acids are nitric acid, hot concentrated perchloric acid, or some mixture that yields free chlorine or free bromine.

In many cases, the sample will not dissolve completely, but the constituent to be determined may readily dissolve out of the insoluble matrix. For example, acid-soluble oxides or sulfides may occur with insoluble silicates. If acid digestion is not sufficient, the residue may be fused by one of the procedures discussed later.

Common Strong Acids for Sample Decomposition

Hydrochloric Acid

Hydrochloric acid, or HCl, is a nonoxidizing, complexing strong acid. Concentrated hydrochloric acid (about 12 M, 37%) is an excellent solvent for many metal oxides as well as those metals below hydrogen in the electromotive series. It is often a better solvent for the oxides than the oxidizing acids. Carbonate and oxide ores of Ba, Ca, Fe, and Mg are directly soluble in HCl. Chlorides are useful as complexing agents to prevent acid-resistant metal oxides from precipitating. Some elements volatilize as chlorides or other halogens when heated to fumes. For example, chlorides of As, Sb, Ge, and B at temperatures >140°C and $AuCl_3$ (gold trichloride) at >265°C will volatilize (Dulski 1996).

Nitric Acid

Concentrated nitric acid, or HNO_3 (about 16 M, 70%), is an *oxidizing* solvent for attacking metals. It will dissolve most common metallic elements except Al, B, Cr, Ga, Hf, In, Nb, Sb, Sn, Ta, Th, Ti, W, and Zr that become passive by forming a film of oxide on the surface of the metal. Nitric acid is more useful in combination with other acids. Some metals, such as metallic Cu, are somewhat insoluble in concentrate nitric acid but readily dissolve in a 1:1 dilution of nitric acid with water.

Perchloric Acid

Hot concentrated perchloric acid, or $HClO_4$ (about 12 M, 72%), is an extremely strong oxidizing agent and solvent. It must be used after nitric acid reaction ceases to prevent any easily oxidizable material from exploding. The hot acid attacks ferrous alloys and stainless steels that are insoluble to the other mineral acids. This acid also dehydrates and rapidly oxidizes organic materials. Dry metal chlorate salts must be wetted with water prior to adding acid for salt dissolution to prevent explosion. The use of perchloric acid requires specially designed fume hoods with water sprays throughout the ductwork to prevent explosive perchloric crystals from forming. A trained technician is required for safe usage.

Hydrofluoric Acid

The primary use for hydrofluoric acid, or HF (about 29 M, 49%), is for decomposition of silicate rocks and minerals *where silica is not to be determined* because the silicon volatilizes from the solution as silicon tetrafluoride. This releases the elements encapsulated within silica grains to be attacked by the other mineral acids. After decomposition is complete, the excess HF is driven off by evaporation with perchloric acid to near dryness. Since HF attacks glass and quartz, polytetrafluoroethylene (PTFE) laboratory ware must be used throughout. **CAUTION:** HF can cause serious painful injury, even death, when exposed to skin. Calcium gluconate ointment should be kept nearby during use and emergency procedures put in place. Only trained personnel should attempt digestions with HF.

Sulfuric Acid

Hot (near boiling point, 340°C) concentrated sulfuric acid, or H_2SO_4 (about 18 M, 96%), is often used as an oxidizing agent; otherwise, it is useful at ambient temperature for partial digestion of oxide minerals. Sulfuric acid is a good desiccant and will dehydrate and decompose most organic materials when concentrated. Sulfuric acid may be used for digestion of ores of Al, Be, Mn, Th, and U.

Mixtures of Acids for Optimal Sample Decomposition

Maximum sample decomposition of minerals is rarely achieved using one type of acid. Blending two or more acids together produces properties, such as oxidizing strength, greater than the sum of the individual acids. The most common of these acid mixtures are discussed in the following sections.

Aqua Regia

The aqua regia digestion method is optimally used with a 3:1 mixture of hydrochloric (HCl) and nitric (HNO_3) acids. The two acids react together and produce synergistic strong oxidizing products: nitrosyl chloride and chlorine gas:

$$3HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$$

Aqua regia is considered adequate for dissolving most base element sulfates, sulfides, oxides, and carbonates but only provides a "partial" extraction for most rock-forming and refractory elements because it does not attack silicates. For example, aqua regia extraction might give complete extraction of Cd, Cu, Pb, and Zn and also the volatile elements (Sb, As, Bi, Se, and Te) while it is known to provide only partial extraction of Cr, Ni, and Ba. These latter elements can only be efficiently recovered by using HF. However, the aqua regia digestion method may be acceptable for scoping these elements when they are not of primary interest. *Aqua regia* (in Latin) means "royal water" because of its ability to dissolve Au and other precious metals. However, this is not the case when organic "preg robbing" carbon is present and a stronger oxidizing digestion is required (e.g., by sodium chlorate salt addition). Other ratios of nitric to hydrochloric are often used for various digestions.

4-Acid Digestion

4-acid digestion is a blend of nitric + hydrochloric + hydrofluoric + perchloric acids and is more vigorous than aqua regia and provides satisfactory dissolution of most silica matrices. A PTFE digestion vessel must be used. This method is used on a hot plate for a near "total" sample decomposition. Perchloric acid decomposes organic or preg-robbing carbonaceous material. The acid mixture with HF will dissolve silica matrices by the following reaction:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

SiF_4 (silicon tetrafluoride) is volatilized and is not measured. This is a very effective method for trace analysis; however, there can be a loss of other volatile elements (e.g., As, B, Ge, Hg, Pb, Sb), and some refractory minerals (especially oxide minerals) are only partially digested or precipitate quickly as metal oxides (Al, Ba, Cr, Hf, Mo, Mn, Nb, Pb, Sb, Sn, Ta, Ti, W, Zr). Excess HF must be volatilized to prevent precipitation of metal fluorides. The use of perchloric acid requires specially designed fume hoods with water sprays throughout the ductwork to prevent explosive perchloric crystals from forming.

Other reagents to aid in sample dissolution are hydrobromic acid and bromine for sulfides and for volatilizing As, Se, and Sb. Hydrogen peroxide (H_2O_2) may be added as a clean oxidant. Potassium chlorate in nitric acid provides a strongly oxidizing mixture but must be used with care by experienced technicians. Citrate and tartrate aid in complexing certain elements to prevent precipitation.

Sample Decomposition/Digestion Techniques

Four common techniques for sample decomposition are hot plate and hot block open-vessel acid dissolution, leaching, microwave digestion, and fusion.

Open-Vessel Acid Dissolution

Following are the two types of open-vessel acid dissolution.

1. **Hot plate** samples are acid-digested in an open Pyrex beaker. PTFE beakers are used when HF is added. Digestion is on a high-temperature hot plate when silicates or other elements are purposefully volatilized.
2. **Hot block** is used for an acid digestion at a lower controlled temperature when the desire is to prevent element volatilization. This technique is useful for preventing loss of volatile elements such as Sb and Se; however, the temperature is not high enough for a total digestion.

Leaching

Leaching techniques are used to determine the soluble fraction of an element of interest under specific leaching conditions. Results are not intended as a total decomposition. Changing leaching condition variables (temperature, time, leachate strength, agitation speed) usually impacts reproducibility and differs from laboratory to laboratory.

Microwave Digestion

Microwave digestion ovens have solved several problems. Digestion in a microwave oven in a closed container is more powerful than hot-plate heating because of the closed pressurized vessels, and the specialized fume hoods for perchloric acid digestions is eliminated. Strong oxidizing conditions are created particularly when H_2O_2 is added and carbon or other carbonaceous material may be digested, liberating Au. Vessels are sealed and volatile elements are retained. When PTFE vessels are used, HF may be added to dissolve silicates; however, one must be cautious with solubilized samples because HF is still active and dangerous. Contrary to popular belief, addition of boric acid does not render HF into a harmless ionic molecule. Boric acid simply acts to complex HF to prevent precipitation of calcium fluoride (CaF_2) and other fluorides. Sample introduction components (i.e., injectors and spray chambers for AA and ICP) must be HF resistant. The downside to microwave digestion is that the number of vessels and the sample size are limited in these systems.

Fusion

Fusion is a technique to decompose all minerals by melting a finely ground sample with a salt-based flux and is reserved for the most refractory material or for eliminating mineral interferences for XRF instrumental analysis. Many elements of interest in ores are often not completely decomposed after a 4-acid total digestion, particularly samples containing Al, Ba, Be, Cr, Ge, Hf, Mn, Mo, Nb, Pb, Re, Sn, Ta, Ti, W, and Zr. High temperature in conjunction with a flux to lower the melting point decomposes the refractory material. The downsides are that (1) the ratio of flux to sample is often 10:1, diluting a sample beyond detection by XRF or producing a solution high in dissolved solids, which is problematic for sample introduction and precision in ICP-OES and ICP-MS; (2) contamination inherent in fluxes requires meticulous blank correction; (3) the Li and Na in flux are quite damaging to instrument quartz torches; and (4) some elements are volatilized at the high fusion temperature. A skillful analyst is able to avoid many of these issues with third-party accessories, but the analysis cost is at least twice the cost of acid digestion.

A complete decomposition of a sample with a flux is achieved by first grinding the sample to a very fine powder. An appropriate flux is selected and mixed well with the sample in a compatible crucible (Table 3) and covered. The temperature is raised slowly in a furnace or over a flame. The maximum temperature used varies considerably and depends on the flux and the sample. Gentle agitation during fusion improves homogeneity. Fusion is complete when a visual inspection shows a total melt without particles. The mass is allowed to cool somewhat and then dissolved into a liquid using a solvent—depending on the method—of water, dilute hydrochloric acid, or nitric acid. Unattacked material may require a change in flux.

Fluxing and fusing into a glass disk or bead is another option if the sample will be analyzed using XRF or laser ablation ICP-MS. Blends of lithium metaborate or tetraborate are mixed well with a sample, fused at about 1,000°C, and poured into a platinum mold. An automated system can produce several hundred glass disks per day for whole rock analysis. Care must be taken when choosing a crucible since fusion crucibles can be a costly consumable. Fusions must have negligible attack on the crucible and the material from which the crucible is made and should not contain any of the elements for which the sample is being analyzed.

The following should be taken into account when choosing a vessel for fusion:

- Platinum crucibles are excellent with lithium meta/tetraborate fusions but are expensive and easy to destroy if one attempts to clean them in aqua regia. However, they can last through hundreds of fusions with no impact if properly used. They should never be used for a sodium peroxide fusion.
- Zirconium, nickel, and iron crucibles may be used for sodium peroxide fusions where Zr, Ni, and Fe are of no consequence in the analysis and temperatures do not need to be much higher than 600°C. Zr is the best for complete fusion of sulfide minerals since Ni and Fe are usually of interest.
- Graphite crucibles are the least costly but have the shortest life. They may be used with caution and for small samples by heating in an induction furnace with an argon purge gas. The recommended flux is lithium metaborate or lithium tetraborate.

The following should be considered when choosing a flux for fusing:

- Alkaline fluxes are used for attack on acidic materials and include sodium carbonate, potassium carbonate, potassium or sodium hydroxide, borates, and sodium peroxide. Sodium peroxide also has oxidizing properties, making it a popular choice. The basic fluxes may be used individually or as mixtures to lower the fusion melting point. Lithium tetraborate is used for dissolving basic oxides such as alumina. Lithium metaborate is more basic and

Table 3 Common fusion fluxes, temperatures, and preferred crucible type

Flux (melting point)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
$Na_2S_2O_7$ (403°C) or $K_2S_2O_7$ (419°C)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Pu, Ta, Ti, Zr, and the rare earths
NaOH (321°C) or KOH (404°C)	450–600	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides
Na_2CO_3 (853°C) or K_2CO_3 (903°C)	900–1,000	Ni, Pt for short periods (use lid)	For silicates and silica-containing samples (clays minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulfates
Na_2O_2	600	Ni, Ag, Au, Zr; Pt (<500°C)	For sulfides; acid-insoluble alloys Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals
H_3BO_3	250	Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels
$Na_2B_4O_7$ (878°C)	1,000–1,200	Pt	For Al_2O_3; ZrO_2, and zirconium ores, minerals of the rare earths, Ti, Nb, Ta, aluminum-containing materials; iron ores and slags
$Li_2B_4O_7$ (920°C) or $LiBO_2$ (845°C)	1,000–1,100	Pt, graphite	For almost anything except metals and sulfides. The tetraborate salt is especially good for basic oxides and some resistant silicates. The metaborate is better suited for dissolving acidic oxides such as silica and TiO_2 and nearly all minerals.
NH_4HF_2 (125°C), NaF (992°C), F (857°C), or KHF_2 (239°C)	900	Pt	For the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr

Adapted from Dean 1995 and Bock 1979

better for dissolving acidic oxides such as silica or titanium dioxide. A blend of both is usually used. Boron oxide (B_2O_3) is used to decompose silicates and oxides when Li, Na, or K will be determined.

- Acid fluxes are the pyrosulfates (of sodium, potassium, and ammonium), bisulfates, potassium hydrogen sulfate, the acid fluorides, and boric acid. They are used for insoluble oxides and oxide-containing samples.
- Oxidizing fluxes contain sodium peroxide, potassium nitrate, sodium nitrate, or potassium chlorate, usually in mixture with alkaline fluxes. They are used for sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; and Cr, Sn, and Zn minerals.
- Neutral fluxes are the most commonly used for destroying silicates and include sodium fluoride, borax, and lithium fluoride.

Table 3 summarizes proper flux and crucibles for different material types.

Sample Decomposition Losses and Contamination

Losses are likely to occur but may be minimized if understood. Acid dissolution may present losses in many ways, such as when complexed ions (e.g., tetrachloroaurate, or $AuCl_4^-$) adhere on glass surfaces. Vigorous shaking of the solution may bring some of the adsorbed species back into solution (Twyman 2005). Plastics also absorb ions, and acids in strengths >10% are recommended for storage. Filter paper can also absorb analytes of interest. Centrifugation is preferable over filtration when the filtrate solution is to be analyzed. Losses from volatilization of halides may be minimized with lower digestion temperatures or the use of closed-vessel microwave.

Silver loss is a common occurrence, usually by precipitation as silver chloride (Equation 1a). The key to consistent Ag analysis is to avoid all chloride or add excess chloride as hydrochloric acid (at least 15%–30% in final solutions) to resolubilize the silver as a very stable silver chloride complex (Equation 1b).

$$Ag^+ + Cl^- \rightarrow AgCl\ (\text{solid}) \qquad \textbf{(EQ 1a)}$$

$$AgCl\ (\text{solid}) + Cl^- \rightarrow Ag(Cl)x\ (\text{aqueous}) \qquad \textbf{(EQ 1b)}$$

Since avoiding chloride is virtually impossible, excess chloride is always required to stabilize Ag (Hg and Pb behave similarly). Very concentrated silver, however, is best measured by a titration method or by fire assay.

Contamination may occur in a variety of laboratory ware. PTFE beakers are difficult to clean when a "sticky" inorganic species is formed such as silver chloride, which may require an ammonium hydroxide rinse. Other contamination of Al, B, Na, and Si is typically found in borosilicate glass test tubes, which should be replaced with plastic when these are elements being analyzed. Dust in laboratory mining labs is a concern as it is drawn into fume hoods. All reagents should be purchased in a quality suited for the purpose.

FIRE ASSAY FOR GOLD AND PLATINUM GROUP METALS

Fire assay is a quantitative method for accurately determining precious metals of gold and platinum group metals (PGMs). Silver is also fire assayed in higher concentrations. Fire assay principles have been used for hundreds of years with little change except for the integration of AAS finish in the 1960s, which brought higher productivity and improved detection limits for gold determination. An advantage of fire assay over other wet chemical methods is that a larger sample may be used, it is relatively inexpensive, precious metals are quickly separated from gangue minerals, and it is widely applicable to ores, concentrates, and rocks.

Edward Bugbee, a professor at the Massachusetts Institute of Technology (United States) and highly regarded author of *A Textbook of Fire Assaying*, believed that a course in fire assaying is the logical place to introduce the study of metallurgy (Bugbee 1922). Many metallurgical principles are utilized within the fire assay process, such as the thermochemistry of the metals, oxide and sulfide ores, the nature and physical constants of slags, the characteristics of refractories and fuels, the principles of ore sampling, the behavior of metallic alloys on cooling, and the chemical reactions of oxidation and reduction. Training in fire assay fundamentals is difficult to find, although Montana Tech (Butte, Montana, United States) offers a course each summer (Montana Tech 2017).

A typical crucible fire assay involves five steps: fluxing, fusion, cupellation, parting, and finish. The sample is mixed with a flux consisting primarily of lead oxide (litharge), as a collector of precious metals, along with other reagents customized for the characteristics of the material being assayed. The sample is blended well in a crucible with the flux mixture and fused at high temperature to produce two molten layers, a complex borosilicate slag and metallic lead. The gangue material follows the slag while the precious metals collect in the lead. The slag is discarded and the lead "button" is placed in a vessel made of absorbent bone ash or magnesia, called a cupel. During cupellation, the lead metal is oxidized to lead oxide and absorbed into the cupel. A bead containing gold, silver, and possibly some of the PGMs remains on the cupel surface. This bead is then "parted" in acid to remove silver and other impurities. The gold remaining after parting is either finished gravimetrically by weighing on a microbalance or digested in acid and the Au measured using AAS or ICP-OES.

The sample weight used in a fire assay charge is referred to as an "assay ton" or some fraction of an assay ton. An assay ton is exactly 29.167 g. The weight in milligrams of precious metal obtained from an assay ton of ore equals the number of ounces to the ton. With modern electronic balances and automated calculations, the concept of using an exact assay ton is obsolete, however the terminology is still used. Half-assay and quarter-assay ton are 14.583 and 7.292 g, respectively, and are used for more difficult sulfides and complex ores.

The five steps of fire assay are described in detail in the following sections.

Fluxing with Litharge

Accurate fire assay requires characterizing the material for proper fluxing. The material is broadly classified as neutral, acidic, basic, oxidizing, or reducing. In general, nonmetals form acidic oxides with SiO_2 and Al_2O_3 being the most common, while metal oxides are basic. Carbonate metals liberate CO_2 during heating, leaving base metals behind. Some metal oxides, such as zinc oxide (ZnO) and Al_2O_3, are amphoteric with both acid and base properties. Table 4 summarizes oxides in the earth's crust (Bugbee 1940).

Table 4 Oxides in order of abundance in the earth's crust

Slag-Forming Constituents	Acid or Base
Alumina, Al_2O_3	Acid
Calcium oxide, CaO	Base
Cuprous oxide, Cu_2O	Base
Ferrous oxide, FeO	Base
Lead oxide, PbO	Base
Magnesium oxide, MgO	Base
Manganous oxide, MnO	Base
Potassium oxide, K_2O	Base
Silica, SiO_2	Acid
Sodium oxide, Na_2O	Base
Zinc oxide, ZnO	Base

Source: Bugbee 1940

Fluxing acidic, siliceous ores is fairly simple and straightforward with only a decision of how much extra sodium carbonate to add, if any. Fluxing basic ores or pyrite and metallurgical products is more complex. Ideal slags are produced when metals are converted to their bivalent state either by (a) oxidation with PbO, (b) oxidation with heat, or (c) reduction to a lower valence using carbon or metallic iron (Beamish and Van Loon 1977). For example,

a. Oxidation to bivalent oxide
$FeS_2 + 5PbO \rightarrow FeO + 2SO_2 + 5Pb$
b. Oxidation of a metal by roasting
$2Cu + O_2 \rightarrow 2CuO$
c. Reduction of a trivalent oxide to a bivalent oxide
(with carbon) $2Fe_2O_3 + C \rightarrow 4FeO + CO_2$
(with metallic iron) $Fe_2O_3 + Fe \rightarrow 3FeO$

Samples with small amounts of pyrite may be reduced to divalent pyrrhotite (FeS) using (d) metallic iron, (e) roasting, or (f) niter (potassium nitrate, or KNO_3) addition. Examples (e) and (f) are more effective for high sulfide pyrite concentrates:

d. $FeS_2 + Fe \rightarrow 2FeS$
e. $4FeS_2 + 11O_2 + \text{heat} \rightarrow 2Fe_2O_3 + 8SO_2\uparrow$
f. $4FeS_2 + 10KNO_3 + \text{heat} \rightarrow 4FeO + 5\,K_2SO_4 + 5N_2 + 3SO_2\uparrow$

Roasting sulfides must be carefully controlled to avoid gold losses to volatilization (Strong and Murray-Smith 1974). Ores containing As, Sb, and Bi as sulfides require special treatment where they are partially oxidized. They must be carefully roasted, starting in a cool muffle furnace and raising the temperature slowly to 650°C and maintaining for 2 hours. In the case of As, the sample must be oxidized only to the trivalent state and not all the way to its pentavalent state. If pentavalent arsenic forms, it will combine with iron to form arsenates, or speiss. Speiss compounds can occlude gold with subsequent losses. Speiss arsenates must be eliminated before progressing to the fusion process. To remove pentavalent speiss arsenate, the sample is roasted again under reducing conditions with carbon to reduce pentavalent to trivalent arsenic where it is volatilized. Samples containing chlorides must not be roasted. Substantial gold losses may occur through volatilization when 10% or more of sodium chloride is present (Young 1980).

The ultimate goal of a proper fusion is to produce a lead button of consistent mass containing all the precious metal, none of the non-precious metals, and separates easily from a highly fluid slag. A lead button weight of approximately 28 g is ideal, although in the range of 25–35 g is acceptable. A button too small may not have collected all the precious metal. Too large a lead button could result in losses during the subsequent cupellation step. A larger lead button, while a waste of lead, is preferable to a button too small, since it may be scorified (see the "Fusion" section later in this chapter) to reduce base metals.

One must determine the reducing or oxidizing power of an ore or other metallurgical material and whether it is acidic, basic, or neutral. The reducing power is the amount of lead that 1 g of sample will reduce when fused when excess lead is available. The oxidizing power is the opposite, the amount of lead that 1 g of sample will oxidize during fusion.

Determining the Reducing or Oxidizing Power of Test Material

Visual examination. Visual examination of the ore as received is often a quick and reliable method of approximating the mineral composition of a sample for an experienced assayer. To understand the composition of the material, beginner assayers must also review the ICP elemental analysis, carbon/sulfur results, X-ray diffraction (XRD) report, and discuss the ore composition with a mineralogist or metallurgist.

Vanning. Vanning is a less common way of classifying an ore using a rapid technique to determine the minerals present when Leco sulfur or ICP analysis is not available. Vanning, applied with a few variations between laboratories, consists of taking 0.5–1 g of the ground sample with a spatula and placing it in a porcelain dish. The sample is moistened with a few drops of water and stirred with a glass rod. Two to three drops of 1:1 HCl are added. Any effervescence is generally due to evolution of CO_2. When effervescence stops, more drops of HCl are added, and any additional effervescence is noted. 1:1 HCl addition is continued until effervescence ceases. While a small fume extractor is recommended, an odor of hydrogen sulfide (H_2S) during vanning suggests sulfides are present and is particularly characteristic of sphalerite. Many sulfides, including pyrite, do not give an odor. Sulfides reduce litharge, and therefore, their presence and amount should be known so that the proper flux components can be selected. A few drops of 10% HNO_3 are then added. Brown fumes of nitrogen oxides (NOx) indicate the presence of sulfides. With practice and experience, the amount of carbonate and sulfide in the sample can be estimated rather closely; this amount determines how much of each flux component should be used. These acid tests are often used in conjunction with a Leco total sulfur and carbon, and carbonate calculation and an ICP-OES analysis to establish the presence of carbonate or sulfide minerals.

Preliminary fusion. A preliminary fusion is first undertaken using the following charge mixed in a small crucible: 2 g ore, 10 g sodium carbonate, 46 g lead oxide, 3 g silica, and 1 g $Na_2B_4O_7$ and the resulting lead button is weighed to determine the reducing power. If, for example, the resulting lead button weighs 10 g, then the reducing power is determined:

$$\text{reducing power} = \frac{\text{Pb button weight}}{\text{sample weight}} = \frac{10\text{ g}}{2\text{ g}} = 5$$

Using a half-assay ton (~15 g) as a sample size, one can calculate the amount of niter (KNO_3) required to add to the charge to oxidize the sample in order to achieve a lead button 28–30 g. From Table 5 the oxidizing power of niter is 4.2.

total reducing effect of ore =

sample weight(g) × reducing power = 15 g × 5	= 75 g Pb
lead button target weight	= 28 g Pb
difference, ore equivalent that must be oxidized by niter	= 47 g Pb
1 g of niter oxidizes (Table 5)	= 4.2 g Pb
niter required = 47/4.2	= 11.2 g niter

Flux components. A general flux usually consists of the following four reagents: litharge (PbO), sodium carbonate (Na_2CO_3), borax ($Na_2B_4O_7$), and silica (SiO_2). Other components are added as needed.

Table 5 Approximate reducing power or oxidizing power of some common minerals and reagents

Mineral or Reagent	Reducing Power	Oxidizing Power
Carbon/charcoal, C	18–30	—
Sugar	14.5	—
Cornstarch	11.5–13	
Pyrite, FeS_2	11	—
Flour	10–11	—
Pyrrhotite, FeS	9	—
Argol (potassium tartrate)	8–12	—
Chalcopyrite, $CuFeS_2$	8	—
Sphalerite, ZnS	8	—
Arsenopyrite, FeAsS	7	—
Stibnite, Sb_2S_3	7	—
Chalcocite, Cu_2S	5	—
Cream of tartar	4.5–4.6	—
Metallic iron, Fe	4–6	—
Galena, PbS	3.4	—
Niter, KNO_3	—	4.2
Pyrolusite, MnO_2	—	2.4
Hematite, Fe_2O_3	—	1.3
Magnetite, Fe_3O_4	—	0.9
Magnetite-ilmenite	—	0.4–0.6

Adapted from Hafty et al. 1977; Bugbee 1940

- **Litharge (PbO)** is also a strong basic flux to react with metallic oxides. It acts as an oxidizing and desulfurizing agent. Together with the addition of flour, it is reduced to metallic lead and collector for precious metals. It is, by far, the most expensive consumable component of the fire assay and must be disposed as a hazardous waste. Litharge should always be tested for impurities. Red granular litharge is preferred over yellow finely powdered litharge from a safety and hygiene aspect because dust is less of a problem.
- **Sodium carbonate or soda ash (Na_2CO_3)** is a powerful basic flux that is usually the principal component of fire assay flux. It reacts with silicates to form alkali glassy slag.
- **Borax (anhydrous sodium tetraborate, $Na_2B_4O_7$)** is an acidic flux component that lowers the fusing point of all flux materials. It forms fusible complexes with limestone and magnesite. It is often used as a cover over the fluxed material to minimize losses due to dusting or overflow. It also protects the crucible from flux attack. Too much borax is detrimental in acidic ores, causing difficulty in separating slag from lead phases.
- **Silica (SiO_2)** is the strongest acid component of the flux and combines with metal oxides to form silicates, the primary component of almost all slags. It also provides an acid constituent for basic ores and protects the crucible from the corrosive action of litharge.
- **Calcium fluoride (CaF_2)** increases the fluidity and is used especially for high-grade aluminum-bearing samples, as much as 8 g. Other samples not necessarily containing high aluminum but requiring an excessive amount (4 g or more) of CaF_2 are black sands, magnetite, and calcium phosphate (bone ash).

Table 6 Suggested grams of flux per 15-g sample

Sample Composition	Na_2CO_3	PbO	SiO_2	$Na_2B_4O_7$	CaF_2	Flour	KNO_3
Basic and ultra-basic rocks, including mineralized basic rocks. Also used for silicates where the Fe and Mg are each 5%–10% or more.	30	35	4	35	1	3.2	0
Quartzite, high silicates	20	50	1	3	0	2.8	0
Copper concentrate	20	100	10	5	1	0	7.5
Pyrite concentrate	30	60	12	10	0	0	30

- **Reducing agent (flour, cornmeal, carbon)** is required to reduce PbO to Pb metal evolving CO and CO_2.
- **Niter (potassium nitrate, KNO_3)** is a strong oxidizing agent. It melts at 334°C, but at a higher temperature it expels oxygen, which oxidizes sulfur, carbon, and many of the metals. The reducing power of the ore must be calculated because excessive amounts of niter may cause excess silver loss and boiling-over of the charge.
- **Inquart metal.** Silver, in the form of either silver nitrate or silver prills, is most commonly added in very quantitative amounts. A few milligrams of silver is "inquarted" into the crucible prior to fusion to protect from gold losses, to aid in handling the precious metal bead, and to facilitate parting of silver and gold following cupellation. The ratio of silver to gold should be about 3:1. Other metals (e.g., palladium and gold) are also used as inquarts to improve silver or other PGM recoveries.
- **Other metal collectors.** In addition to lead, other metals may be used, particularly for collection of PGMs. Nickel sulfide is used for PGMs because all six PGMs are collected and the fusion temperature is lower. The disadvantage is that gold recovery is not as good as with lead. Other collector metals include tin, copper, and iron, but these are not as effective as lead for gold. Silver, platinum, and palladium are good collectors but uneconomical.

In-depth flux calculations for all material types are beyond the scope of this chapter and are covered in other sources (Shepard and Dietrich 1940; Lenahan and Murray-Smith 2001; Bugbee 1940; Hafty et al. 1977). Table 6 lists a few common metallurgical types of samples and appropriate ratios of flux components for a half-assay ton.

Fusion

Crucible Fusion

Once the charge is mixed well, the crucible is loaded into a fusion furnace initially set at about 800°C and finishing at 1,100°C for about 1 hour when slag is thoroughly fluid. The lower start temperature prevents rapid CO_2 evolution. The crucible contents are poured into a conical mold or the slag onto a metal table and the lead into a button mold. After cooling, the slag is discarded and the lead button is pounded into a cube shape to simplify moving with tongs and to remove adhering slag particles.

Scorification Fusion

If the lead button is brittle, residual sulfur and base metals may still be present, which will impact cupellation losses. The brittle lead button must be scorified to remove sulfur and base metals. Scorification is an oxidizing fusion carried out in a shallow fire-clay dish called a scorifier. The button is placed in the scorifier with test lead, borax, and sometimes silica. The dish is placed in the furnace under appropriate conditions for scorification to take place. Scorification may also be performed instead of a crucible fusion but is limited to very small sample sizes.

Cupellation

Cupellation is the separation of precious metals from lead. The lead button is placed in a preheated cupel. A cupel is a porous vessel made most commonly of bone ash or magnesia. Under proper temperature conditions, the lead oxidizes to PbO. The molten PbO is absorbed by the cupel. One to two percent of the PbO volatilizes and is captured in a baghouse. Precious metals are not absorbed and a small precious metal bead, also referred to as the doré, remains in the cupel. Cupels should weigh about one-third more than the lead button.

Once cupellation begins and the buttons appear to have melted, the furnace door is cracked open to allow air to flow over the cupels. Very pure lead requires a cupellation temperature of 850°C and impure lead requires higher temperatures of 1,000°C. The rate of cupellation should be about 1 minute per gram of lead. Crystals of litharge resembling feathers on the sides of the cupel are an indication of correct cupellation temperature. The temperature is increased by 100°C toward the end to drive off the last of the lead. Experience is required to recognize brightening and other signals indicating completion of cupellation.

Cupellation losses are inherent in the cupellation process. There is always some loss of gold but not as much as silver. Temperature is the most important factor influencing precious metal losses. Losses are more pronounced when the temperature is too high or when the lead button is too large and cupellation goes on too long. Silver is added to protect against gold losses. Impurities including As, Sb, Se, Bi, Te, Tl, and especially Cu interfere and must be removed by scorification prior to cupellation. Extensive discussion of approaches to minimize losses may be found in fire assay texts (Bugbee 1940; Shepard and Dietrich 1940).

Parting

Parting is the separation of silver from gold alloys by dissolution of silver in hot, dilute nitric acid. Less common are the few special methods that use sulfuric acid. Acids must be free from any form of chlorides, as they tend to precipitate the dissolved silver or even combine with the nitric acid to dissolve gold. (This is not a problem if instrumental finish is used.) Either of these reactions would adversely affect the outcome of the gravimetric finish assay. The most frequent strength of nitric acid used ranges from a ratio of 1:4 to 1:8 parts acid to water. If the parting is incomplete, it is likely due to the incorrect ratio of silver to gold. The ratio of silver to gold must be about 3:1. Too much silver causes the bead to break into pieces and losses are likely, while too little silver will mean parting may be incomplete. In many determinations, a secondary parting using a stronger acid is needed to ensure a complete separation of the silver–gold alloy. The completion of the parting process is indicated when the evolution of nitrogen oxide gas bubbles has ceased. At this time, the presence of platinum may be evident by a brown-colored solution, while the presence of palladium is indicated by a distinctive orange color.

Finish

The finish is usually determined by the grade of precious metals present in the final bead after parting. A large bead will be by a gravimetric finish, while small beads will be digested and follow an instrumental finish for lower detection.

Gravimetric Finish

The gold that remains after parting in dilute nitric acid is black in color or is a large, brassy mass. Annealing the gold in a muffle furnace at 700°C for 5 minutes changes it to the more familiar gold color. This also avoids the possible effect of absorbed gases, preventing added weight other than gold. The final bead is weighed on a microbalance accurate to 0.000001 g (1 µg). Gravimetric finish is suggested for gold concentrations >5 ppm and always for bullion analysis. There is a possibility of other metals (e.g., Ag, Pb, Pt, and other PGMs) interfering with the final weight.

Instrumental Finish

The doré bead is cleaned, pounded flat, and placed in a test tube. One mL of 1:1 dilute HNO_3 is added and test tube is heated in a water bath at 80°C for 15 minutes to dissolve Ag. The gold bead remaining is then dissolved in the same test tube by adding 1 mL of concentrated HCl in a water bath at 80°C. After 15 minutes, 8 mL water is added for a final total volume of 10 mL. Silver chloride solids are separated by centrifuging. The solution is read using AAS or ICP-OES. Measuring metals in solution by AA or ICP-OES only measures the element of interest. Instrumental finish is recommended for gold concentrations <5 ppm or when other metals are suspected to be present. The AA finish has an approximately 10× lower reporting limit than the gravimetric finish.

Screen Fire Assay

Screen fire assay should be performed when apparent coarse particulate gold causes poor reproducibility between same samples or when the concentration of gold is greater than 15 ppm and very accurate results are required. The sample preparation requires significantly more time to complete. One kilogram of sample is screened through a 200-mesh (75-µm) screen. Screen size may vary depending on gold particle size. The weights of each fraction are recorded. The oversize portion contains the coarse gold and is assayed in its entirety. The undersize fraction is rotary split and portions are assayed in duplicate. The assay results are multiplied by the weight fraction of each and added together. A gravimetric finish is typically used.

Gold and other precious metals may be by-products associated with other industrial metal products such as those related to aluminum, bismuth, cadmium, chromium, copper, indium, iron, lead, molybdenum, nickel, palladium, platinum, rhodium, silicon, silver, tantalum, tin, titanium, tungsten, vanadium, and zinc. Appropriate analytical procedures for measurement of precious metals and impurities may be found in standard reference books (Dillon 1955; Furman 1962; (Young 1971).

ELEMENTAL PHASES AND DIAGNOSTIC TESTING BY CHEMICAL DISSOLUTION

Chemical phase analysis determines, by chemical dissolution, a characteristic of an element within a rock or ore. That characteristic might be its oxidation state or a separation of an element associated with a particular mineral. Diagnosing the phase of an element is of interest in hydrometallurgical process optimization and plant design. Sometimes called hydrogeometallurgy, chemical phase analyses are not a replacement for full mineralogical evaluations but offer quick, inexpensive, qualitative results for testing many samples. They are seldom quantitative because of partial solubility of other minerals within the same material. The key to meaningful results is performing these analyses under consistent and reproducible conditions (e.g., leach time, temperature, agitation speed, leach concentration, solid-to-liquid ratio, and particle size).

Gold Diagnostic Testing

Gold by fire assay is the preferred method of analysis for total gold concentration. However, process development and ore control may require other gold leaching tests.

Cyanide-Soluble Gold

Cyanide-soluble gold (AuCN) is the amount of gold soluble in a defined concentration of cyanide. The ratio of cyanide-soluble gold to total gold by fire assay, often referred to as the "cyanide-to-fire ratio," is an important parameter in process development and in ore control. Results from the AuCN procedure is an indicator of non-refractory gold that is amenable to cyanide leaching and is not a predictor of actual deposit Au recovery. For assay results of Au >0.1 ppm, cyanide-soluble gold (AuCN) may be determined by measuring the Au soluble in 30 mL of 0.3% NaCN and 0.3% NaOH solution (or another agreed-upon concentration) mixed for 1 hour at room temperature using 15 g or more of finely ground sample. The result will give an indication of leaching difficulty due to several factors that may include the presence of sulfides, large particulate Au, preg-robbing organic carbon or clay content. Samples containing particulate gold will require averaging of replicates and larger sample sizes and cyanide leachate volumes. Strong cyanide leaching (>3% sodium cyanide solution) is used for testing of material from deposits found to contain free gold >50 µm and some Cu/Au deposits during early stage development. Stronger cyanide (3% NaCN [sodium cyanide] plus 1% NaOH [sodium hydroxide]) is required to appropriately characterize the Au. This test is for characterization of non-refractory free Au and is not a predictor of actual Au extraction.

Preg-Robbing Cyanide

Preg-robbing analysis in cyanide is a diagnostic test for estimating the preg-robbing characteristic for gold (AuPR). It is identical to the AuCN test but also contains a gold spike. The spike concentration of 3.4 ppm (0.10 opt [ounces per ton]) is commonly used. The AuPR index, which is calculated using the AuCN and AuPR assays, typically applies to any deposit containing organic carbon. The cyanide concentration used in the AuPR must match the cyanide concentration in the AuCN test. The degree of preg-robbing is determined by a preg-robbing index (PRI). Preg-robbing may also be expressed as a spike recovery percentage.

Table 7 Selective pretreatment leach stages and the minerals destroyed

Pretreatment Stage	Minerals Likely To Be Destroyed
1. NaCN washes	Precipitated gold
2. NaCN	Gold
3. Na_2CO_3	Gypsum and arsenates
4. HCl	Pyrrhotite, calcite, dolomite, galena, goethite, calcium carbonate
5. HCl/$SnC1_2$	Calcine, hematite, ferrites
6. H_2SO_4	Uraninite, sphalerite, labile copper sulfides, labile base metal sulfides, labile pyrite
7. $FeCl_3$	Sphalerite, galena, labile sulfides, tetrahedrite, sulfide concentrates
8. HNO_3	Pyrite, arsenopyrite, marcasite
9. Oxalic acid washes	Oxide coatings
10. HF	Silicates
11. Acetonitrile elution	Gold adsorbed on carbon, kerogen, coal

Source: Lorenzen 1995

- PRI = 3.4 (spike solution) + AuCN – AuPR
- If PRI = 0, material is non-preg-robbing
- If PRI > 3, material is extremely preg-robbing

Bulk Gold Diagnostic Testing

Bulk Au diagnostic testing is performed when Au mineral associations are unknown and troubleshooting a process requires knowledge of gold deportment. Detailed diagnostic testing is performed on a large sample (0.5–1 kg). The sample is chemically treated to liberate Au associated with various mineral phases (Table 7). All the mentioned pretreatment stages can be varied according to the matrix of the material. Temperature, potential, concentration, treating time, and so on, play a major role in the selection of the desired pretreatment stage. Details are thoroughly discussed in Tumilty and Schmidt (1986) and Lorenzen (1995).

Copper Mineral Phases

Total Cu >0.02% is leached to estimate its behavior under metallurgical processes. Unlike total Cu, partial digestions have a much higher degree of error. Consistency is the key to useful data for estimating Cu mineral variability. Stronger leach solution, aggressive agitation, leach temperature, agitation time, and particle size are all variables that affect results. These mineral-selective leaches are run in sequence on a single sample to semiquantitatively identify the potential recovery by various copper ore processing methods. The actual amount of each mineral dissolved in each leach may vary, depending on the sample mineralogy, grain size, and other physical characteristics. Detailed differences between laboratories must be agreed upon before analysis and meticulously documented. Cu mineral assumptions should be confirmed with scanning electron microscopy (SEM).

Acid-Soluble Copper (CuAS) Test

Ore is typically leached with weak sulfuric acid (100 g/L) for 1 hour at room temperature. CuAS estimates easily leachable oxidized copper minerals such as malachite, azurite, chrysocolla, and portions of cuprite and tenorite as well as “acid-soluble” content of copper in secondary copper sulfides as a result of ferric iron oxidation. If the purpose is to differentiate oxide copper from sulfidic copper in a float process, then the copper oxide (CuOX) test is more appropriate. In this case, ferric iron is chemically reduced to ferrous to prevent oxidation. Addition of citric acid minimizes oxidation of chalcocite from Fe(III).

Copper Oxide (CuOX) Test

Ore is leached with weak sulfuric acid plus a reducing agent (100 g/L H_2SO_4 + 15 g/L sodium sulfite) for 1 hour at room temperature. CuOX is reported since the ferric iron is reduced to ferrous, and the copper from secondary sulfides is not leached. Alternatively, sulfurous acid may be used but is more costly.

Copper Quick Leach Test (CuQLT)

Ore is leached with weak sulfuric acid plus Fe(III) (100 g/L H_2SO_4 + 5 g/L ferric ion as sulfate) for 1 hour at room temperature. The CuQLT estimates easily leachable copper, such as in a dump leach, and includes oxide and some portion of copper secondary sulfides. The CuQLT has utility for bioleaching applications.

Cyanide-Soluble Copper (CuCN) Test

Ore is leached with a solution of 3% NaCN/3% NaOH for 1 hour at room temperature. Cyanide leach will dissolve the oxides (with the exception of chrysocolla, which is only partially digested), secondary sulfides including chalcocite and covellite, and most bornite and enargite. The chalcopyrite content in ores will remain largely undissolved. Cyanide consumption from copper minerals can be estimated.

Sequential Copper Leach (Cu-Seq) Test

This leach is a combination of CuAS, CuCN, and total Cu measured on a single sample aliquot sequentially. This is a special request assay used occasionally to estimate copper minerals present.

Water-Soluble Copper (CuWS) Test

With this method, copper ore is leached in deionized water. This is sometimes used in conjunction with other copper leaches, including EDTA (ethylenediaminetetraacetic acid) as a leach reagent, for characterizing oxidized ore (i.e., stockpiled ore) to understand low recovery or potential environmental impacts.

Sulfur and Carbon Phases

Total carbon and sulfur are first measured on combustion infrared analyzers. A second aliquot of the same sample undergoes a leach, or roast, and the residue is again measured for sulfur and carbon on the combustion infrared analyzers. The leach solution and/or the roast temperature depend on the sulfur mineral, and a knowledge of mineralogy is required to make the best decision. Table 8 summarizes sulfur-phase methods, assumptions, and mineral interferences for each method.

Sulfur Phases

Sulfide sulfur and sulfate sulfur are required on samples for both metallurgical process selection and environmental assessments, such as acid generation potential estimation. Determination of sulfide sulfur can be challenging and a variety of methods are used by different laboratories. It may be measured directly or through subtraction of sulfate sulfur from total sulfur.

Table 8 Sulfide sulfur assay procedure mapping

Assays	Procedure	Assumption of Method	Minerals Determined	Minerals Interference
S(total)	Leco	All sulfur is converted to gas and measured	All sulfur minerals	No interference
Sulfide sulfur	Method A	SS=SCIS	Refer to SCIS	
	Method B	SS=SCIS/HCl	Refer to SCIS/HCl	
	Method C	SS=S(tot)-SAP 550°C	Refer to SAP 550°C	
	Method D	SS=S(tot)-SAP 650°C	Refer to SAP 650°C	
	Method E	SS=SAI	Refer to SAI	
	Method F	SS=SAICONC	Refer to SAICONC	
Sulfate sulfur	Method G	SO$_4$=S(tot)-SCIS	Refer to SCIS	
	Method H	SO$_4$=S(tot)-SCIS/HCl	Refer to SCIS/HCl	
	Method I	SO$_4$=SAP 550°C	Refer to SAP 550°C	
	Method J	SO$_4$=SAP 650°C	Refer to SAP 650°C	
	Method K	SO$_4$=S(tot)-SAI	Refer to SAI	
	Method L	SO$_4$=S(tot)-SAICONC	Refer to SAICONC	
SCIS	Sodium carbonate digestion, filter/Leco sulfide	Sulfate dissolves and sulfides remain.	Sulfur contained in pyrite, pyrrhotite, marcasite, and base metal sulfide minerals measured as sulfide	Barite, alunite, and lead sulfate do not fully dissolve, resulting in high-sulfide results. Orpiment and realgar dissolve, resulting in low-sulfide results.
SCIS/HCl	Sodium carbonate digestion, filter, dissolved arsenic sulfides precipitated with HCl, filter/Leco sulfide	Sulfate minerals and orpiment and realgar dissolve, sulfides filtered, orpiment and realgar are re-precipitated during acidification and filtered.	Sulfur contained in pyrite, pyrrhotite, marcasite, orpiment and realgar, and base metal sulfide minerals measured as sulfide	Barite, alunite, and lead sulfate do not fully dissolve, resulting in high-sulfide results.
SAP 550°C	Pyrolysis at 550°C/Leco sulfate	Sulfides are lost, leaving sulfate.	Sulfur contained in pyrite, pyrrhotite, marcasite, and base metals—except copper, lead, and zinc—are volatilized, sulfate remaining measured	Carbonate minerals adsorb sulfur dioxide, resulting in high-sulfate results. Copper minerals are not volatilized, giving high-sulfate results. Jarosite may be partially lost, resulting in low-sulfate results.
SAP 650°C	Pyrolysis at 650°C/Leco sulfate	Sulfides are lost, leaving sulfate.	Sulfur contained in pyrite, pyrrhotite, marcasite, and base metal sulfide minerals are volatilized. Remaining sulfate is measured.	Carbonate minerals and lime adsorb sulfur dioxide, resulting in high-sulfate results. Jarosite may be partially lost, resulting in low-sulfate results.
SAI	HCl digestion, filter/Leco sulfide	Sulfates are dissolved; sulfides remain.	Pyrite, marcasite, and base metal sulfides measured as sulfide in residue	Pyrrhotite dissolves in acid, leading to low-sulfide results. Barite, alunite, and lead sulfate are not fully dissolved, leading to high-sulfide results.
SAICONC	Strong HCl digestion, filter/Leco	Sulfates are dissolved; sulfides remain.	Pyrite, marcasite, and base metal sulfides	Pyrrhotite dissolves in acid, leading to low-sulfide results. Barite, alunite, and lead sulfate are more fully dissolved, leading to improved sulfide results.
Elemental S <5%	Chloroform/ultraviolet-visible	Elemental sulfur dissolves and is measured in solution.	Elemental sulfur	Elemental S ≥5% will not dissolve in chloroform. Smaller weight can improve results.
Elemental S ≥5%	Carbon disulfide/gravimetric	Elemental sulfur dissolves and is measured in solution residue.	Elemental sulfur	Elemental S <5% poor precision.

HCl = hydrochloric acid
SAI = sulfur-hydrochloric acid–insoluble
SAICONC = sulfur-strong acid–insoluble after digestion (represents sulfide in a concentrate)
SAP = sulfur after pyrolysis
SCIS = sodium carbonate–insoluble sulfur (represents sulfide sulfur in most cases)
SS = sulfide sulfur

If a roast, or pyrolysis, technique is selected for measuring sulfate sulfur, it may be determined by roasting to drive off sulfide sulfur and then measuring the residue, also referred to as sulfur after pyrolysis. The temperature used to roast sulfides must be agreed upon prior to analysis and documented since 550°C is used for estimation of acid generation potential from pyrite while 650°C is used for total sulfide estimation (ASTM E1915 2013). Another approach to determining sulfide sulfur is to hot leach the soluble sulfates with dilute sodium carbonate or dilute HCl to report sodium carbonate–insoluble sulfur or hydrochloric acid–insoluble sulfur. The sulfide residue is washed, dried, and measured on the combustion infrared analyzer. XRD analysis should be completed before selecting an appropriate method since sulfide sulfur can be overstated or understated, depending on which sulfur-bearing minerals are present. Common interfering minerals for selecting a sulfide sulfur method are alunite, barite, jarosite, orpiment, realgar, pyrrhotite, and carbonates. See Table 8 to determine the most appropriate method for determination of sulfide sulfur.

Elemental sulfur or native sulfur is occasionally present naturally in some ores or is a product of a metallurgical process. If elemental sulfur is present in amounts >0.01%, the assumptions in Table 8 are invalid and will require discussion of appropriate sulfide determination with a project metallurgist. Elemental sulfur is considered to be a potentially acid-generating mineral for stockpile and waste rock characterization.

Carbon Phases

Organic and inorganic carbon are of interest in gold process development. Organic carbon, also called acid-insoluble carbon (CAI), is determined by hot leaching a sample with dilute HCl, driving off CO_2, and measuring the residue by combustion infrared analysis. Organic carbon is detrimental in the gold cyanide extraction process and CAI may be used to predict preg-robbing potential of an ore. CAI analysis may also include non-preg-robbing graphitic carbon and is correlated with the preg-robbing index to be certain. Graphitic carbon may be determined by roasting followed by an HCl wash. Graphitic carbon is also separated using thermogravimetric analysis. CAI subtracted from total carbon represents inorganic carbon (carbonate carbon) and is used to estimate the acid neutralization potential in tailings from an environmental perspective.

Mineral Phases of Other Materials by Chemical Dissolution

Use of XRD, SEM, and other mineralogical tools simplify identification of mineral phases. However, when mineral identification instrumentation is unavailable, chemical methods for phase separation are still useful for hydrometallurgy and ore control. Full mineralogical assessment should be performed to validate chemical phase assumptions. A shortened list of lixiviants used for quick phase identification of elemental phases in multiple ore types is shown in Table 9. More detail of each is available in Steger (1976).

CLASSICAL WET CHEMICAL ANALYSES

Prior to about 1960, classical wet chemical analysis was the only means of determining the chemical composition of minerals. Such analyses were limited by the factors previously discussed in terms of sampling size, although techniques were developed for analyzing very small samples. It is important for the extractive metallurgical student to recognize that many hydrometallurgical processes (i.e., dissolution, separation, concentration, purification, and metal plating) involve chemical principles of oxidation, reduction, chelation, hydrolysis, and so on. These steps are also found in traditional analytical chemistry; thus, it is possible to regard hydrometallurgy as applied analytical chemistry with the only difference being the scale of the involved steps. The identification with analytical chemistry suggests that the solutions to the relevant industrial unit operations may be found in the procedures already developed by analytical chemists.

Wet chemical analyses always involve dissolving the mineral into a solution. In order for the dissolution to take place completely, the mineral is usually first ground into a fine powder (to increase surface area) and the appropriate solvent must be used. Wet chemical analysis can be classified into three types: gravimetric, volumetric, and colorimetric.

Gravimetric Analysis

Gravimetric analysis is where the element of interest is precipitated as a compound. The precipitate is then weighed to determine its proportion in the original sample (e.g., $BaSO_4$ [barium sulfate] precipitation for sulfate measurement).

Volumetric Analysis

Volumetric analysis is a quantitative chemical analysis that is used to determine an unknown concentration of an analyte. A titrant is prepared as a standard solution. A known concentration and volume of titrant reacts with a solution of analyte. The volume of titrant reacted is recorded and the concentration of unknown is calculated. Following are common titrations routinely used in an analytical laboratory on metallurgical samples:

- Silver nitrate titration for free cyanide, where Ag forms the $Ag(CN)_2^-$ complex. Another example is silver nitrate titration for free chloride where Ag^+ and Cl^- are precipitated together as silver chloride (AgCl). A silver electrode measures the change in potential in both titrations.
- Short iodide titration is a very accurate method for determining Cu in copper concentrates for settlement between shipper and buyer. Cu is first dissolved in mixed acid. Cu(III) oxidizes potassium iodide (KI) to I_2. Sodium thiosulfate ($Na_2S_2O_3$) is then used to titrate I_2, equaling the moles of Cu present.
- Dimethyl glyoxime precipitates nickel followed by titration with EDTA for settlement of Ni in nickel concentrates.
- Redox titration of Fe in iron ore by acid decomposition, followed by reduction with stannous chloride and then titration with an oxidant such as potassium dichromate.

Colorimetric Analysis

In colorimetric analysis, a reagent is added to the solution that reacts with the element of interest to produce a color change in the solution. The intensity of the color is proportional to the concentration of the element of interest, and thus, when compared to standard solutions in which the concentration is known, the concentration of the element in the unknown solution can be determined (e.g., thiocyanate complexed with ferric iron).

Many classical wet chemical analyses require a skilled analytical chemist, and tests are usually very time-consuming and costly when performed for metal content on settlement material between buyer and seller. These types of testing are usually used only where extremely high precision and accuracy are required.

The high dollar value of concentrate and bullion shipments means that the regular analytical methods used for other stages of mineral resource development are not appropriate and classical wet chemical methods must be used. As an example, the splitting limit for %Cu in a copper concentrate is 0.15%–0.2%. This represents a requirement for less than 1% relative accuracy and precision in the analysis. As a result, the analytical procedures for these types of samples are much more rigorously controlled. To ensure that high accuracy and precision are obtained, the QC protocols are expanded. Four

Table 9 Chemical phase analysis of ores and rocks

Mineral Associated with ...	Treatment	Mineral Separation
Aluminum	Determined by rates of dissolution in KOH (potassium hydroxide)	Bauxite minerals, gibbsite, boehmite, and diaspore, and "available aluminum"
	NaOH + HCl	Gibbsite only
	Boiling (1:1) HCl	Aluminum phosphate minerals such as crandallite and millesite separated from kaolinite
Antimony	Tartaric acid	Antimony oxides separated from sulfides
Beryllium	3% HCl and roasting	Multiple beryllium minerals are separated
Bismuth	5% Thiourea solution in 0.5N H_2SO_4	Bismuth oxide minerals from other bismuth minerals
	0.1M Silver nitrate in 0.5–1.0M nitric acid	Native bismuth from other bismuth sulfide
Calcium	Sucrose solution	Free CaO is extractable from $Ca_3(PO_4)_2$, CaF_2, $CaCO_3$, and $CaSO_4$
	5%–10% acetic acid	Calcite, $CaCO_3$, can be selectively dissolved in the presence of fluorite, CaF_2
Copper	Dilute HCl in ethanol plus stannous chloride	Cuprite, Cu_2O, selectively extracted from ores that contain native copper and tenorite, CuO
	Ferric chloride in 3M HCl	Native Cu from tenorite
	(a) 1% Solution of unithiol in 5% HCl	Azurite, malachite, and cuprite from other Cu minerals
	(b) 2% Sodium sulfite in 3% H_2SO_4 after (a)	Chrysocolla from Cu sulfides
Germanium (in coal ash)	0.1M Ammonia	GeO_2 from other Ge minerals
Indium	Water	$In_2(SO_4)_3$
	3% Bromine solution in methanol	In_2S_3
	3M HCl	In_2O_3
Iron (in reduced ores)	Bromine in alcohol	Metallic Fe
Iron	HCl in an inert atmosphere, then ferrous titrated with dichromate	FeO and Fe_2O_3 in reduced iron ores (after metallic Fe removed)
	1% HCl in H_3PO_4 plus hydrogen peroxide	Magnetite separated from hematite
	Mixture of sulfuric and hydrofluoric acid or ammonium vanadate. Ferrous is titrated with permanganate.	Ferrous separated from ferric iron in rocks and ores
	Bromine in methanol	Pyrrhotite, chalcopyrite, and bornite extracted from pyrite
Lead	25% sodium chloride solution	Anglesite, $PbSO_4$
	15% Ammonium acetate solution in 3% acetic acid	Cerussite, $PbCO_3$
Manganese	6N Ammonium sulfate acidified with H_2SO_4 to pH 2	$MnCO_3$ separated from MnO_2
Molybdenum	20%–50% Ammonia solution	MoO_3 from roasted MoS_2
Nickel-cobalt	Ascorbic acid–hydrogen peroxide	Ni, Co, and Cu sulfide minerals in rocks
Tantalum-niobium	Mixture of HF and HCl at slightly elevated pressure	Pyrochlore and microlite from simpsonite
Uranium	5% Solution of tri-n-octylamine in xylene	U(VI) separated from U(IV)
Zinc	Boiling 5% acetic acid	Oxidized zinc from sphalerite

Adapted from Steger 1976

or six replicates are analyzed with matrix-matched certified reference samples. This ensures that no matrix-caused bias affects the analytical result.

The mineralogical makeup of the reference samples should be as similar to that of the samples as possible. Titer proofs (pure metals titrated along with samples to monitor the concentration of the titrating solution in instances of volumetric control assay work) can also be performed as one determination. It is important that the buyer or seller discusses all requirements with the analytical scientists to ensure that the data generated are adequate for their intended uses.

ANALYTICAL TESTING OF HYDROMETALLURGICAL SOLUTIONS

Controlling hydrometallurgical processes requires analysis of different streams of solvents. Leaching processes may include a variety of leaching reagents. The most commonly used leaching agents are sulfuric acid (Cu, Zn), sodium carbonate (U, V, Mo, W), sodium hydroxide (W), ammonia (Cu, Ni), cyanide and thiosulfate (Au, Ag), sulfite (Sb, Hg), and chlorine and chloride (PGMs and rare earth metals; Bazhko 2009). The elements of interest, the solvent itself, and often the degradation created from the solvent must be measured.

For the most accurate results, solvents containing elements of interest must first be digested to destroy the solvent, usually in aqua regia, before instrumental analysis. Measuring solvents directly by flame-AAS, ICP-OES, ICP-MS, while common practice, often causes erratic results because of solvent decomposition during sample introduction. XRF may sometimes be considered and does not require predigestion. Calibration standards must contain the same solvent and digestion matrix as the samples.

Analytes of interest are difficult to measure in matrices with large concentrations of other elements. Separating metals may be accomplished by precipitation or ligand complexation. Solvent extraction techniques have been developed for analytical purposes to separate elements. Chelating agents added to organic solvents, resins, or filter papers are used to preferentially separate trace elements from major interfering elements. Details of separating metals through chelation may be found in Rydberg et al. (2004).

Measuring ions in solution is necessary for a variety of reasons, including process control, cost estimation, and environmental assessment.

Instrumentation for Analytical Measurement of Hydrometallurgical Solutions

Ion Chromatography

Ion chromatography (IC) is a process used to separate ions into their constituents based on their affinities for column material. A common application is utilizing a conductivity detector to measure the response for Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^-. Detectors and columns may be customized for other anions or cations.

Discrete Analyzers

A discrete analyzer is an automated chemical analyzer that measures a chemical change in a discreet sample vial instead of a continuous flow. Measuring nitrite, nitrate, or ammonia/ammonium using colorimetric chemistry in process or wastewater is a common application.

Ion-Specific Electrode

A sensor converts the activity of a specific ion in a solution into an electrical potential. The voltage is dependent on the logarithm of the ionic activity, according to the Nernst equation. Common applications are pH, Cl^-, and F^-.

Continuous Flow Analysis

Continuous flow analysis, or similarly, flow injection analysis, is a process to measure ions in solution. A sample is injected into a flowing carrier solution passing rapidly through small-bore tubing. The sample is mixed with a reagent, which reacts to form a color or form a gas, as is the case in weak acid dissociable (WAD) cyanide measurement. The gas passes through a semipermeable membrane where an amperometric Ag electrode detector measures change compared to standard solutions.

Cyanide measurement. Flow injection analysis is used to measure cyanide complexes. Accounting for cyanide losses presents its own set of unique challenges. Reporting cyanide consumption is an important parameter for operational cost estimation of leaching, as well as the cost of detoxification of cyanide in tailings pond and mill water. Cyanide forms both strong and weakly bound complexes with transition and precious metals (Table 10). Measuring cyanide complexes and understanding the terminology for these complexes is necessary for gold process development. Cyanide is measured and reported as free WAD cyanide, or total cyanide, and includes the following:

free cyanide = CN^- and HCN

WAD cyanide = free cyanide + weak and moderately strong metal–cyanide complexes

total cyanide = free cyanide + WAD cyanide + strong metal–cyanide complexes

Table 10 Cyanide metal complexes

Free Cyanide	WAD Cyanide Weak and Moderately Strong Metal–Cyanide Complexes			Strong Metal–Cyanide Complexes
Not Complexed	Log β (stability constant) <30			Log β (stability constant) >30
HCN	$Ag(CN)_2^-$	$Cu(CN)_2^-$	$Ni(CN)^+$	$Au(CN)_2^-$
CN^-	$Ag(CN)_3^{-2}$	$Cu(CN)_3^{-2}$	$Ni(CN)_4^{-2}$	
		$Cu(CN)_4^{-2}$	$Ni(CN)_5^{-3}$	$Co(CN)_5^{-2}$
				$Co(CN)_6^{-3}$
	$Cd(CN)^+$	$Hg(CN)^+$	$Zn(CN)^+$	
	$Cd(CN)_3^-$	$Hg(CN)_2^0$	$Zn(CN)_3^-$	$Fe(CN)_6^{-3}$
	$Cd(CN)_4^{-2}$	$Hg(CN)_3^-$	$Zn(CN)_4^{-2}$	$Fe(CN)_6^{-4}$
		$Hg(CN)_4^{-2}$	$Zn(CN)_5^{-3}$	

Table 11 Analytical techniques for cyanide deportment analysis

Analyte	Technique
Free CN^-	Titration with silver nitrate or flow injection analysis
WAD CN^-	Flow injection analysis
Total CN^-	Flow injection analysis after ultraviolet digestion
Anions	Ion chromatography (NO_3^-, NO_2, Cl, F, SO_4, SCN^-, OCN^-, $SeCN^-$)
NH_4	Ion-specific electrode
OxySulfur	Ion chromatography (S_2O_3, S_4O_6, SO_3, S^{2-}, etc.)
Metals	ICP-OES for Ag, As, Ca, Cd, Co, Cu, Fe, Hg, Mo, Na, Ni, Se, Tl, Zn

"Total cyanide" analysis does not include oxidized forms of cyanide such as cyanate, thiocyanate, or selenocyanate. A complete cyanide deportment analysis is accomplished by measuring all cyanide complexes and oxidized cyanide decomposition products. A variety of ways exist to measure each component. The preferred methods are listed in Table 11.

Other environmental analytical testing. Extensive procedures and policies to ensure protection of the environment must be determined. Underground, open pit, and tailings can become unstable or hazardous over time as they weather and deteriorate. When stable un-oxidized material is exposed to the atmosphere, it can become reactive and hydrolyze, generating acid and potentially liberating toxic elements into the environment. Artificial leaching to simulate rainwater action is an example of short-term laboratory tests used to predict long-term models. Analytical testing for water balance and meeting discharge limits is also an important part of a process development plan. Details of acid–base accounting, tailings management, and testing procedures for predicting tailings reactivity are found in other chapters of this handbook.

DATA MANAGEMENT AND QUALITY

Laboratories using a laboratory information management system (LIMS) will be more efficient and organized, resulting in better quality of data. Analysts can dedicate more time to sample analysis and less to menial tasks. A LIMS speeds up the retrieval of information and includes other data such as analytical laboratory costs, data trends, outstanding work, and sample turnaround times. Transcription of data errors can be eliminated. Tracking the location of each sample and each sample movement effectively creates a chain of custody with time, date, and operator identification stamping. Storage location of each sample is known at any given time if additional analyses are added.

With few exceptions, instrumentation must be calibrated with a series of calibration standards traceable to a certified standard, within the expiration window, and their calibrations validated with a second source (different from the source used to prepare calibration standards). The laboratory must establish acceptability criteria for each analyte and determine appropriate wavelengths or mass, linear range, limit of quantification, limit of detection, correlation coefficients, and relative standard deviations, and determine frequency of measuring the continuing calibration verification and certified reference materials.

Limit of Detection

The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample that can be detected but not necessarily quantified as an exact value. One approach is to determine the signal-to-noise ratio by comparing measured signals from samples with known low concentrations of analyte with those of blank samples and by establishing the minimum concentration at which the analyte can be reliably detected. A signal-to-noise ratio of 3:1 is generally considered acceptable for estimating the detection limit. The limit of detection (LOD) must not be confused with method detection limit, a number higher than LOD, and takes into account variables such as the matrix of the actual sample, the instrumentation at a particular laboratory, skill level of staff, and chemicals used.

Limit of Quantification

Lower detection is achieved in a "clean" matrix but quantifying the same analyte in a solution with high TDS is a different story. The limit of quantification (LOQ) of an individual analytical procedure is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy in sample matrices of interest. Determination of the signal-to-noise ratio is performed by comparing measured signals from samples with known low concentrations of analyte with those of blank samples in similar matrix and by establishing the minimum concentration at which the analyte can be reliably quantified. A typical signal-to-noise ratio is 10:1.

Quality Control Checks

After instrument configuration and method development are complete, an ongoing quality program is followed, including insertion of internal QC checks. These are essential for continual assessment of analytical procedures. QC analyses include the use of blanks, internal standards, check standards, matrix spikes, duplicates, replicates, check samples, certified reference materials, initial calibration verification, and continuing calibration verification standards. The frequency of insertion of QC samples depends on how the data are used. Greenfield exploration samples will have less QC insertions than metallurgical accounting data. Participation in control charting and proficiency testing programs are also prudent and a requirement for accreditation.

ISO/IEC 17025 Accreditation

ISO 9001 (2015) is a management tool to evaluate quality systems but does not evaluate the technical competence of a laboratory and does not assure you or your customers that the test, inspection, or calibration data are accurate and reliable. International standard ISO/IEC 17025 (2005) is used for evaluating laboratories throughout the world. This standard specifically addresses factors relevant to a laboratory's ability to produce precise, accurate test and calibration data. It includes several components (e.g., technical competency of staff, validity and appropriateness of the methods, traceability of measurements and calibrations to certified standards, appropriate application of measurement uncertainty, calibration and maintenance of test equipment, sampling and handling of test items, quality assurance of test, inspections, and proficiency testing).

Analytical procedures used to analyze samples for metal accounting or commodities exchange should, where relevant, be accredited to the ISO/IEC 17025 (2005) standard. Accreditation boards have been established in most countries with significant mining and metallurgical operations. Accreditation is seen as a requirement for laboratories performing analyses on payable material such as concentrates that are part of a commercial transaction between a buyer and seller and for other materials that are part of a metal accounting system. To maintain accreditation, a laboratory's quality management system is thoroughly evaluated on a regular basis to ensure continued technical competence and compliance with ISO/IEC 17025 (2005). Accreditation improves the reputation and image of the laboratory. A laboratory may achieve accreditation for just a few methods of analysis. Achieving accreditation in a research laboratory with a large variety of test methods is a business decision and not necessarily a requirement for delivering high-quality data.

COSTS FOR ANALYTICAL TESTING

Building an analytical chemistry laboratory with a proper ventilation system and building code compliance is estimated to cost between US$388–US$430 per gross square foot (Gering 2015). Instrumentation and sample preparation equipment costs to support a *small* operation would add another US$1–US$2 million in capital. Table 12 lists a few pieces of common equipment used in the analytical laboratory with price ranges.

Operating expenses for an on-site laboratory include costs associated with labor, consumables, maintenance, utilities, waste management, and other miscellaneous items. Justification for building an on-site laboratory for a new operation must be weighed against many factors, including but not limited to the estimated mine life, distance to off-site laboratories, turnaround time requirements to meet the mine plan, and availability of skilled workers. Even with the relatively large expense of building and operating an on-site laboratory, the decision may be worth the investment. Babacan (2001) describes experiences at the Çayeli Bakir İşletmeleri A.S.

Table 12 Capital cost of common laboratory equipment

Common Laboratory Equipment	Range of Cost, US$, in thousands
Crusher/rotary splitter combination	60–80
AA	15–30
ICP-OES	75–120
ICP-MS	120–220
Leco C/S analyzer	50–70
Fire assay furnace	10–30
WDXRF	150–250

on-site laboratory in Turkey and demonstrated that a minesite analytical laboratory has a very high rate of return on investment and makes a great contribution to the operation and the community. The author strongly advised that a laboratory be established early in the life of any mining project.

Commercial laboratories, on the other hand, may be the only option in many cases. They publish list pricing for all services. Typical costs may include shipping, sample preparation, test preparation (e.g., digestion or fusion), instrumental measurement, and sample storage or shipping return. Other costs may include quarantine services for soils. Rush charges can be significant and may range from a 300% upcharge for one-day turnaround to a 100% upcharge for a less-than-two-week standard turnaround.

Analytical costs for a short-term metallurgical project can be a large portion of the overall budget. Estimating those project assay costs can be an arduous task and, in general, are directly proportional to the complexity of the ore. Table 13 lists many of the tests and current associated costs per sample required to characterize ore for a complex gold project using a commercial (ISO/IEC 17025 certified) analytical/geochemistry laboratory. Pricing for large amounts of analytical test work is usually negotiated.

SUGGESTED ANALYTICAL TESTING PLAN FOR COMMON COMMODITIES

Gold Ore

For the recommended analytical testing plan for gold ore, see Table 13.

Copper Ore

Following is the suggested analytical testing plan for copper ore:

- Full 62-element suite using 4-acid digestion and ICP-OES/ICP-MS: Ag, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Fe, Ga, Gd, Ge, Li, Mn, Mo, Ni, Pb, Re, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Zn
- Metaborate fusion for major analytes by XRF: Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, TiO_2
- Au by fire assay
- Acid-soluble copper
- Ferric sulfate–soluble copper
- Hg by combustion AAS
- F by carbonate fusion and ion-specific electrode
- Cl analysis
- C and S by Leco analysis
- Sulfide sulfur

Iron Ore

In world practice, no minimum standards have been set for iron, silica, alumina, calcium, and magnesium percentages in commercial iron ores, although certain generalizations can be made (Dobbins and Burnet 1982).

Total Fe in iron ore is measured in many ways. Titration with potassium dichromate following reduction is a common method. The iron ore is first digested in HCl. Stannous chloride, a strong reductant, is added slowly dropwise until the dark ferric color changes to a light ferrous yellow, indicating complete reduction of iron. Strong H_2SO_4 and H_3PO_4 (phosphoric acid) are added to prevent air oxidation. Ferrous iron is then titrated with standardized potassium dichromate using barium diphenylamine sulfonate indicator to a purple color. Ferrous Fe (FeO) is measured similarly but without the stannous chloride reduction.

Table 13 Analytical testing plan for a complex gold project with approximate cost per sample

Analytical Test	Description of Test	Approximate Cost per Sample, US$
Sample prep: drill core, rock, and chip samples	Crush to 70% less than 2 mm, riffle split off 1 kg, pulverize split to better than 85% passing 75 μm.	8.60 plus 0.75/kg
Specific gravity	Pycnometer reported as a ratio	12.25
Au—ore grade	Fire assay, 30 g, AA finish	16.60
Pt, Pd—ore grade	Fire assay, 30 g, ICP-MS finish	21.00
Cyanide-soluble Au, Ag, Cu	Cyanide leach, 30 g, AA finish	9.85 plus 4.90/element
Preg-robbing of Au	Au spike cyanide leach, 30 g, AA finish	11.00
Au on carbon	Au on carbon by ashing, aqua regia digestion, and AAS; duplicate analysis	39.25
Au and Ag in a concentrate	Au and Ag by fire assay and gravimetric finish, 30-g sample weight required	85.00
Au and Ag in bullion	Routine (non-umpire) bullion assays by fire assay with gravimetric finish	129.80
Multi-element analysis	33 Elements using 4-acid digestions, ICP-OES finish	20.85
Hg in ore	Acid digestion and ICP-AES	73.60
Paste pH	Paste pH on 10-g sample saturated with water	7.50
Whole rock analysis for use with mineralogy/XRD reporting	14-element package by lithium borate fusion and XRF	30.65
Total C and S	Total carbon and sulfur by Leco furnace	20.55
C (noncarbonate) and S (sulfide)	Organic carbon and sulfide sulfur by HCl (25%) leach of carbonates and sulfates, Leco furnace	27.45
Acid–base accounting for predicting tailings behavior	Nevada Bureau of Land Management's acid–base accounting requirements. Includes the Nevada modified Sobek neutralization potential (NP) method, the siderite-corrected NP method, total sulfur, and inorganic carbon.	216.15
Storage	Storage of samples after testing is complete	0.30/sample/month

Adapted from ALS 2017

*Extra costs for rotary splitting, cleaning between samples with silica sand, or handling extra-large samples.

Iron ore samples are also fused with $Na_2B_4O_7$ and the fused beads are measured by XRF. Major analytes of interest are Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2, LOI, and S as SO_3. Other impurities, Ba, Co, Cu, Mg, Mn, Ni, P, Pb, Ta, V, Zn, and Zr, are acid digested and run by ICP-OES. C and S are determined by high-temperature combustion with infrared detection. Chloride content is determined by a gravimetric method in accordance with internal testing procedures. The recommended limits are

- $Na_2O + K_2O < 0.8\%$,
- $Zn < 0.02\%$,

- $P < 0.04\%$, and
- Cd and $S < 0.01\%$.

Silica and alumina, as well as small amounts of sulfur and phosphorus in iron ore, have significant deleterious effects during processing and in the final properties of products. Mineralogical study using XRD and microstructure determination using SEM and/or FEG-SEM (field emission gun scanning electron microscopy) is prudent.

Coal and Coke

Following is the suggested analytical testing strategy for coal and coke:

- **Proximate and sulfur analysis.** The proximate and sulfur analysis is basic to all coal and coke evaluations. The proximate analysis consists of the following suite of tests: moisture, ash, volatile matter, and fixed carbon (by difference).
- **Ultimate analysis.** Coal is analyzed for the following as part of an evaluation for its use as a fuel: carbon, hydrogen, nitrogen, oxygen (by difference), ash, and sulfur.
- **Ash chemistry.** Major elements of coal or coke ash provide important information for blast furnace and coal utility operations. The following elements are typically tested: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O, P_2O_5, MnO_2, SO_3, BaO, SrO.
- **Trace elements analysis.** Trace elements analysis is critical to evaluating coals for environmental regulations. The following are often requested: As, B, Be, Cr, Hg, Pb, Se, V.

Uranium

Laboratories must be qualified and experienced in handling samples of naturally occurring radioactive material in the jurisdiction with active uranium exploration and mining. The recommended analytical testing plan for uranium is as follows:

- Full 62-element suite using 4-acid digestion and ICP-OES. Table 14 lists the typical specifications for uranium concentrates.
- Pb isotope analysis by aqua regia and ICP-MS.
- U by lithium borate fusion and XRF.
- Other radiometry tests as needed.

Clays, Limestones, and Dolomites

Following is the suggested analytical testing plan for the industrial minerals of clays, limestones, and dolomites:

- Samples are fused with $Na_2B_4O_7$ and the fused beads measured by XRF.
- Major analytes by XRF: Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, TiO_2.
- LOI at 1,000°C.

Rutile, Zircon, and Ilmenite

Following is the recommended analytical testing strategy for the industrial minerals of rutile, zircon, and ilmenite:

- Samples are fused with $Na_2B_4O_7$ and the fused beads measured by XRF.
- Major analytes by XRF: Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, Nb_2O_5, P_2O_5, SiO_2, SO_3, TiO_2, V_2O_5, ZrO_2 (add HfO for zircons).
- LOI of 1,000°C.

Table 14 Typical specifications for uranium concentrates*

Concentrate Composition	Maximum Impurities Permissible
Impurity	Weight percent based on the U_3O_8 content
Na	7.5
H_2O	5.0
SO_4	3.5
K	3.0
Th	2.0
Fe	1.0
Ca	1.0
Si	1.0
CO_3^{2-}	0.50
Mg	0.50
Zr	0.50
PO_4^{2-}	0.35
Cl, Br, I	0.25
V_2O_5	0.23
Rare earths	0.20
P	0.15
Mo	0.15
As	0.10
B	0.10
Extractable organic matter	0.10
Insoluble U	0.10
Ti	0.05
^{226}Ra	740 Bq/g (20,000 pCi/g)
Particle size	6.35 mm (¼ in.)

Source: IAEA 1992, reprinted with permission from IAEA.
*Minimum U_3O_8 content, with a partial size of 65%. Only natural uranium concentrates (nonirradiated material) containing 0.711 wt % of the isotope 235U are acceptable.

Nickel Laterites

The following plan is recommended for analytical testing of rare earths:

- Samples are fused with $Na_2B_4O_7$ and the fused beads measured by XRF.
- Major analytes by XRF: Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, TiO_2, V_2O_5.
- Major analytes by 4-acid digestion for As, Co, Cu, Ni, Pb, and Zn by ICP-OES.
- LOI at 1,000°C.
- Chloride by silver nitrate titration.
- C and S by Leco analysis.

Phosphate Rock

Fertilizer capabilities for phosphate rock include nutrients such as nitrogen, phosphates, and potassium. The following plan is recommended analytical testing of phosphate rock:

- Acid, insoluble
- Al, Ca, Cd, Fe, K, Mg, Na, P, SiO_2
- Water analysis (moisture content)
- Organic matter
- Carbonate fusion and ion-specific electrode for fluoride
- Forms of sulfur analysis
- ICP trace metals

- Specific gravity
- Total nitrogen analysis
- LOI at 1,000°C
- Total suspended solids
- Viscosity

Rare Earths

Following is the suggested analytical testing plan for rare earths:

- Samples are fused with $Na_2B_4O_7$ (or sodium peroxide) and the fused beads are measured by XRF.
- Major analytes by XRF: Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, TiO_2, V_2O_5.
- Minor analytes by XRF: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Th, U, Y. (The elements are recalculated as oxides and reported as such.)
- LOI at 1,000°C.

Bauxite

Lithium borate fusion followed by XRF is the industry-standard analytical method for bauxite analysis. Results are reported on a dry weight (110°C) basis. The suggested analytical testing plan for bauxite is as follows:

- Fused-disc XRF
- Major analytes by XRF: Al_2O_3, Fe_2O_3, SiO_2, TiO_2
- Minor analytes BaO, CaO, Cr_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SO_3, SrO, V_2O_5, Zn, ZrO_2
- Total organic carbon
- Reactive silica
- Available alumina
- Multiscreen sizing to determine the optimum screen size for recovery and subsequent wet beneficiation
- Hot hydroxide leach for soluble Al by ICP-OES
- Sodium oxalate leach for measuring organic carbon contaminants by ion chromatography
- LOI at 1,000°C

For reporting, bauxite = $Al_2O_3 + SiO_2 + Fe_2O_3 + TiO_2$ + LOI + trace elements.

Lithium

Lithium-hosted minerals, pegamites and jardites, as well as lithium-bearing clays and sediments can co-occur with economic grades of rare earth elements and other rare metals such as cesium and rubidium. Li in sedimentary rocks dissolves easily in aqua regia and may be a simpler approach when other analytes are not of interest. Li is not typically determined by XRF because it is such a light element. The suggested analytical testing plan for lithium is as follows:

- Samples are fused in sodium peroxide and measured for multi-elements on ICP-OES and ICP-MS.
- Major and minor analytes are measured by ICP-OES and/or ICP-MS (depending on concentration): Ag, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Ho, In, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Re, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, and Zn.

If material has been determined to contain rare earth elements or other economic elements, further analytical testing of major analytes is appropriate. Samples are fused with sodium peroxide, and analytes are measured by ICP-OES: Al_2O_3, As, B, CaO, Co, Cr_2O_3, Cu, Fe_2O_3, K_2O, Li, MgO, MnO, Na_2O, Ni, Pb, S, SiO_2, TiO_2, and Zn.

Lithium Brine Analysis

Lithium brines have their own unique set of analytical difficulties due to viscosity and because Li is such a light element surrounded by much heavier elements. The suggested analysis for lithium brine is as follows:

- Slurries are digested with aqua regia and measured by ICP-OES and ICP-MS.
- ICP-OES analytes include Al, As, B, Ba, Ca, Co, Cr, Cs, Fe, K, Li, Na, Ni, Mg, Mn, Na, P, Pb, S, Sc, Se, Sr, Ti, V, and Zn.
- ICP-MS analytes include Br, Cs, I, and Rb.
- Cl by silver nitrate titration
- F by ion-specific electrode
- PO_4 (phosphate) and NO_3 (nitrate) by colorimetric method
- pH
- Conductivity
- Total dissolved solids
- Sulfate (calculated from S)
- HCO_3 (bicarbonate) and NH_4 (ammonium) by volumetric method

Potash

Potash ores are used primarily in the fertilizer industry but also in various chemical applications in different potassium forms. Most potassium forms are water soluble but major impurities are not. XRF is suggested for total analysis of major analytes. Following is the suggested analytical testing plan for potash:

- Samples are fused with lithium metaborate fused-disc XRF.
- Major analytes by XRF: Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, SrO, TiO_2
- Additional 4-acid digestion for penalty elements, As, Cd, Ce, Cr, La, Pb, Se, Sm, Th, U, Y, Yb
- Combustion analyzer for Hg
- Carbonate fusion and ion-specific electrode for F
- Chloride by silver nitrate titration
- Color, visual
- Moisture content
- Particle hardness
- pH
- Potassium content (K_2O, KCl)
- Screening
- Forms of sulfur
- Water residues (water-insoluble matter)
- LOI at 1,000°C

Chromite and Manganese Ores

The extreme refractory nature of these materials prevents the use of simpler acid digestions. Following is the suggested analytical testing plan for chromite and manganese ores:

- Samples are fused with lithium metaborate, fused-disc XRF.
- Major analytes by XRF include Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SO_3, SrO, TiO_2.
- LOI at 1,000°C.

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