ROCKS TO RESULTS

A PRACTICAL GUIDE TO LABORATORY OPERATIONS
The technical excellence, unparalleled global network and unequaled breadth of service that is now SGS Minerals Services coalesced in the early 2000s from diverse roots. The pedigree of this handbook, *Rocks to Results*, lies in these roots. Created originally in the 1990s by the analytical staff of Analabs, this reference manual became a valuable desktop resource to Australian geologists.

In 2007, SGS decided to revisit this reference book, as we believed that the new generation of minerals industry professionals would see value in an up-to-date version. Included now are new sections detailing the new analytical technologies and test procedures used in the testing industry today. This completely revised volume was produced by Kate Jackson and Shaileen Stanley with technical input from the global SGS laboratory group, including lengthy contributions from Dr. Nick Turner on ICP-AES and ICP-MS, Ms. Pierrette Prince on Sample Preparation, Dr. Hugh de Souza on Mineralogy and Diamond Exploration testing, and Dr. J. M Richardson on Sampling. In addition, we asked Dr. Wesley Johnson of Quality Analysis Consultants to provide overall editorial management and to contribute specific updates on current laboratory practices for Quality Control and Quality Assurance.

Geochemical sampling and analysis is the basis for many decisions in exploration. When you need to be sure of procedures, protocols or lab practice, we hope that you will turn to this book. If you would like personal advice, please call: we have over 150 labs globally (listed in www.sgs.com/geochem) and we will be pleased to help, anywhere, anytime.

Russ Calow
Vice President, Global Geochemistry
SGS Minerals Services
Lakefield

Cover: ICP-MS lab in SGS Toronto office on a background of sphalerite-marble ore from Hudbay Minerals Inc.’s Balmat zinc mine in Governeur, NY. This region has produced over 40 million tons of 9.4% zinc ore since 1908. Sample collected by J. M. Richardson in 1985.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>SELECTING ANALYTICAL OPTIONS</td>
<td>7</td>
</tr>
<tr>
<td>2.1</td>
<td>Grassroots Exploration</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Target Definition</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>Resource Estimation (Prefeasibility and Feasibility)</td>
<td>12</td>
</tr>
<tr>
<td>2.4</td>
<td>Production</td>
<td>14</td>
</tr>
<tr>
<td>2.5</td>
<td>Concentrate and Bullion Analysis</td>
<td>15</td>
</tr>
<tr>
<td>2.6</td>
<td>Sampling</td>
<td>16</td>
</tr>
<tr>
<td>2.7</td>
<td>Summary</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>QUALITY CONTROL AND QUALITY ASSURANCE</td>
<td>19</td>
</tr>
<tr>
<td>3.1</td>
<td>Good Field Sampling Plans and Protocols</td>
<td>19</td>
</tr>
<tr>
<td>3.2</td>
<td>Good Laboratory Practices</td>
<td>21</td>
</tr>
<tr>
<td>3.3</td>
<td>Assessing Precision</td>
<td>22</td>
</tr>
<tr>
<td>3.4</td>
<td>Assessing Accuracy</td>
<td>23</td>
</tr>
<tr>
<td>3.5</td>
<td>Laboratory Assessment</td>
<td>26</td>
</tr>
<tr>
<td>3.6</td>
<td>Method Validation and Fit-For-Purpose</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>LABORATORY OPERATIONS</td>
<td>29</td>
</tr>
<tr>
<td>4.1</td>
<td>Sample Preparation</td>
<td>29</td>
</tr>
<tr>
<td>4.2</td>
<td>Digestion</td>
<td>38</td>
</tr>
<tr>
<td>4.3</td>
<td>The Fire Assay Process</td>
<td>41</td>
</tr>
<tr>
<td>4.4</td>
<td>Analytical Methods and Instrumentation</td>
<td>46</td>
</tr>
</tbody>
</table>
5  PETROLOGY AND MINERALOGY AS APPLIED TO MINERAL EXPLORATION AND MINING  57

5.1  Rock and Mineral Identification  57
5.2  Mineral Chemistry  61
5.3  EXPLOMIN™  62
5.4  Geometallurgy  63
5.5  Refactory Gold  63
5.6  Diamond Exploration Services  65
5.7  Mineral Sands  68

6  SGS AUDIT POLICY - EXTERNAL 2ND PARTY AUDIT  69

6.1  Policy Scope  69
6.2  Confidentiality  69
6.3  Auditor Identification  69
6.4  Photographs and Access  70
6.5  Health and Safety  70
6.6  Advance Notice  70
6.7  Audit Objectives, Scope and Criteria  70
6.8  Audit Conduct  70

7  CONCLUSION  71

8  ENDNOTES/REFERENCES  72

9  APPENDICES  76

9.1  Metal Oxide/Metal Conversion Factors  76
9.2  Standard Test Sieve Series  77
9.3  Frequently Requested Equivalents  78
9.4  Drill Core Specification  78
9.5  Glossary of Terms  78
9.6 Periodic Table 80
9.7 Unit Conversion Factors 82
9.8 The Assay Ton 82
9.9 Field Tests 83

FIGURES

Figure 2.1: SGS Services available across the value chain 8
Figure 2.2: Data generated through geometallurgical mapping populates the block model 14
Figure 2.3: Sample weight 18
Figure 3.1: The X or Shewhart control chart 25
Figure 4.1: Summary of sample preparation procedures 29
Figure 4.2: The Jones riffle splitter 32
Figure 4.3: An automated comminution system 37
Figure 5.1: Indicator mineral extraction flowsheet 66

TABLES

Table 2.1: Approximate sample size required for rocks of given grain size 17
Table 2.2: Analytical options available for different development stages 18
Table 4.1: Chute width recommended for top particle size of sample to be split 33
Table 4.2: Percent relative error introduced by different sample splitting techniques 34
Table 4.3: Contaminants introduced from grinding equipment composed of various materials 35
Table 4.4: “Nugget Effect” of gold particle sizes versus sample weight 45
This manual was written to provide geoscientists with an introduction to geoanalysis. This document will address questions such as:

- What type of analysis should I ask for at the grassroots exploration, resource estimation, prefeasibility or feasibility stage?
- What accuracy and precision can I expect from this analytical method?
- What should I look for when deciding upon an analytical lab?
- How can I ensure that the lab will provide me with the accuracy and precision I need?
- Will the data be fit for my purpose?

The laboratory must select methods to analyze a set of samples. The decisions that must be made include:

- How large a test portion should I take for analysis?
- What digestion method should I use?
- What instrument should I select to measure the target element concentrations?

For the geoscientists and the analysts to make the correct decisions when considering questions and options, both must have some understanding of the other’s field. This manual was written to help with this.

No matter how competent each party is, or how much they know of the other’s field, it is critical that there be a thorough discussion between the geoscientist and the analyst. Only in this way can the best choices be made to ensure the data generated by the analytical work are fit-for-purpose.
1 INTRODUCTION

The analytical laboratory plays an integral role in the entire mineral exploration and mining industry process from grassroots exploration of a prospect to the analysis of bullion and/or concentrates. Geoscientists are involved in all of the steps, from exploration to product shipment, and so must have a basic knowledge of how the laboratory fulfills its role.

Most of the decisions made during the exploration for, and development of, a mine are made with reference to analytical information. These decisions can be made confidently only when the decision-makers have confidence in the reliability of the information upon which the decision is based. That is, the precision and accuracy of the analytical work must be adequate to support the decision. Laboratory quality control and quality assurance programs are designed to ensure that the analytical data are fit-for-purpose and to assure the decision-maker of the reliability of the data.

DATA REQUIREMENTS

Geologists working at different stages in the development of a mineral resource have different analytical requirements. For example, exploration work will not need the same precision and accuracy required at the reserves development stage, which, in turn, is less demanding than the grade-control stage. Concentrate and bullion shipments are the most demanding in terms of data quality and, as a result, this analytical work involves extensive quality control. It is much more expensive.

QUALITY SYSTEMS

Credible mineral analysis laboratories follow the analytical principles outlined in Sibilia\(^1\), Johnson and Maxwell\(^2\), Potts\(^3\) and Riddle\(^4\) and participate in an international quality standard known as ISO/IEC 17025\(^5\). For a laboratory to successfully comply to this standard, it must demonstrate to independent technical assessors that it meets the quality requirements of the standard. These requirements are divided into two sections. The first is almost identical to the more familiar ISO 9000\(^6\) management system certification. The second is a series of laboratory specific technical requirements.

The management requirements include policies and procedures for the management system, such as organizational structure and authority, customer confidentiality and communication, document control, complaints and feedback, purchasing of supplies and services, acting on non-
conformances using corrective action reports and potential non-conformances using preventive action reports, demonstrated continuous improvement, annually scheduled internal audits and management review plus additional procedures and policies that any organization holding ISO 9000 qualifications would recognize.

ISO/IEC 17025’s additional technical requirements provide a more comprehensive technical component than the ISO 9000 series. The ISO/IEC 17025 standard is specific to testing and calibration laboratories. These requirements include adequately trained staff with specific responsibilities and authorized proficiency to perform the tests. Test methods must be appropriately selected, suitably documented with demonstrated validation and associated measurement uncertainty to be deemed fit-for-purpose. Test methods must be traceable to international measurement units with records of calibration and verification as necessary. Quality control and quality assurance must be statistically demonstrated from the sub-sampling stage through to the data reporting with sufficient frequency for insertion of screen checks, duplicate and replicate samples, certified or suitably characterized reference materials and scheduled proficiency testing by a recognized PT provider.

Laboratories holding ISO/IEC 17025 are reassessed every two years by an external, recognized accreditation body to ensure the laboratory is maintaining the management and technical requirements needed to produce competent results. By following these practices, laboratories can be expected to provide reliable analytical services to clients.

There is still the requirement that the geoscientist and the laboratory come to a joint agreement on what constitutes ‘fit-for-purpose’ (in terms of accuracy and precision), the numbers of samples to be submitted, and what turnaround time and costs are acceptable. Most geoscientists have an ongoing dialogue with the laboratory to make sure that these questions are answered.

This manual will help geoscientists:

• Select a satisfactory laboratory.
• Be aware of what can be done in the field to facilitate the rapid delivery of analytical work.
• Understand the process that samples will undergo when sent to the laboratory.
• Request the optimum analytical package.
• Evaluate the final data.
Projects go through several developmental steps as they move forward, each requiring a different analytical approach. It is critical for those carrying out the assessment and development of the resource to understand these different analytical approaches.

Given the wide range of methods and instrumentation available in modern geochemical laboratories, method selection can seem daunting. However, the choice of method is very much a question of what the goal of the exploration program is and what questions need to be answered. Commercial laboratories have brochures and websites that describe the different analytical options. These methods have differing elemental options, precision and accuracy parameters and they were developed to provide data fit-for-purpose at each operational stage. Discussions with the laboratory ensures the geoscientist will get data that are fit-for-purpose at each stage.

SGS offers a wide range of services to each operational stage in a project’s development (Figure 2.1). Geochemistry is an important component of each stage.
SGS SERVICES FOR THE MINERALS INDUSTRY

Figure 2.1: Services available at each stage of project development from SGS.
2.1 GRASSROOTS EXPLORATION

Early-stage exploration can be divided into two phases, each with differing geochemical requirements. Regional-scale evaluations assess prospective areas to determine if there is the potential to host mineralization. Such surveys rely on regional geology combined with geophysical and geochemical mapping. Prospect-scale work then follows. Detailed geophysical and geochemical surveys are then used to locate mineralized zones that can be drilled.

On a regional scale, samples selected for analysis can vary tremendously, depending on landscape, surficial weathering and nature of the soil and overburden, either residual or transported. Types of material analyzed at this stage can include stream or lake sediments, till samples, soils and rock or chip samples. Analysis often focuses on the more resistant minerals (often in a heavy mineral concentrate) that survive transport or weathering, and requires total multi-element geochemical analysis using methods such as Instrumental Neutron Activation Analysis (INAA). Currently, fusion Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) methods provide a larger number of elements and are very effective in combination with Au, Pt and Pd by fire assay. Weak partial extractions, such as Mobile Metal Ion Technology™ (MMI), have a role at this stage of exploration as they delineate target geological units in areas of deep cover.

2.1.1 Orientation Survey

An orientation survey (including an MMI orientation survey) involves the collection and testing of a series of samples to ensure that the sampling procedures and analytical methods proposed will produce expected geochemical results. An orientation survey may also help characterize the nature of the geochemical response, particularly where this deviates from the norm.

Ideally, samples are taken from the undisturbed overburden and soil profile above an area of known mineralization that is geologically and environmentally similar to the survey area. Samples from each soil horizon are selected to compare elemental response. These samples are chemically analyzed and the elemental data are plotted to gain an understanding of the correlations among the three dimensional dispersal pattern of elements in the overburden
and the anomalous mineralization in the bedrock below. These dispersion patterns or secondary dispersion halos of elements are formed from chemical and mechanical weathering of the bedrock and subsequent dispersal into the overburden via ground water movement or other transport mechanisms.

In addition to establishing correlations, the background or non-anomalous element levels in the survey area and beyond are established to determine the extent of the dispersion pattern in the overburden. To help determine the zones with the greatest concentration of target elements (the optimal sampling depth), the soil and overburden profile of each sample should be noted and mapped. Also, samples should be screened and each size fraction analyzed to determine the specific size fraction associated with each target element. Samples in an orientation survey can be split and analyzed in pairs to help measure the uncertainty associated with the process of reducing the sample volume for the laboratory.

2.1.2 Lithogeochemical Survey

Lithogeochemical studies identify potential magmatic assemblages that have potential for developing mineralized systems. An example would be the search for volcanic massive sulphide (VMS) deposits in volcanic sequences. Here, the aim is to identify specific petrochemical assemblages that could host VMS mineralization. Analysis required might include high-precision whole rock geochemistry (RSD of better than ±5%) using a combination of X-ray fluorescence (XRF) for major and minor elements and trace elements by fusion ICP-MS. Indicator mineral analysis is also used in regional exploration.

2.1.3 Hydrogeochemical Surveys

Hydrogeochemical studies also play a significant role in regional exploration in some environments. ICP-MS technology provides low-cost, high-precision, multi-element data on suitably collected water samples.
2.1.4 Packages and Analytical Measurement

Grassroots exploration programs can involve the collection of thousands of soil or till samples to identify potential drill targets. The goal is to identify anomalies generated by mobile elements, sometimes at very low parts-per-billion (ppb) levels. Because of the number of samples needed, the cost of the analytical packages is an issue. Packages chosen at this stage, such as aqua regia digests, extract the labile (mobile) elements. The digests are then analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) or ICP-MS for ultra-trace level determinations and are complemented by Au, Pt and Pd by fire assay. Precision and accuracy are normally ±10%. Over the last decade, very weak partial extractions such as MMI Technology™, have become popular because of their ability to identify anomalies in areas covered by deep or transported material. Biogeochemical methods can also be used at the prospect scale.

When ICP-MS is unavailable, specialized Atomic Absorption (AA) methods can provide similar quality data for key pathfinder elements, such As, Sb, Se, Te and Bi, using hydride generation methods or doing Hg by a cold-vapour method. Both of these methods have low ppb or even sub-ppb detection limits.

For ICP and AA instrumental measurement techniques the samples must be in a liquid state so they can be introduced into the instrument. How this is achieved is the subject of much discussion and development (see Section 4.2). It is critical that the selection of the digestion process be the subject of a thorough discussion between the geoscientist and the laboratory scientists to ensure that the appropriate digestion option is selected for the geological conditions and the exploration objectives.

Sample preparation techniques are available for extracting different mineral fractions, or to concentrate solubilized (dissolved) elemental fractions using a secondary extraction procedure. These aid in the identification of anomalies and/or improve detection limits of the instrumental methods mentioned above. These procedures range from complete digestions using alkali fusions to leaches using very weak extractions (such as MMI Technology™) that target weakly adsorbed elements soil and/or sediment surfaces.
One extraction method that has seen little change is the fire assay pre-concentration of gold, platinum and palladium into a silver prill. The use of AAS, ICP-AES or ICP-MS to analyze the prill once it has been dissolved has lowered detection limits substantially, when compared to the traditional gravimetric finish. The cyanide leaching of large samples (BLEG), aqua regia digestions and INAA are all used in gold exploration programs. Nickel sulphide collection with subsequent ICP-AES or ICP-MS measurement is used in platinum group element (PGE) exploration work.

2.2 TARGET DEFINITION

Once an anomaly is identified, a more detailed examination of the occurrence begins. This can involve closer spaced soil and/or sediment sampling, channel sampling of outcrops or even limited drilling. Fewer samples and a smaller number of elements might be required at this stage, but the extraction and measurement techniques selected will, for the most part, be identical to those used at the orientation stage. Drill core analysis will normally require similar packages, precision and accuracy.

When a mineralized zone has been discovered, analytical requirements may change again because the data may be used in resource calculations. Partial digests using aqua regia or multi-acid digest might still be the norm, but higher precision and accuracy of ±5% may be necessary. When metal levels exceed the upper limits of the method, better quality data are necessary and assay methods are used.

Other data that can be gathered at this stage include mineralogical characterization, specific gravity and other tests that predict metallurgical performance.

2.3 RESOURCE ESTIMATION (PREFEASIBILITY AND FEASIBILITY)

During prefeasibility and feasibility assessment, the deposit is assessed for profitability and production potential. The grade and tonnage are proved up and quantified to support significant future investment in the infrastructure needed for mining. The analytical work used for these stages needs to be of assay quality – that is, better than 5% relative precision and accuracy.
The objective of resource estimation is to determine if the mineral resource is economic in terms of grade and size. This means that calculations, grades of ore, the physical distribution of the resource and the metal recovery must be very reliable. These estimates will only be as reliable as the testing that the calculations are based on. As several billion dollars are typically spent developing a mine, it is critical that estimation of the size of the orebody and the associated grades and recovery be as reliable as possible. This is dominantly based on good sampling, sound analytical practice and testing and reliable statistics. To achieve these goals, companies use

- aggressive “total” analytical digestions
- advanced quality control procedures
- technologies such as EXPLOMIN™
- geometallurgy
- geostatistics and 3D data handling.

To achieve this quality of analytical work, sample digestion techniques that are aggressive or “near total” (4 acid digest) or “total” (fusions) are used to ensure complete digestion of the important economic elements (see Section 4.2). These methods are thought to generate data that reflects the metallurgical “recovery” of the target element. Sometimes this can be the case, but this assumption is often incorrect so it must be assessed for each deposit.

The laboratory must implement more stringent quality control provisions to ensure that the analytical results meet disclosure requirements and scrutiny of Qualified Persons. AMEC\(^8\) indicates that the norm in 2007-8 for control sample insertion is about 20% to meet regulatory guidelines. Each batch of 20 samples should include one blank, one duplicate and one certified reference material (CRM) plus field duplicates. As the project advances, additional Quality Control measures include field and sample preparation duplicates and check samples sent to another laboratory.

EXPLOMIN™ is a mineralogy package that provides the routine, automated documentation of mineralogy, alteration and texture on core and crushed samples, for a statistically robust comparison. See Section 5.3 for more details.
Geometallurgy is used to define domains and quantify variability within an ore deposit. The data generated from EXPLOMIN™ can be used to populate 3D models, leading to reduced technical and financial risk. See Section 5.4 for more details.

Geostatistics broadly encompasses the use of statistical methods to describe correlations among sample data. These data are then used in various types of spatial models. Geostatistics changes the emphasis from estimation of averages to mapping spatially-distributed populations. Correlations can be analyzed using correlograms, covariance functions and variograms. In essence, data are associated with a location in the ore deposit and there is an implied connection among location, data, the distance to which the data can be extended through the ore deposit and the related uncertainties.

2.4 PRODUCTION

Once a mine is in production, analytical work is used for grade control to distinguish between ore grade and waste rock. In addition, mill heads, concentrates and tailings are analyzed to calculate metallurgical balance and performance. Samples taken within the mill are used to control the processing plant. All of these applications require quality assay work with rapid turn-around. This is traditionally done on-site and such laboratories are often sub-contracted.
The analytical work involved in these applications will not be much different from that used in earlier stages except for more rigorous digestion procedures and more detailed quality control practices are used.

Production forecasting and optimization is the application of geometallurgical data to predict, plan and optimize production throughput (tonnes per hour and post-primary crush 80% passing size – tph and P₈₀) and recovery with a measured degree of accuracy and precision. Production optimization consists of:

- Sampling
- Flotation and grinding tests to determine geometallurgical parameters
- Merging geometallurgical parameters into the block model
- Forecasting performance using simulation
- Valuing blocks, planning mining activities, reconciling forecast to production
- Refining and optimizing

Companies can contract only the mill control or metallurgical accounting aspects of production, or hire subcontractors to provide the complete metallurgical management of the mill.

Companies also may subcontract environmental analysis of their site during production. The resulting data allows them to routinely monitor air, water and soil are routinely monitored to ensure regulatory guidelines are met.

### 2.5 CONCENTRATE AND BULLION ANALYSIS

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 (see also Section 4.4.6). The splitting limits (the accepted spread of analytical results agreed upon by concentrate seller and buyer) are determined by negotiation but, as an example, are on the order of 0.15% to 0.2 % copper for a 30% copper concentrate. This represents a requirement for substantially 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. In addition, to ensure such accuracy and precision are obtained, the quality control protocols are expanded. Four or five replicates are analyzed with matrix-matched reference samples. This ensures no matrix-caused bias affects the analytical result.
As well, the mineralogical make-up of the reference samples should be as similar to that of the samples as possible. Titre 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 discuss all requirements with the analytical scientists to ensure the data generated is adequate for its intended use.

### 2.6 SAMPLING

A fundamental question that supersedes the selection of any analytical method is what is the optimum sample size? Also, is it representative of the material that it came from? Was the host material homogeneous at the scale at which the sample was taken? The first control on this is, of course, in the field, when sampling is first anticipated...what is the grain size of the material and is it homogenous at the scale of the sampling process? The second control is in the lab, when the received sample is crushed and split for testing.

The size of the sample taken is dependent on the

- Grain size of the material to be tested.
- Mineralogical composition with respect to the element of interest.
- The distribution of the minerals that contain these target elements.
- The concentration of the target elements in the least abundant minerals in the samples.

Rocks in which the target elements are concentrated in a mineral that is both of low abundance and irregularly distributed are very hard to sample representatively (see the nugget effect discussion in Section 4.3.7). This typically applies to gold, PGE alloys, zinc and the rare-earth element minerals thorite and monazite.

There are two approaches to sampling, one is a “rule of thumb for field use” (Table 2.1) and the other is a rigorous statistical treatment that uses Gy’s Theory.
Table 2.1: Approximate sample size required for rocks of given grain size\textsuperscript{13}

<table>
<thead>
<tr>
<th>GRAIN SIZE</th>
<th>SAMPLE SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine grained (&lt;1 mm-1 mm)</td>
<td>100 – 500 g</td>
</tr>
<tr>
<td>Medium grained (1 mm-1 cm)</td>
<td>1 kg</td>
</tr>
<tr>
<td>Coarse grained (1 cm-1 dm)</td>
<td>2 – 10 kg</td>
</tr>
<tr>
<td>Porphyritic (1-3 mm)</td>
<td>500 g – 1 kg</td>
</tr>
<tr>
<td>Porphyritic (3-6 mm)</td>
<td>2 – 10 kg</td>
</tr>
</tbody>
</table>

Gy's equations relate sample weight to particle size. This is shown graphically in Figure 2.3.

The Safety Line represents the minimum amount of sample that can be collected or subsampled safely for a given sample size. Typically, the sample is collected in the field, sent to the lab, where it is crushed, pulverized and resampled several times before analysis. These operations are shown as steps on the left side of Figure 2.3.

Safe sampling practice requires all such steps be plotted to the left of the Safety Line. Equating the grain size of a field sample to the particle size parameter can result in a margin of safety, but if extensive reductions in sample size are anticipated (i.e. due perhaps to mineral separations), much larger samples should be collected\textsuperscript{14}. 
Table 2.2: Analytical options available for different development stages.

<table>
<thead>
<tr>
<th>DEVELOPMENT STAGE</th>
<th>DIGESTION TYPE</th>
<th>RELATIVE PRECISION/ACCURACY</th>
<th>INSTRUMENT SELECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grassroots exploration</td>
<td>Mild digestion for weakly adsorbed species</td>
<td>15-20%</td>
<td>AAS, ICP-AES, ICP-MS, INAA for multi-element work</td>
</tr>
<tr>
<td>Target outline</td>
<td>Stronger acid attack for minerals</td>
<td>10%</td>
<td>AAS, ICP-AES, XRF for selected elements</td>
</tr>
<tr>
<td>Reserves development and production</td>
<td>Strong acid attack or fusion for complete digestion</td>
<td>&lt;5%</td>
<td>AAS, ICP-AES, XRF for selected elements</td>
</tr>
<tr>
<td>Concentrate and bullion shipments</td>
<td>Strong acid attack or fusion for complete digestion</td>
<td>&lt;1%</td>
<td>AAS, ICP-AES, XRF, classical methods</td>
</tr>
</tbody>
</table>

2.7 SUMMARY

Table 2.2 summarizes many of the above points and is included to provide a framework for the selection of the appropriate methods. It is not intended to be a substitute for discussions with analytical scientists but rather as a guide to focus those discussions.
3 QUALITY CONTROL AND QUALITY ASSURANCE

Quality control consists of the activities undertaken to ensure that a laboratory’s sub-sampling and analytical process are in control and that the accuracy and precision of the results are fit-for-purpose. Quality assurance is the quality system framework under which the analyses are conducted and includes the organization of the quality control data and the presentation of the information in such a way to prove that the data are fit-for-purpose and the assurance that the data are reliable for the intended use.16, 17, 18, 19

There are numerous quality control activities that must be undertaken to ensure the sampling and analysis programs supply reliable results. These include measures to minimize both random and non-random (blunders for example) errors, sources of variance and error and to minimize any systematic bias.

3.1 GOOD FIELD SAMPLING PLAN AND PROTOCOLS

It is critical that the data control begins when the sample is collected. It is important to assess for nugget effect (in Section 4.3.7). One estimate of the amount of uncertainty introduced is given by Dr. Ed Paski20:

- Field sampling 10% to >100%
- Storage, transport <1% to >100%
- Sample reduction (sub-sampling) 10% to >100%
- Chemical preparation (sample decomposition) 5% to 20%
- Measurement 1% to 10%
- Reporting <1%

From this, it is clear that the geoscientist has to ensure field sampling, as well as sample storage and shipment, are done properly to minimize uncertainty in the data.

The geoscientist should have a sampling plan that includes21:

- When, where and how to collect samples.
- Sampling equipment and its maintenance and calibration.
- Sample containers – type, cleaning, addition of stabilizers, and type of storage.
• Criteria for acceptance and rejection of samples.
• Criteria for the exclusion of foreign objects.
• Sample treatment procedures such as drying, and handling prior to shipment.
• Sub-sampling procedures.
• Sample record-keeping such as location, labelling, recording and auxiliary information.
• Chain-of-custody requirements.

To this can be added aspects related to shipping:

• Ensuring rugged packaging so the samples do not arrive at the laboratory as “one super sample” due to bag breakage.
• A well organized and complete chain of custody form that lists all samples, the analyses required and any special treatment needed.
• Instructions as to whom to report the results to and whom to invoice.
• The addition of duplicate samples collected on the field (to assess sampling precision).

Each sample collected in the field must have a unique identification and description that should include:

• Date, weather, sampler and companions.
• Geographic location (GPS coordinates).
• Unit name (group, formation, etc.).
• Description of field setting of sample (sketch, photographs if possible).
• Characteristics of units that make up the sample site (outcrop rock type, layer thickness etc.).
• Description of primary features – grading, banding, etc and in the case of soils – soil profile, horizon, etc.
• Description and measurement of secondary features such as bedding, cleavage, fossils, etc.
• Description of the sample.
• Sample number, reason for sampling and photograph number.
• Results of field tests (magnet, ultraviolet light, acid, etc.).

Once the geologist has ensured the quality of the field work and that the samples are submitted properly to the laboratory, the quality control and quality assurance responsibilities of the laboratory begin.
These measures, when combined with the field information, give the geoscientist the tools needed to evaluate the results based on reliable information.

3.2 GOOD LABORATORY PRACTICES

3.2.1 Good Measurement Practices

Good measurement practices are the steps laboratory analysts take every day to ensure an analysis is done properly. The geoscientist should audit to make sure that the laboratory’s standard practices involve:

- Using clean, Class A, calibrated glassware (as appropriate) and reagents of adequate purity.
- Good housekeeping to minimize potential contamination.
- Proper weighing and volumetric techniques with demonstrated verification checks and actions taken when necessary.
- Correct instrument calibration and operation.
- Establishing measurement traceability.
- Good documentation of methods, sample handling and analyst responsibility.
- Training records.

Good measurement practices are the habits and work practices that well trained and experienced analysts come to accept as second nature. Those new to the profession must learn these. For this reason, accreditation bodies stress training programs and analyst evaluation.

3.2.2 Control Sample Insertion

Control samples are inserted to assess accuracy (reference samples), precision (sample replicates), contamination (blanks) and, in some cases, recovery (target element spikes). When selecting a laboratory, one should ask to have control samples inserted during routine analysis and the resulting data reported.
3.2.3 Proficiency Testing

Defined as the “determination of laboratory testing performance by means of inter-laboratory comparisons\textsuperscript{23}”, proficiency testing is a key part of any quality control program. It demonstrates the agreement among independent analytical systems on identical samples.

The results of a laboratory’s participation in proficiency testing schemes should be available for client inspection as independent proof of the laboratory’s capabilities (or lack thereof) as compared to others. The geoscientist should ask to review a laboratory’s proficiency results.

3.3 Assessing Precision

Because standard deviation is a measure of the range in analytical results that result from taking the same measurement more than once, precision is estimated by the use of replicate analyses. The most robust estimate of precision is made by inserting samples at each stage of the process – field sampling, sample crushing and splitting through to the final measurement. The standard deviations calculated from these replicate results include the uncertainty of the sampling at the stage at which the duplicates have been inserted, as well as uncertainty due to random variations in all subsequent processes.

Analysis of this replicate data permits the estimation of the uncertainty at each stage. The relative precision is usually smaller for the analytical processes than the sample preparation stage, which again is smaller than the variation introduced in the field sampling process (see Section 3.1). The geoscientist should insist on knowing the precision at each stage of the process. This includes both field sampling (which he or she controls) and laboratory operations. The geoscientist should insert field replicates to assess the precision of the field sampling process. This is usually the largest source of variance and should not be ignored. The laboratory should be able to supply an estimate of the uncertainty (standard deviation) arising from its work as required by the ISO/IEC 17025 standard.

Useful tools to visualize the precision of the laboratory’s work are plots of the difference (range) between duplicates as a function of concentration. The geoscientist can plot this information from replicate results reported by the laboratory.
3.4 ASSESSING ACCURACY

Once an analytical system has been developed to the point that it has satisfactory precision, bias can be assessed. Bias is a measure of accuracy and is defined as “the difference between the expectation of the test results and an accepted reference value.” Precision controls the size of bias detected; bias smaller than the standard deviation of the results cannot be detected. Suitable precision is necessary to prove that the accuracy of the analysis meets the established criteria.

3.4.1 Reference Materials

Reference materials are used to assess a measurement method. More specifically, reference materials are used to assess the accuracy (bias) of the measurement process. This assessment cannot be any better than the quality of the reference material. Neither the JORC code, nor NI 43-101, nor CIM’s Exploration Best Practices Guidelines set minimum operational, analytical or statistical criteria for reference materials. They require only that reference materials be used.

The geoscientist should ensure the following guidelines concerning reference materials are followed in the laboratory and in external quality programs:

- The certification process should meet ISO Guide 35 guidelines if possible.
- The reference material should be matrix-matched and therefore be subject to the same potential sources of error as the samples.
- The reference material must be homogeneous enough that the test portions are virtually identical within the degree of precision of the measurement system used.
- The reference material must be stable with respect to the elements of interest over its intended period of use.
- In order for it to be used to identify a bias, the confidence interval of the standard value must be less than the bias to be detected.
- A certified value and a description of how it was determined should be given for each element of interest.
- The target element concentration in the reference material must be similar to that of the samples being analyzed.
- The reference material must be plentiful enough to allow its use over a long time period.
Reference samples must be tested by several laboratories to give the geoscientist a reliable assessment of the laboratory’s results. If the geoscientist has submitted the candidate reference material to only one laboratory, there can be no guarantee that the sample result does not have an analytical bias. The results from several laboratories should be combined and an “accepted value” calculated with a standard deviation. In addition, various digestion techniques extract elements from a sample to different extents (see Section 4.2.4). If this fact is not taken into consideration, comparisons of results from different laboratories and different methods can lead to misleading conclusions. Because of this the certificates accompanying the internationally used CANMET soil standards list different element concentrations for different digestions.

3.4.2 Control Charts

Control charts are used to determine whether or not a process is in a state of statistical control. If analysis of the control chart indicates that the process is not in control, the source of variation can be determined and then eliminated to bring the process back under control\textsuperscript{55}. Accuracy is monitored through the use of warning and control limits on control charts and their associated rules for construction. These include:

- Ensuring the measurement process is in statistical control and that the precision is adequate.
- Inserting internal or in-house reference materials (IRM) or certified reference materials (CRM) in to routine analytical runs as early in the process as possible (e.g. weighing sample pulps).
- When a minimum of 20 results have been accumulated, calculating the mean and standard deviation (“s”).
- Constructing a graph as shown in Figure 3.1 with lines at the mean concentration and at ±2s and ±3s above and below the mean.
- Plotting subsequent results obtained from the reference material as they are generated.
The control chart contains a centre line that represents the mean value for the in-control process. The vertical axis of the Figure 3.1 is the value of the target element being measured in the reference material (e.g. concentration). The horizontal axis is the measurement sequence in which the data were obtained. The lines at ±2sd (standard deviation) above and below the mean are known as the Upper and Lower Warning Limits (UWL and LWL). Those at ±3sd are the Upper and Lower Control Limits (UCL and LCL). These control and warning limits are chosen so that most of the data points will fall within these limits as long as the process remains in-control.

The rules concerning the interpretation of these charts are based on the confidence levels built into the 2sd and 3sd control limits. They are as follows:

- No data should fall outside of the control limits (UCL and LCL) and if so, must be investigated.
- No more than 5% (1 in 20) of the data should fall outside the warning limits (UWL and LWL).
- Two successive data outside of the UWL and/or LWL may signify a loss of control and must be investigated.
- More than five successive data on one side of the mean or the other may signify a bias trend and must be investigated.
- A sudden increase in the variation of values about the mean signifies a loss of precision.

If a measurement process results in data that break any of these rules when plotted on a control chart, all measurements (known samples, blanks and reference materials) made since the last time control was demonstrated must be discarded and remedial action undertaken.

Figure 3.1: The X or Shewhart control chart
The cause of the lack of control must be identified, the problem resolved, and the measurement system once more proven to be in control. Only then can the unknown samples be repeated. This is one of the requirements of ISO/IEC 17025 and the geoscientist should ask to see documentation reflecting such QC protocols.

3.5 LABORATORY ASSESSMENTS

Because geoscientists make critical decisions based on data from a laboratory, it is important that they choose the laboratory carefully. This means assessing the prospective laboratories.

So just what should be considered when making such an assessment? One strong indication that a laboratory can produce acceptable results is conformance to the ISO/IEC 17025 standard. This is an internationally recognized quality standard. This means that a laboratory meeting the criteria of the national accrediting body in Australia, Mexico or Russia has met the same standards as one accredited in Canada, South Africa, the United States or anywhere else.

A lot of effort has gone into developing the laboratory assessment scheme that is as part of the ISO/IEC 17025 accreditation program. This standard can be used as a valuable guide to a geoscientist’s assessment process. If an accredited laboratory is not available, the requirements of the standard can be used to make an evaluation and, ultimately, select a laboratory. The most important things to look for are:

- A well documented quality system that has a quality manager responsible for its overall operation.
- A quality manual that describes the quality system and that includes top management’s signed commitment to the laboratory quality system.
- Employees’ signed commitment to a code of ethics, avoidance of conflict of interest and commitment to the laboratory quality system.
- An operational and well-documented non-conformance, client complaint, preventive action and corrective action program.
- A formal process for evaluating requests for quotes to ensure the laboratory has the facilities, staff and equipment required to fulfill commitments made to clients.
- Analytical staff trained to be knowledgeable and skilled enough to perform the work in a timely and satisfactory way. Records must be available to document this.
- Analytical facilities that are appropriately designed for the efficient flow of samples with a minimum chance of cross-contamination, equipment failure and other disruptions. The geoscientist should conduct a tour of the laboratory and confirm good housekeeping, proper dust control and smooth sample flow from receiving to reporting. There should be provision for the separation of equipment used for geochemical exploration work and that used for the assay of ore grade samples.
- Standard operating procedures that are documented, approved and controlled in a formalized way that allows no unauthorized deviations when performing the tasks.
- Methods that have been validated to prove that they generate data that are fit-for-purpose. Validation files should be available for inspection by a prospective client.
- Laboratory equipment that is well maintained with logs detailing maintenance and calibration history.
- Generation of data that are traceable to SI units or to internationally recognizable certified reference materials (such as those produced by CANMET, NIST, SARM and others). Documentation should be available to confirm traceability.
- Regular participation in inter-laboratory comparisons or proficiency testing programs. In cases where there was a failure in a result, the corrective actions taken are documented. Records of this participation should be available for inspection by a geoscientist.
- Control data should be accessible and readily control charted. Control data should be made available to the geoscientist on all reports including the observed values and the expected values. The results of replicate determinations should also be reported.
- A sampling plan that ensures a reliable sub-sample such that it is representative of the larger sample from which it has been taken.

3.6 METHOD VALIDATION AND FIT-FOR-PURPOSE

A laboratory’s method validation files provide evidence of their capability in generating data that is fit-for-purpose. The geoscientist should review these files with consideration of the required data quality. Important requirements to anticipate and understand include detection limit, the analytical concentration range likely to be encountered, accuracy and precision across this concentration range.
Method validation files should contain the raw data and the data interpretation to demonstrate that the methodology used meets the criteria established. Experiments such as replicate measurements (commonly between 7 and 10 repeated independent tests)\textsuperscript{27} to establish the method performance should be available. Ideally, the laboratory should have a file that contains replicates of analyses of reference samples at low, medium and high regions of the anticipated target element concentration range for each target element. The detection limit as well as the accuracy and precision at each concentration range, can be assessed from this data.

To confirm the performance characteristics of a method, the geoscientist should look for:

- A calibration graph for each target element over its expected concentration range. This will establish the linearity and sensitivity of the instrumental response.
- A comparison of the observed concentration versus the established concentration for the reference samples. This is used to assess method accuracy.
- The effectiveness of the digestion for the different target elements for the low, medium and high concentration levels.
- The standard deviation from the replicate analyses will establish the method precision at different concentration levels.
- Replicate analyses of blank or low concentration samples are used to establish detection and reporting limits (if appropriate).

If these values meet the criteria established for the project, the data generated from a given method can be expected to be fit-for-purpose.

However, no checklist can take the place of a thorough discussion with the geoanalysts about your requirements in terms of accuracy, precision, sample numbers, turn around time and target element selection. Only when all of these are clearly identified, can the best solutions be found. This will involve method selection, sample preparation options, digestion techniques to be used and instrumentation choices. At this point, laboratory capabilities can be evaluated and analytical costs established.
4 LABORATORY OPERATIONS

4.1 SAMPLE PREPARATION

Sample preparation includes all the steps taken in the laboratory to reduce the sample into a form suitable for chemical analysis, but not including the point where the portion for analysis is taken. Figure 4.1 summarizes much of this activity for different geological sample types.

Figure 4.1: Summary of sample preparation procedures.28
4.1.1 Receiving

After the samples are received and opened by the laboratory, they are sorted and the numbers are compared with the list supplied by the geoscientist. Any discrepancies or problems (such as sample bags breaking due to poor packaging) are noted and the submitter is notified immediately. A log is kept of this type of information.

When problems are resolved, the laboratory enters the samples into the laboratory system, usually a laboratory information management system (LIMS). This process consists of assigning an internal laboratory tracking identifier (usually a lot number for the set of samples received and ascending integers in addition to the geoscientist’s number to identify individual samples within the lot). The analytical work requested on the sample submission form is also entered, along with pertinent information such as date received, problems noted, special instructions and any request for “rush” sample treatment. Then, work lists are compiled for the different sections of the laboratory.

The geoscientist submitting the samples should ensure that the samples are packaged securely and that complete documentation including special instructions, accompanies the samples. Then there will be no delays in entering the samples into the LIMS and the work can begin immediately.

4.1.2 Drying

Samples are often received wet. In this case, they must be dried before they can be crushed and pulverized. This usually involves placing the samples in trays that will not cause contamination (for example, we avoid zinc contamination that arises from galvanized trays). The trays are put on racks in an oven at a specified temperature, usually 100° ±10°C. If mercury is a target element or if the sample is high in sulphides, the drying temperature should be lower. Excessively hot drying can lead to the loss of volatile species, combined water and CO₂, the oxidation of some sulphide minerals and the partial ashing of organic material.
4.1.3 Ashing

Vegetation is typically ashed to remove carbon. The samples are placed in a cool muffle furnace (<100°C) and temperatures are raised slowly to char the material. Heating too quickly will cause combustion and result in sample loss. Cross contamination can result if samples are ashed together. Ashing is usually finished when the sample is dull red, which indicates a temperature of around 500°C. Ashing is also done to remove sulphur from high sulphide samples. In either case, care must be taken not to lose volatile constituents such as mercury, arsenic or antimony.

4.1.4 Compositing

In some instances, and upon relevant instructions, more than one sample is combined to form a composite. This is done by collecting similarly sized sub-samples from samples known to be homogeneous and combining them. This is usually done after pulverization to maximize the degree of homogeneity.

4.1.5 Crushing

The most common primary crushing tool in geoanalytical laboratories is the jaw crusher. Laboratory crushers accommodate rock chunks up to about 15 cm and can reduce most rocks down to about 85% passing 2 mm.

Jaw crushers have an open flow for the samples (that is, the sample falls through the bottom of the crusher when it has been reduced to a small enough particle size), and, as a consequence, the crusher can be effectively cleaned between samples. However, damp, or clay-laden samples can coat the jaws and can be difficult to remove. This can cause cross contamination if operators do not notice this and clean the equipment thoroughly.

Some laboratories use a roll crusher following a jaw crusher as a second crushing stage to provide a smaller particle size prior to the splitting step. Such contamination is a serious problem with roll crushers since they are extremely difficult to clean. Many labs refuse to use them for this reason. If a roll crusher is being used, the geoscientist should ensure the crushing procedure specifies a cleaning step between samples to prevent cross contamination.
Organic samples are reduced in size using a macerating hammer mill. This consists of blades attached to a central shaft that flail the sample and break it up as the shaft rotates. This makes organic material easier to homogenize and representative sub-sampling easier.

4.1.6 Splitting

After crushing, a smaller portion of the crushed material is split or selected for pulverizing. If due care is not taken, splitting during sample preparation can result in a sub-sample that is not representative of the primary sample (see Figure 2.3). Duplicate splits should be analysed and the results scrutinized to ensure the samples have been crushed to a suitably small particle size before splitting.

In any sub-sampling procedure, it is better to take many small increments, or splits, to reach a designated sub-sample size than to do a few large splits. General sampling theory states “The composition and distribution variance components for the mean of n primary increments are n times smaller than the variance for single increments.”

Figure 4.2: The Jones riffle splitter.
4.1.6.1 Jones Riffle Splitter

The most common splitting equipment found is the Jones riffle splitter. It is shown in Figure 4.2.

The size of the chutes should be significantly larger than the top particle size of the sample to be split. Table 4.1 gives a guide for this rule.

Table 4.1: Chute width recommended for top particle size of sample to be split\textsuperscript{31}.

<table>
<thead>
<tr>
<th>TOP PARTICLE SIZE (MM)</th>
<th>CHUTE WIDTH (MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 – 20</td>
<td>50</td>
</tr>
<tr>
<td>10 – 13</td>
<td>30</td>
</tr>
<tr>
<td>5 – 10</td>
<td>20</td>
</tr>
<tr>
<td>2.4 – 5</td>
<td>10</td>
</tr>
<tr>
<td>&lt; 2.4</td>
<td>6</td>
</tr>
</tbody>
</table>

A Jones riffle splitter is simple and gives reliable sample division as long as the chute widths are large enough and the sample is poured through equally across all of the chutes. This is accomplished by ensuring the sample is spread evenly along the bottom of a pan that is the same width as the splitter. The sample is then poured out of the long side of the pan as it is held parallel to the side of the splitter onto the top of the chutes.

Some difficulties with the Jones riffle splitter include the following:

- The division ratio is 1:2 so the sample must often be passed through the riffles several times to get the appropriate sub-sample.
- Dust losses are difficult to control.
- There is some segregation parallel to the chutes in the rectangular splitter pan. This tends to bias towards the outer chutes. For this reason there should be an even number of chutes.
- The final pan must all be taken as the sub-sample with no sample material discarded.
- The Jones riffler is difficult to clean except by forced air.
4.1.6.2 Rotary Dividers

Rotary dividers yield a more representative split of the original sample than the Jones riffle splitter (see Figure 4.2). These dividers can be arranged to give a series (often 8) of similarly sized fractions of the original sample. Alternatively, the divider can be programmed to give a set sample size fraction (say 500g for example) with the remainder of the original sample going into a reject container. There can be some dust loss with this type of divider and cleaning may be difficult.

4.1.6.3 Coning & Quartering

Coning and Quartering consists of manually flattening out a heap of material and dividing it into quarters. The alternate quarters are combined. One is the sample portion and the other is the reject. If the sample portion is still too large, the process can be repeated.

These manual methods are subject to bias because particles of different sizes and densities segregate during the movement. They are also more subject to human error.

A comparison of the relative levels of uncertainty introduced by the different methods of reducing sample volume/size is shown in Table 4.2.

Table 4.2: Percent relative error introduced by different sample splitting techniques33.

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PERCENT RELATIVE ERROR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone and Quarter</td>
<td>22.7 %</td>
</tr>
<tr>
<td>Jones riffle splitter</td>
<td>3.4 %</td>
</tr>
<tr>
<td>Rotary splitter</td>
<td>0.42 %</td>
</tr>
</tbody>
</table>

4.1.7 Pulverizing

Several different techniques are available to reduce sample particle size to a pulp (usually taken to be <75 μm). Ring and puck (also called vibratory or ring and disk) are the most frequently used mills because they have the following advantages:

- High sample throughput
- A range of bowl sizes
- Narrow particle size distribution of the pulverized material
- Ease of cleaning
Automated mortar and pestles, rotating plate mills and other mills are also occasionally used.

Ring and puck mills consist of a bowl in which there are one or more rings, a puck and 50g to 5kg of sample, depending on the size of the mill. A lid is put on and the entire assembly is clamped into a device that vibrates. The rings and puck move rapidly and grind the sample, usually in about 3 minutes or less. The resulting material is mostly <75 µm and is homogeneous.

Mills are made of a variety of materials. This allows one to avoid specific contaminants by selecting the appropriate type of mill material (see Table 4.3). There is very little dust loss if the tops are sealed and the bowls are emptied carefully. A thorough brushing of the mill followed by a fast processing of cleaning sand (30 seconds) between samples effectively prevents cross contamination. This fast processing is also known as a “blank wash”.

Table 4.3: Contaminants introduced from grinding equipment composed of various materials.

<table>
<thead>
<tr>
<th>BOWL TYPE</th>
<th>SAMPLE SIZE</th>
<th>MAIN CONTAMINANTS</th>
<th>MINOR CONTAMINANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild Steel</td>
<td>To 3.5 kg</td>
<td>Fe, Cr</td>
<td>Mo</td>
</tr>
<tr>
<td>Cr-free Steel</td>
<td>500 to 1500 g</td>
<td>Fe</td>
<td>Mn</td>
</tr>
<tr>
<td>Zirconia</td>
<td>100 g</td>
<td>Zr, Hf</td>
<td>Al</td>
</tr>
<tr>
<td>Tungsten Carbide</td>
<td>150 g</td>
<td>W, Co</td>
<td>Ta</td>
</tr>
<tr>
<td>Agate</td>
<td>100 g</td>
<td>Si</td>
<td></td>
</tr>
</tbody>
</table>

Grinding bowls get very hot and high sulphide samples decompose during pulverization. To avoid this, labs rotate bowls so that each can cool in turn.

Alternative pulverizing equipment is occasionally used in a laboratory. Rotating disc pulverizers and blasters (hammer mills) are examples. They are difficult to clean which results in an enhanced possibility of cross contamination. In addition, rotating disc pulverizers contribute serious contamination from wear of the metal discs themselves. In both types of equipment, loss of the very fine portion of the sample can be a serious problem.
4.1.8 Automated Comminution

Recently, automated comminution equipment has become available that permits automated jaw crushing, rotary splitting, ring mill grinding and even analytical portion weighing in a continuous operation. In the past, these systems have been plagued with cross contamination issues. This was an on-going deterrent. However, automated sample preparation systems are changing to reduce the amount of cross contamination as well as increase sample throughput. The advantage of these systems is that the quality of the final product surpasses that derived from the manual sample preparation methods. As well, significantly fewer personnel are needed to operate and maintain the units overall.

Some automated systems have surpassed the quality objectives of the geoscientist. The quality can be monitored at all stages of the system, as well as on the contamination levels and the wear rates. The robot and the robust nature of these systems reduce many of the inherent day-to-day problems typically associated with manual sample preparation.

Fully automated robotic systems are incorporated as standard equipment into modular systems which allows a robotic arm operated by PC-based software to support flexible and dynamic operations of the system. Figure 4.3 highlights a typical arrangement which incorporates a sample weighing and fluxing system for XRF sample preparation. The arrangement consists of one robotic arm for 2 crushers and 6 pulverizers as well as rotary sample dividers, a cleaning station, and a labeling and filling station. The pulp produced from this system is then transferred before being weighed for the automated fluxing system. A glass bead is eventually produced for XRF analysis.
Figure 4.3: An automated comminution system.
4.2 DIGESTION

As most exploration samples are solid, and most instruments require the sample to be inserted in a liquid form (two exceptions being XRF and INAA), samples must be digested and converted into a solution.

The digestion technique used varies depending on the end use of the data. In some cases, a very weak extraction is desired to enhance an anomaly. In other cases, total analysis may be required and a digestion that fuses the sample to ensure a complete dissolution will be necessary. There are many digestion techniques available between these two extremes, depending on the need.

4.2.1 Weak Partial Digestion

4.2.1.1 BLEG Leaching

BLEG (bulk leach extractable gold) is a partial extraction based on a cyanide leach of a large (1 to 5 kg) sample. The gold concentration in the leachate is measured by AAS or an ICP-based method with detection limits of 0.05 ppb. Sample preparation is minimal, and is usually restricted to the removal of large chunks. The precision can be good because of the large sample size, but the accuracy (leaching effectiveness) is sample dependent. The cost is usually mid-range for analyses.

4.2.1.2 Weakly Adsorbed Element Extractions

There are numerous extractions specially designed to extract elements that are only weakly adsorbed on sediment and/or soil particles. The objective is to enhance the anomalous element signature above the background values so that it can be traced to an unexposed mineral deposit. These weak extractions have been used for several decades. They have matured from the early dilute mineral acid, organic acid (such as citric acid) and hydroxylamine-based extractions to the more recent multi ligand-based techniques such as Mobile Metal Ion (MMI™) extractions. MMI Technology™ extracts only the metal ions that are most weakly adsorbed onto soil and/or sediment particles.

The extracts resulting from such digestions are analyzed by ICP-MS, the most sensitive technique available, as extracted metal levels are usually in the sub-ppb range.
4.2.2 Strong Acid Digestion

4.2.2.1 Aqua Regia

Aqua regia is a 3:1 mixture of hydrochloric acid and nitric acid. It is a strong oxidizing mixture that dissolves many base metal sulphide minerals as well as gold and platinum. However, it is a partial leach that leaves undigested silicate and aluminate residue as well as refractory minerals such as garnet and spinel. It is possible to vary the sample size from less than 1 g up to 20 to 50 g depending on the target elements and their expected concentration. Sub-ppb detection limits are possible and base metal detection limits of low ppb are common.

Aqua regia digestion can result in the partial loss of volatile arsenic and antimony species. Insoluble sulfates such as those of barium and lead can precipitate when sulphide is converted to sulfate by oxidization. This is common since aqua regia is a strong oxidizing agent.

4.2.2.2 Aqua Regia Plus Perchloric Acid

Adding perchloric acid to aqua regia accomplishes two things. First, the resulting high temperature and strong oxidizing conditions help to digest some minerals that aqua regia alone cannot completely dissolve. Second, virtually all metal perchlorates are soluble so lead, barium and silver will not precipitate. This means the data will not be biased low. Base metal minerals are dissolved using this mixture of acids. A disadvantage is that HClO₄ solutions precipitate antimonic acid, tungstic acid and the equivalent acids of Nb and Ta thus giving low results for these elements. There is also the possibility of the volatilization of chromyl chloride from boiling HClO₄ solutions containing chloride ions. These effects will bias results low for some elements.

4.2.2.3 Aqua Regia, Perchloric Plus Hydrofluoric Acid

The advantage of adding hydrofluoric acid to the previous mixture is that HF dissolves silicate minerals. However, this digestion can leave some base metal minerals undissolved, typically sulphide or oxides. Silica however, is lost as volatile SiF₄. Some refractory minerals are only partially digested.
4.2.3 Fusion

4.2.3.1 Fusion for AAS and ICP

The fusion of samples using alkali fluxes decomposes very refractory minerals such as garnets, spinels and other oxides. Dissolving the fused material in acid yields solutions in which virtually all of the metals are dissolved. A very effective flux mixture is sodium carbonate, sodium peroxide and sodium hydroxide. This very basic, strongly oxidizing mixture renders most refractory minerals soluble. Sodium peroxide fusion is now commonly used to decompose the most refractory minerals. Low sample/flux ratios and a suitable dilution produces a solution with acceptable levels of total dissolved solids for ICP analysis. A major advantage is that the fusion is done at low temperatures (about 500°C), thus avoiding the loss of volatile elements.

There are some exceptions to the effectiveness of the mixed sodium salt flux. These include the precipitation of a few elements depending on the absence or presence of sulfates (barium for example) and other potentially complicating anions. These problems can usually be avoided by using metaborate or tetraborate salts of sodium or lithium.

Some elements such as tungsten, barium, rare earth elements, niobium, tantalum and chromium usually occur in highly refractory minerals. They can be effectively decomposed and solubilized using the borate fluxes. There are problems with high sulphide samples, but a pre-roasting step can usually resolve that complication. The solutions from weak hydrochloric or nitric acid dissolution of the borate fusions are ideally suited for subsequent multi-element ICP work. High purity lithium borate salts are available, so solutions have limited contaminants.

4.2.3.2 Fusions for XRF

The fusing of samples with lithium borate salts and casting of the melts into glass discs yields a sample that is ideal for subsequent XRF analysis. This is useful for major element or whole rock analyses and the determination of elements not easily determined by alternative methods (such as some rare earth, tungsten and tantalum). XRF is capable of determining concentrations up to 100% with a reliability of better than ±2% RSD using fused discs.
4.2.4 Refractory Metals

The various digestions discussed above (partial, weak acid, strong acid and different acid combinations) reflect a continuum of easy-to-difficult dissolved minerals and mineral assemblages\(^40\). Some metal oxides are easily dissolved in acids (CuO for example) while others are not (Al\(_2\)O\(_3\)). Some silicates dissolve easily whereas some, such as garnets, do not. Many minerals are not dissolved, or are only partially dissolved, in specific digestion conditions. Often, digestions are designed to take advantage of such behaviors for mineral speciation studies\(^41\).

Most strongly basic alkali fusions using salts such as sodium peroxide (Na\(_2\)O\(_2\)) and lithium metaborate (LiBO\(_3\)) will dissolve oxide and sulfide minerals but not refractory minerals such as garnets and spinels. The metaborate fusions used for ICP-AES, ICP-MS and XRF work do dissolve even these minerals however.

4.3 THE FIRE ASSAY PROCESS

Fire assay fusion is used for gold, platinum and palladium (the precious metals) exploration work, because it can accommodate a larger sample size 30g to 50g being common. This is necessary as the target elements occur at very low levels and so require an effective pre-concentration step. The reliability of the extraction and the low detection limits that can be achieved (5 ppb Au by AAS for example) are also attractive features of this technique. The standard fire assay method has been unchanged for decades, its reliability is well established and it is widely trusted\(^42\), \(^43\), \(^44\), \(^45\). The time-tested chemistry of the fusion and cupellation steps is still used successfully to extract the precious metals from any type of sample matrix.

4.3.1 Fluxing

The assayer must judge the balance needed of the various acid, basic, oxidizing and reducing reagents to ensure a successful fusion. Most commercial laboratories use a premixed flux that gives a suitable fusion for a large percentage of the samples submitted. When a slag indicates a poor fusion or a lead button is too large or small, the assayer will re-fuse the sample with an adjusted flux mixture.
For silver analysis, a few milligrams of silver, known as an inquart, are added to the fusion mix. This inquart ensures that the bead is large enough to be seen and handled. It also provides the silver-to-gold ratio of 3:1 that is required to dissolve the silver from the bead, leaving the gold.

### 4.3.2 Fusion

The reagents used in the fusion must be selected to effectively attack the sample matrix, form a slag that dissolves the base metals and then create a 30g lead button. This ensures that the slag separates easily from the lead button. Different types of samples will require different flux recipes to meet these objectives.

Once the sample has been mixed with the appropriate flux, it is put into the fire assay furnace to fuse at 900°C. The fusion is a complex pyrometallurgical process in which the flux breaks down the mineral matrix and thus frees the precious metals. The fusion is done under reducing conditions to reduce the elemental lead in the litharge (one of the reagents). The droplets of lead combine with the metals released from the sample matrix and then collect at the bottom of the crucible. When the fusion is complete (45 to 60 minutes), the melt is poured into a conical mold and the lead again sinks to the bottom.

Note: Although most laboratories have adequate pot cleaning procedures, the geoscientist should ask how the pots are tracked. Pots used for higher grade samples should not be reused to avoid contamination of subsequent samples.

### 4.3.3 Cupellation

After fusion and the separation of the lead button from the slag, the lead is separated from the precious metals in a process known as cupellation. This step involves the rapid oxidation of elemental lead into lead oxide in a cup-like cupel at 840°C. The lead oxide is molten at this temperature and it is absorbed selectively into the cupel. This leaves a precious metal alloy on the surface as a small, spherical globe known as a prill.

The silver and gold in the prill remaining from the cupellation step are then measured to “finish” the analysis. There are a number of alternative methods to select from.
4.3.4 Gravimetric Finish

The prill remaining after cupellation consists of an alloy of the inquart silver and the gold that was in the sample. At one time, the silver as well as the gold concentration of the sample was determined gravimetrically from the prill. This is not commonly done now unless it is very high grade, because the silver is more reliably determined by other methods.

The gravimetric step involves lifting the prill from the cooled cupel, cleaning it and flattening it with a small hammer and anvil. If silver is to be determined gravimetrically, the prill is weighed. It is then treated with hot, dilute nitric acid to dissolve the silver, leaving the gold. The metallic gold is washed, annealed, cooled and weighed. This separation of the silver from the gold is called “parting”. The silver concentration can be calculated by difference, corrected for the inquart and reported along with the gravimetric gold determination.

Many geoscientists insist on the gravimetric gold method, but this is an advantage only when gold values are above about 10 mg/kg (ppm). Current instrumental finishes are capable of much lower detection limits than this. In addition, below about 10 mg/kg, instrumental precision is significantly better than that of the microbalances used to weigh the gold in the gravimetric finish.

Platinum and palladium cannot be determined gravimetrically.

4.3.5 Instrumental Finish

If the gold (or platinum and palladium) concentration is to be determined instrumentally rather than gravimetrically, one of two procedures is used. If the instrumental finish is instrumental neutron activation analysis (INAA), the prill is picked from the cupel, cleaned and submitted to an INAA facility.

If the finish is AAS, ICP-AES or ICP-MS, the prill is picked out of the cupel and placed in a test tube. It is dissolved in aqua regia, diluted to volume and introduced into the instrument for measurement. The detection limit for gold by AAS is in the low ppb range and sub-ppb (if using ICP-MS), assuming reagent blanks are sufficiently low.
4.3.6 Screen Metallics

This method, also known as “pulp metallics,” is used when coarse metallic gold is present in the ore. In this case, it is extremely difficult to get a reproducible result from standard sample preparation fire assay techniques. The screen metallics method is then used to obtain better reproducibility. Because of the labour-intensive nature of this technique, and the extra analyses required, the geoscientist should expect a significant surcharge when requesting this procedure.

This process consists of crushing and coarse grinding (to about 150 or 100 mesh, 106 or 150 µm) a weighed large portion (1 kg is common) of the sample. The sample is then passed through a 100-mesh screen. The oversize portion (the sample is generally ground to a target weight about 30g of oversize) is weighed and analyzed separately. The undersize is weighed and analyzed (usually in duplicate). The weights of the oversize plus the undersize portions will be less than the original weight due to the inevitable formation of dust and its loss during crushing, pulverizing and sieving. The concentration of gold in the original sample is calculated and reported, ensuring the correction for dust loss (usually assumed to be part of the undersize fraction).

This same technique can be used with samples containing other native metals such as copper, silver, palladium and platinum.

4.3.7 Nugget Effect (see also Section 2.6)

The problems arising from the presence of metallic particles are commonly known as the “Nugget Effect”. Nugget Effect is caused when particles of a mineral with a high concentration of the element to be determined are sparsely distributed in a sample (such as in the case of native metals or alloys being unevenly distributed in the sub-sample and test portions). This results in a test portion with one or more of the native metal particles having much higher results for that element than other test portions with fewer particles. The potential for problems with reproducible results in the case of gold analyses can be seen in Table 4.4.
Table 4.4: “Nugget Effect” of gold particle sizes versus sample weight.

<table>
<thead>
<tr>
<th>GOLD GRAIN SIZE (CUBES)</th>
<th>WT. OF ONE GOLD PARTICLE (MG)</th>
<th>CHANGE IN CONC. (PPM) 15 G SAMPLE</th>
<th>CHANGE IN CONC. (PPM) 30 G SAMPLE</th>
<th>CHANGE IN CONC. (PPM) 50 G SAMPLE</th>
<th>CHANGE IN CONC. (PPM) 100 G SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 (2 mm)</td>
<td>88</td>
<td>5870</td>
<td>2930</td>
<td>1760</td>
<td>879</td>
</tr>
<tr>
<td>20 (850 mm)</td>
<td>11</td>
<td>733</td>
<td>367</td>
<td>220</td>
<td>110</td>
</tr>
<tr>
<td>28 (600 mm)</td>
<td>4</td>
<td>267</td>
<td>133</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>48 (300 mm)</td>
<td>0.50</td>
<td>33.3</td>
<td>16.7</td>
<td>10.0</td>
<td>5.01</td>
</tr>
<tr>
<td>65 (210 mm)</td>
<td>0.17</td>
<td>11.3</td>
<td>5.67</td>
<td>3.40</td>
<td>1.70</td>
</tr>
<tr>
<td>100 (150 mm)</td>
<td>0.061</td>
<td>4.07</td>
<td>2.03</td>
<td>1.22</td>
<td>0.61</td>
</tr>
<tr>
<td>150 (105 mm)</td>
<td>0.021</td>
<td>1.40</td>
<td>0.70</td>
<td>0.42</td>
<td>0.21</td>
</tr>
<tr>
<td>200 (75 mm)</td>
<td>0.0078</td>
<td>0.52</td>
<td>0.26</td>
<td>0.16</td>
<td>0.080</td>
</tr>
<tr>
<td>325 (45 mm)</td>
<td>0.0017</td>
<td>0.11</td>
<td>0.057</td>
<td>0.034</td>
<td>0.017</td>
</tr>
<tr>
<td>400 (38 mm)</td>
<td>0.0010</td>
<td>0.067</td>
<td>0.033</td>
<td>0.020</td>
<td>0.010</td>
</tr>
<tr>
<td>20 mm</td>
<td>1.56x10^-4</td>
<td>0.010</td>
<td>0.005</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>5 mm</td>
<td>2.41x10^-6</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>2 mm</td>
<td>1.56x10^-7</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

4.3.8 Nickel Sulphide Fire Assay

The nickel sulphide fusion is used to determine platinum group elements (PGE). It is slow, expensive and involves the use of highly toxic carbonyl nickel powder. Its advantage is that, when combined with ICP-MS detection, it gives reliable results for all of the PGE at low detection limits because these metals are quantitatively extracted into the nickel button.

The method involves mixing nickel powder, sulfur, sodium carbonate, borax and sample pulp together in a crucible and fusing it at over 1000°C for an hour. As the NiS matte button forms, it extracts the PGE from the sample. There are several options for determining their concentrations:

- Powder the button and put it into a container for INAA finish.
- Dissolve the powdered matte button in HCl, filter off the PGE-containing residue on a membrane, dissolve it in aqua regia and finish with ICP-AES or ICP-MS analysis.
- Dissolve the powdered matte button, add tellurate and reduce this to elemental tellurium to concentrate the PGE. The PGE are analyzed using ICP-AES or ICP-MS after digesting the tellurium precipitate in aqua regia.
The advantage of the nickel sulphide collection is that the PGE are concentrated more effectively than is the case with the standard lead-based fire assay procedure. Thus it is more accurate. This is especially true for osmium, ruthenium and iridium. Detection limits using ICP-MS are at the sub-ppb level.

4.4 ANALYTICAL METHODS AND INSTRUMENTATION

Once a geological sample has been crushed, sub-sampled (if required) and pulverized, the next stage is the actual elemental determination. A portion of the sample is weighed and then treated as appropriate for the final instrumental determination. In the case of XRF and INAA, the pulverized sample can be measured directly. In most instances, however, the sample must be digested by one of the techniques described in Section 4.2.

4.4.1 Atomic Absorption Spectrometry (AAS)

This technique was introduced commercially in the early 1960s and it is still a common analytical tool. The name “atomic absorption” is an indication of how it works.

Samples are introduced in a liquid state through a nebuliser into a flame.

- The flame conditions are adjusted so that the target element atoms in the sample are converted into the ground (unexcited) elemental state.
- Light from a light source (commonly a hollow cathode lamp or an electrodeless discharge lamp) made of the target element is shone through the flame.
- The instrument response is calibrated with calibrating solutions to relate the absorption signal to the target element concentration in the sample.
- The ground state atoms of the target element that are in the flame absorb some of the light.
- The amount of light absorbed is a function of the number of absorbing atoms and thus of the concentration of that element in the sample.

A modification of the instrument is the introduction of a graphite furnace to replace the flame as a source of ground-state target element atoms. This lowers the effective detection limit of AAS from the ppm range to the ppb range.
Another modification is the introduction of hydride generation techniques for the analysis of relatively insensitive elements such as arsenic, antimony, tellurium, selenium and a few others. In this modification, the volatile hydride (for example arsine – AsH₃) is reduced from the liquid sample solution. The hydride is swept along in an inert gas stream into a heated cell in the path of the light from the lamp. The hydride molecules decompose, and the target element atoms in the light path absorb the light from the lamp thus resulting in a signal. The combination of hydride generation with the use of an electrodeless discharge lamp gives much lower detection limits for these elements than does flame AAS.

There are numerous advantages to atomic absorption spectrometry (AAS).

- It is less expensive than alternative methods.
- It can give very precise and accurate results from ppm to percent concentration levels.
- AAS can be used over a wide concentration range – from sub- ppm up to percent levels with dilutions and other method modifications.
- Flameless AAS can achieve detection limits in the low ppb range.
- Most metallic elements can be run on AAS.
- When determining five or fewer elements per sample, it can give fast results.
- There is little inter-element spectral interference.
- Many AAS instruments can be operated in the atomic emission mode to overcome the lack of a specific hollow cathode lamp.
- It can tolerate a high level of dissolved solids in solutions.
- Automatic sample changers and diluters enable reduced labor costs.
- The operating technicians do not need to have extensive training.
- It is robust so can be appropriate for remote mine-site laboratories.

Some disadvantages exist.

- It is slow and cumbersome for multi-element packages and detection limits are higher than ICP-AES or ICP-MS.
- The sample must be in solution to be analysed quantitatively. This means that there can be possible loss or incomplete dissolution of some elements due to digestion procedures.
- The REE can be run by AAS but their detection limit is very poor.
- AAS has a short linear response range and sample dilutions are often required.
• AAS instrumentation requires frequent calibrations and drift checks.
• Chemical and spectral background interferences can be a problem.
• An element-specific hollow cathode lamp is required to provide the light beam that will be absorbed for each element to be measured (some lamps are multi-element but their intensity is lower).

4.4.2 Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is a powerful technique for the analysis of geological samples, due to its high throughput and multi-element capabilities47, 48. ICP-AES is often referred to as ICP-OES (Optical Emission Spectroscopy) or even ICP, although, with the development of ICP mass spectrometry, “ICP” is ambiguous and should not be used. Most commercial laboratories employ ICP-AES instruments that measure virtually all elements simultaneously.

ICP-AES uses the ICP as an energy source to excite atoms and ions. The standard or sample is introduced by pneumatic nebulization into an argon plasma generated in a radio frequency field and is thus excited. The high temperatures of the plasma causes the sample to atomize and ionize. As the ions return to the ground state, they emit light at characteristic wavelengths. The intensity of the light is measured using an appropriate detector. Polychromatic radiation (the light) passes into the spectrometer, where the light is directed onto an Echelle diffraction grating. This high resolution grating splits the light into its constituent wavelengths, with each wavelength being specific to a certain element. The diffracted light intensity, unique to each element, is measured using two segmented-array Charge-Coupled-Device (CCD) detectors (one designed for the ultraviolet range and one for the visible range of the electro-magnetic spectrum). By comparing the intensities of the wavelengths for each element in the sample with those in a standard containing known quantities of each element of interest, the concentrations of those elements in the sample are determined.
ICP-AES has many advantages over AAS techniques:

- All elements in an ICP package are determined in one aspiration. This is advantageous in terms of analysis time and sample consumption.
- The large linear response (e.g. measurement range) of ICP-AES minimizes the number of calibration standards and the amount of dilution required.
- The excellent resolution of the Echelle diffraction grating means that there is very little inter-element spectral interference.
- The instruments are stable and thus long term variability is minimal, facilitating extended automated runs using sample changers.
- Virtually all elements, the REE and S and P can be determined.
- It can give very precise and accurate results from ppm to percent concentration levels on the same solution with no additional calibration.
- Interferences from chemical matrices are minimal because the high plasma temperature readily ionizes molecules.
- Only light enters the instrument, so the optical system does not get “dirty”. Thus strong acid digestions can be analysed as well as fusion matrices. This leads to lower detection limits, more versatile methodology and less contamination.
- Automatic sample changers and diluters reduce labor costs.

There are some disadvantages to using ICP-AES instrumentation:

- The nebulizer system can not handle high dissolved solid solutions as easily as AAS.
- The instrumentation is much more expensive than AAS.
- Instrument technicians need to be well trained to be able to operate and maintain the instruments properly.
- To maintain instrument stability, there must be good environmental controls in the laboratory (temperature, humidity, electrical supply and others).
- If the instrument does not have the high-resolution Echelle grating monochromator, inter-element interferences must be addressed. This increases the complexity of instrument set-up significantly.
- Typically, the sample has to be in solution to be analysed quantitatively. This means that analysis can be compromised due to the digestion procedure and the possible loss or incomplete dissolution of some elements.
4.4.3 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

The second plasma-based technique used in the analysis of geological samples is Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). ICP-MS has the advantage of offering very low detection limits (sub-ppb) for elements. In addition, the instruments and the data produced are reliable and well accepted.

ICP-MS uses the plasma as an efficient heat source for the formation of positive ions. The plasma is positioned horizontally and the ions enter the system through sampler and skimmer cones which are generally made of nickel. These cones select a small portion of the ion beam and allow it to enter the mass spectrometer. A vacuum pump extracts the rest of the sample. The spectrometer consists of a lens system to focus the ion beam, a quadrupole mass spectrometer to isolate the ion of interest and a detector to measure these ions. These are housed in the analyser region that is kept under high vacuum by a turbo-molecular pump (typically 10^-5 Torr or less).

Once in the spectrometer, the ion beam is focused using a cylinder to which a positive voltage is applied. It forces the ions to the central axis. The ion beam then passes into the quadrupole mass spectrometer, where ions are separated based on their mass-to-charge ratio. By changing the frequency on the quadrupole, ions are deflected off-axis by a change in resonance. Only the ion of the correct mass will pass through the quadrupole and hit the dynode detector. The detector is often a two-stage detector that allows the measurement of small and large signals. This gives the ICP-MS a wide analytical range. The first-stage measures high concentrations directly, while the second stage has an electron multiplier for amplification of small signals. A cross-calibration between the two stages enables the measurement of sub part per trillion and part per million concentrations using the same calibration. By measuring the signal produced at a specific mass and comparing it with the signal produced from a standard of known concentration, the concentration of an element in the sample can be determined.
ICP-MS has become widely used in the analysis of geological materials for several reasons:

- The sensitivity of the instrument allows for the determination of many elements in the sub-ppm range (e.g. rare earth elements).
- The multi-element capabilities allow for the analysis of a wide range of elements at different concentration levels in one analysis.
- Interferences, although present, are predictable and easily overcome.
- The selection of elements that can be determined by ICP-MS is very wide and only a few lie outside its capabilities.

The technique is subject to some limitations:

- As a portion of the sample actually enters the instrument, ICP-MS cannot handle the level of dissolved solids of the ICP-AES and many samples require dilution before analysis.
- Target elements must form positive ions. Some elements ionize more easily than others and consequently will be more easily determined.
- The instrument measures elements sequentially, as the quadrupole “scans” by changing frequency. The larger the number of target elements, the longer the analysis will take.
- Because of the very low detection limits reached by ICP-MS, potential sources of contamination must be monitored closely (e.g. glassware, lab environment, reagent quality).

4.4.4 X-ray Fluorescence (XRF) Spectrometry

XRF finds its main application in the determination of major and minor elements - those that make up 97% of most rocks.

X-rays form part of the electromagnetic spectrum with wavelengths from 0.1 to 50 Angstroms (Å) - i.e. photons in the energy range of 0.25 keV to 12 keV. This energy range is higher than that of the visible to UV range used for AAS and ICP-AES spectroscopy techniques. While the electronic transitions of the absorption (AAS) and emission (AES) instruments are from outer valence electrons, those measured in XRF are the much higher energy transitions of electrons in orbitals close to the nucleus of the atoms (k, l and m shells).
The name X-ray Fluorescence is a description of how these analyses are accomplished. The sample is exposed to a primary beam of X-rays generated by a source (usually an X-ray tube or a radioactive element). The atoms of the sample absorb specific wavelengths from the primary beam and become excited. When returning to their ground electronic state, they emit secondary X-rays specific to each element in the sample. The secondary X-rays are separated on the basis of wavelength or energy (in a wavelength or energy dispersive instrument respectively). The intensity of each wavelength is proportional to the concentration of its element in the sample. The concentration of the target element is determined by a calibration that relates X-ray intensity to concentration through a set of calibration standards.

Sample preparation is rapid and simple and in many cases non-destructive. The simplest method is referred to as the pressed powder briquette.

With this technique, a portion of the pulverised sample is placed in a mould with a backing material such as boric acid. This is then compressed using pressures of 10 tonnes or more to form a solid briquette. A binder such as polyvinyl alcohol can also be added to the sample. After mixing, the pulp is compressed and dried. The latter method forms a more stable sample briquette. Typical preparation time is 1-2 minutes per sample.

Alternatively, the sample can be fused to form a glass disc\(^6\). The flux used is usually a mixture of lithium metaborate and lithium tetraborate or some mixture of lithium carbonate and lithium borate. Typically, a sample-to-flux ratio of 1 to 5 is used and the fusion is carried out in Pt-Au alloy crucibles at 1100°C. On completion of the fusion process, the melt is poured into a mould and rapidly quenches to produce a solid glass disc, which is ready for immediate analysis.

The advantages of the glass disk method include:

- Most elements at major and minor concentrations can be determined on the disc.
- Small sample weights can be used – 0.4 grams or less.
- The flux is universal for most matrices.
- Analysis time is fast.
- Synthetic standards can be cast for unique sample matrices.
- Automated fusion systems are now available.
- Discs can be stored indefinitely for re-analysis.
As with all methods, there are disadvantages but most of these can be controlled or eliminated:

- Refractory minerals are sometimes slow to dissolve during fusion.
- High sulphide samples must be roasted prior to fusion and this can cause losses.
- Dilution adversely affects the detection limits in trace analysis.
- The Pt/Au alloy crucibles and moulds are expensive and are easily damaged by samples containing high levels of S, As and Sb.
- During borate fusion, microsegregation can occur.
- Buttons can break.
- Samples containing high levels of sulphide minerals do not fuse readily.

4.4.5 Instrumental Neutron Activation Analysis (INAA)

When samples are exposed to neutrons in a reactor, the nuclei of some atoms interact with the incoming neutrons to form radioactive isotopes (radioisotopes). Instrumental Neutron Activation Analysis (NAA) relies on changes in the nuclear configuration of the sample rather than changes in the electron shells. As the nucleus is extremely small (one ten thousandth of the diameter of the atom itself), a large number of neutrons must bombard the sample (neutron flux) to achieve sufficient activation – hence the use of a nuclear reactor. Even so, most of the neutrons pass straight through the sample and only a fraction of one percent of the total atoms are activated.

The radioisotopes generated by bombardment are unstable and begin to decay at a constant rate which is defined by their half-life. This half-life may range from seconds to years. This decay is often accompanied by the emission of high energy gamma rays. The energy levels of these rays are distinctive for each radioisotope and so, by measuring the gamma ray energy spectrum with a high resolution detector linked to a multi-channel analyser, a nuclear fingerprint of the elements in the sample is built up. As both the elapsed time after irradiation and the half-lives of the radioisotopes are known precisely, it is possible to accurately determine the concentrations of the original elements in that sample based on a master calibration that relates all element activity to a single measurement of neutron flux.
The advantages of INAA include:

- It is a multielement technique that can accommodate a 30g or larger sample.
- It is simple to do. There are only three steps – sample encapsulation, activation and analysis.
- It can measure as low as 5 ppb Au with no sample treatment or preconcentration.
- It can report 28 elements including the gold pathfinder elements As, Sb and W.
- It gives a total elemental analysis.
- One activation permits the determination of numerous elements at low (ppb to ppm range) concentrations at or below crustal abundances.
- It is remarkably free of interferences and those that exist are well known and can be avoided.
- The analysis is non-destructive and, after allowing the radioactivity to decay, the sample can be archived or used for subsequent analyses.

The disadvantages of the method include:

- It requires access to a nuclear reactor as a neutron source.
- The samples are radioactive after irradiation and proper radiation protection is mandatory until the activity has decayed to a safe level.
- Samples high in uranium can not be activated.
- Samples high in carbon give poor detection limits because carbon absorbs neutrons.
- It cannot measure some base metals (e.g. Pb), and it is difficult to measure others (e.g. Cu, Na).
- Turnaround is slowed by the need to wait for some of the short-lived isotopes to decay before the sample can be counted. Typically counting can not begin until 7-8 days after irradiation.

4.4.6 Classical Umpire Analysis

Classical umpire analysis is used for the analysis of high value materials such as base metal concentrate, gold and silver bullion or cathodes of copper, nickel etc. (see also Section 2.5). In these cases, precision and accuracy are critical and must be tightly controlled for sampling and analytical work. If the buyer and seller do not agree within the concentration range established by contract (splitting limits), a portion of the sample is sent to a mutually agreed upon umpire analysis laboratory whose result is accepted.
4.4.6.1 Gold and Silver Bullion Analyses

The reliable analysis of bullion is dependent on proper sampling. Once the molten bullion is poured into a mold, it begins to quench from the edge to the centre. Thus the portion in contact with the mold walls becomes solid first. The highest melting point elements will freeze first, concentrating the lower melting point elements in the remaining melt. The bar thus changes in composition from the outside edges in towards the upper centre.

As a result, bullion should be sampled while it is still molten. The most reliable technique is known as pin sampling and requires the use of a vacuum sampler. This consists of a thin evacuated glass tube. When dipped into the molten gold, the tube breaks and the molten metal is sucked into the tube. The tube is withdrawn and the metal solidifies as a thin rod or “pin” which becomes the sample. This step is usually done at least twice to give replicate samples.

Gold bullion samples are usually about 0.5g in size and are cupelled with enough Ag to give a Ag:Au ratio between 2:1 and 4:1. This will result in a successful parting. The bead remaining after cupellation is rolled into a very thin strip called a coronet. The Au result is obtained by parting (dissolving the silver with nitric acid to leave the gold) the coronet in dilute nitric acid. This dissolves Ag but not Au, and the remaining Au is weighed. A sample of proof Au of the same weight as the sample is treated at the same time. The sample result is corrected for any gain or loss (called the surcharge) according to the result from the proof gold. Samples are usually run at least in duplicate.

Silver bullion analyses can be analyzed by cupellation, by chemical titration, or by a combination of chemical titration and instrumental techniques. The cupellation process is subject to volatilization errors that must be corrected for. A piece of Ag (called a “proof”) of a weight similar to that anticipated for the weight of Ag in the sample is cupelled beside the sample. The sample weight of Ag is corrected for a loss as determined by the weight loss of the proof Ag cupelled. As in the case of Au bullion, the sample is run at least twice.
The errors inherent in the cupellation method can be avoided by the wet chemical method. This method, commonly known as the Gay Lussac Method, consists of dissolving a 1 g sample of bullion in nitric acid. About 99.8% of the Ag is precipitated with 100 ml of a standardized NaCl solution. After this stage, the finish can be either titration or instrumental.

For the titration method, a 1/10th dilution of the original NaCl solution is added gradually until AgCl is no longer precipitated. This is determined by watching closely for a slight cloudiness due to an AgCl precipitate forming after the addition of a few drops of the dilute NaCl solution. The instrumental finish involves measuring the remaining un-precipitated Ag with AAS or ICP-AES after the 99.8% of the Ag has been precipitated with the NaCl solution. The total Ag result is then reported.

4.4.6.2 Base Metal Concentrate Umpire Analyses

Sampling for base metal concentrate shipments has been addressed in many books and articles on sampling. It will not be discussed in this manual. In all cases, it is necessary to measure the moisture content of the samples and correct the results accordingly.

The analysis of base metal concentrates has not substantially changed over the last decade and most methods used are published as standard methods from organizations such as ISO, IEC, ASTM and British Standards. Examples of such standard methods are:

- Zinc concentrates: ISO 13658 – EDTA Titration
- Copper concentrates: ISO 10469 – Electrogravimetric analysis
- Copper cathode: ASTM B-115
- Lead concentrate: ISO 11441 – EDTA after precipitation of PbSO₄
- Nickel concentrate: ISO 12169 – Classic DMG separation followed by electrogravimetric analysis
- Molybdenum ores: BS 6200-3.19.3 and International Molybdenum Association (IMOA)
- Iron ores: ISO 2597 – Dichromate titration
- Cobalt concentrates: ISO 11653 – Volumetric titration
5 PETROLOGY AND MINERALOGY FOR MINERAL EXPLORATION AND MINING

Mineralogical studies are a key adjunct to geochemical analysis. Together, they yield a full petrological understanding of rocks and soils. They can indicate where, and in what form, elements are located and what reactions could have taken place in the transport and capture of these elements into mineral matrices. Numerous case histories exist where identification of a particular mineral species has provided a definitive vector to mineralization. The absence of a mineral can avoid wasting exploration dollars. While there is an added cost of mineralogical services, it is very small compared to the overall exploration budget and it can add considerable value to validating data obtained by geophysical or geochemical methods.

Mineralogy is a fundamental component of exploration models, environmental investigations and the development of metallurgical flowsheets. The success of any of these applications is rooted in understanding the ore alteration and primary mineral suites and their textures and deportments. This has been a key factor driving the development of the latest generation of automated mineralogical instrumentation.

A wide array of other tools are available for mineralogical studies from the macro to the atomic scale. Described below are just a few of the more common methods available.

5.1 ROCK AND MINERAL IDENTIFICATION

The most basic examination of rocks is in a thin or polished section. These are examined by a mineralogist using a polarized light (petrological) microscope either in reflected or transmitted light modes. These petrographic studies provide information on mineralogy and textures for rock classification and genesis.
5.1.1 Modal Analysis

Mineral modal abundances are obtained using point counting methods usually based on 500 points and can be displayed as pie charts. Ore microscopy has particular application in the field of extractive metallurgy. This can yield detailed knowledge of the physical relationships between ore and gangue minerals, vitally important when determining the appropriate extractive processes required to optimize metal recovery.

5.1.2 High Definition Mineralogy

High-Definition Mineralogy is the quantitative study of minerals, using technologies such QEMSCAN™, X-ray diffraction analysis (XRD), image analysis and other automated techniques. Parameters such as mineral abundance, chemistry, grain size, texture, deportment, association and liberation are determined in a statistically robust manner as opposed to traditional manual methods such as point counting or optical petrography which are more subjective and time intensive. High Definition Mineralogy data can be quantitatively compared with similar data from different tests and the interpretation and use of such data adds significant value to many applications, and especially for metallurgical testing. Systems such as QEMSCAN™, electron microprobe, image analysis and quantitative XRD are mere tools - High Definition Mineralogy is the product. Therefore it is extremely important that the mineralogical laboratory employ experts to both ensure a quality product and, from grassroots exploration to production support, provide significant interpretive value.

5.1.3 Automated Digital Imaging Systems (ADIS)

Sized mineral products can be examined optically using a petrological microscope equipped with an automated digital imaging system (ADIS). ADIS assigns imaging thresholds based upon colour and intensity to individual mineral species. Minerals such as chalcopyrite, pyrrhotite, galena, sphalerite, magnetite, hematite and pyrite are easily measured. Silicate minerals are grouped as non-opaque gangue minerals and are differentiated from the epoxy background using a coating technique.
5.1.4 SEM/EDS

Improved resolution can be acquired from backscattered electron (BSE) images produced by electron beam instruments (computer-controlled scanning electron microscopes with energy dispersive analyzers (SEM/EDS) or the electron microprobe) simultaneously with elemental mapping data from the EDS. Elemental X-ray maps of elements can be combined with BSE images allowing more detailed and extensive petrographic examination. For example, this can allow the identification of fine-grained alteration minerals or poorly crystalline rocks such as laterites, to facilitate accurate classification.

When equipped with image analysis capability and advanced interpretive software, these instruments are capable of precise and accurate automated quantitative data based on hundreds of thousands of points to determine bulk mineral content or modal analysis, textural studies, mineral associations, a range of mineral liberation parameters and trace mineral identification. These data are used to provide metallurgically important outputs such as mineralogically limiting grade-recovery and ore mineral liberation curves. They assist in establishing grind size criteria and other mineral processing factors, thus providing a powerful linking of mineral textures to metallurgical performance.

5.1.5 X-Ray Diffraction

Basic mineral identification is also done by X-ray diffraction (XRD). This provides rapid identification of minerals and is useful for identifying fine gained phases which are difficult to identify optically, SEM/EDS or QEMSCAN™. XRD analysis can be performed on a pulverized sample and this is an easy way to obtain mineralogical data for chemical analysis. Until fairly recently, quantitative data were difficult to obtain, but this is changing with Rietveld quantification methods and powerful computers.

XRD is also the preferred method for clay mineral identification particularly swelling clays such as smectites. Clay mineralogy has sometimes provided a critical indicator of the presence of mineralization. For instance, exploration for uranium in the Athabasca Basin has been guided by alteration mineral assemblages and clay mineral species.
5.1.6 QEMSCAN™ Modes of Analysis

QEMSCAN™, which is the most powerful of the tools available for process mineralogy, is an acronym for Quantitative Evaluation of Materials by Scanning Electron Microscopy, a system that is configured to measure mineralogical variability based on chemistry at the micrometer-scale. QEMSCAN™ utilizes both the back-scattered electron (BSE) signal intensity as well as an Energy Dispersive X-ray Signal (EDS) at closely spaced measurement points on the surface of polished grain mounts. It thus makes no simplifications or assumptions of homogeneity based on the BSE intensity, as many mineral phases show BSE overlap. EDS signals are used to assign mineral identities to each measurement point by comparing the EDS spectrum against a mineral species identification program (SIP) or database. Up to a 100,000 data points may be analysed in less than 1 hour. There are two general types of measurement: those using the linear intercept and those based on particle mapping.

Bulk mineral analysis (BMA) is performed using the linear intercept method, and is used to provide statistically abundant data for speciation and mineral distribution. The electron beam is rastered at a pre-defined point spacing (nominally 3 micrometers, but variable with particle size) along several lines per field, and covering the entire polished section at any given magnification. This measurement provides a robust data set for determination of the bulk mineralogy, with mineral identities and proportions, along with grain size measurements.

The Field Stitch (FS) mode of measurement also uses the linear intercept method to map a core sample that has been mounted as a polished section. It collects a chemical spectrum at a set interval within the field of view. Each field of view is then processed offline and a pseudoimage of the core sample is produced.

Particle mapping modes including Particle Mineral Analysis (PMA), Specific Mineral Search (SMS) and Trace Mineral Search (TMS) collect information about the spatial relationships of minerals including liberation and association data. They also provide a visual representation of mineral textures. The particle mapping modes of measurement allow for advanced analysis of the minerals of interest, including grade vs. recovery relationships and mineral release curves.
PMA is a two-dimensional mapping analysis aimed at resolving liberation and locking characteristics of a generic set of particles. A pre-defined number of particles are mapped at a point spacing selected in order to spatially resolve and describe mineral textures and associations. This mode is often selected to characterize concentrate products, as both gangue and value minerals report in statistically abundant quantities to be resolved.

SMS is a modified PMA routine in which a phase that occurs at minor to trace levels can be located by thresholding of the back-scattered electron intensity. SMS assumes target phases will be present in every field; any accompanying phases of similar and higher brightness are also mapped. This mode of measurement would be selected in ores of low sulphide grade, searching specifically for particles containing sulphide minerals.

Trace Mineral Search (TMS) is an additional mapping routine, where a phase occurring as a trace constituent can be located by thresholding the back-scattered electron intensity. TMS assumes target phase/s will not be present in every field – a rapid scan of each field is used to determine if the target phase is present. Barren fields are rejected, thus increasing analytical efficiency. The outputs are otherwise identical to the SMS routine. This mode of measurement is often used for gold or PGE ore types, or trace minerals such as molybdenite.

In the SMS and TMS modes results pertain only to the target minerals. PMA must be selected if quantitative gangue characterization is required. For example, in some sulphide ores, it may be more efficient to reject barren pyrites in favour of copper-bearing minerals. However, the data captured in this manner will not reflect the true pyrite content, as only the pyrite associated with the copper-bearing minerals will be represented.

5.2 MINERAL CHEMISTRY

Mineral chemistry can play an important role in exploration programs. The use of kimberlite indicator mineral chemistry in identifying diamond bearing kimberlites and favourable mantle geotherms for diamond occurrence and grade prediction is a classic example. The majority of these data are generated by electron microprobe but, when only major element chemistry are required, SEM/EDS can provide rapid and acceptable data. The addition of a wavelength dispersive (WD) spectrometer to the SEM allows acquisition of good quality minor and trace element data.
Frequent quality control (QC) checks (up to 30% of the analytical run) are normally performed as part of the routine microanalytical protocol. Silicate and oxide check standards similar in composition to the minerals being analyzed are used. Blank check samples (such as sodium in synthetic rutile) and duplicate grain analysis in a second run can also be performed. Previously analyzed minerals can also be used as QC checks. In this case, it is best if compositions are verified at other microprobe facilities. Some laboratories participate in the Open University GeoPT round robin for electron microprobe labs.

Trace element determination has also relied on proton probe (PIXIE) or ion probe (SIMS). Rapid development in laser ablation ICP-MS technology is also enabling easy acquisition of good quality trace element data for a large number of elements in minerals.

5.3 EXPLOMIN™

EXPLOMIN™ is a mineralogy package done on the QEMSCAN™ (Quantitative Evaluation of Minerals via Scanning Electron Microscopy). The measurements are done on polished sections of core or crushed material. EXPLOMIN™ provides the routine, automated documentation of mineralogy, alteration and texture on core or crushed samples, for a statistically robust comparison. The data can then be used for 3D mapping and manipulation. EXPLOMIN™ supports the consistent logging of new and legacy core for:

- Ore, silicate and alteration assemblage mapping
- Vectoring-to-ore using mineral and alteration suites
- Reinterpretation of exploration models and their application
- Informing metallurgical scoping studies
- Due diligence on logging prior to acquisition
- Environmental planning
- Mineralogy (primary, alteration and ore suites)
- Textures (genetic, alteration, metamorphic, ore)
- Metallurgical liberation and recovery
- Environmental parameters

EXPLOMIN™ can also be used to define domains for geometallurgy, and can contribute to traditional metallurgical scoping studies.
5.4 GEOMETALLURGY

Geometallurgy is

- the geologically informed selection of a number of test samples for metallurgical testing.
- the distribution of these parameters through an orebody using an accepted geostatistical technique in support of metallurgical process modelling.

The distribution can be influenced by the geological structure of the orebody, because the geological environment can influence the distribution of metallurgical parameters.

Geometallurgy quantifies the variability of an ore deposit in terms of process parameters such as ore grindability, flotation kinetics and leach kinetics. The data are then applied to the deposit block model or the mine plan, typically through use of geostatistics. Risk profiles for many variables can then be calculated.

Geometallurgy complements, but does not replace, the traditional metallurgical approach during the development and operation of a mine. Geometallurgical information is used to:

- inform flowsheet design
- size equipment
- assist in plant design
- optimize plant and mine to plant performance
- forecast production and energy use over life-of-mine
- reduce risk during feasibility, preproduction and operation.

5.5 REFRACTORY GOLD

The extractive metallurgy of gold is controlled and often complicated by mineralogical factors such as:

- particle size
- mineral associations
- coatings
- presence of cyanicides, oxygen consumers and preg-robbers (mineral phases that remove gold from solution)
- presence of refractory gold minerals
- locking of submicroscopic gold in sulfide mineral structures
Understanding the deportment of refractory gold or gold locked in pyrite, arsenopyrite or other minerals in gold ores or mill products is critical to troubleshooting low gold recovery. Submicroscopic gold is a major form of gold in many refractory ores, particularly Carlin-type ores and some epithermal gold ores.

### 5.5.1 Gold Mass Balance

To determine the character of refractory gold and a mass balance between refractory and free-milling gold in a sample, a sequence of separations and analyses are performed to provide a complete overview of the mass balance of gold in the sample. While the protocol is complex, the sizing, pre-concentration and final concentration steps are crucial to yielding a sample large enough to be both statistically valid and still able to quantify the gold present in the sample.

Following gravity separation, the gold is characterized into 3 fractions: liberated gold, gold associated with sulphide minerals and gold associated with non-sulphide minerals. Gold associated with sulphide minerals can be further divided into microscopic gold and submicroscopic gold. Mineralogical analysis can be used for this characterization, depending on whether the gold is microscopic or submicroscopic.

A microscopic gold study will utilize the conventional analysis which includes fire assay, optical microscopy or High Definition Mineralogy. This can be used for any of the fractions except submicroscopic gold. An instrument called a SIMS (Secondary Ion Mass Spectrometry) characterizes the submicroscopic, gold component of the sample. For each major gold-bearing sulfide mineral (mainly pyrite and arsenopyrite), the gold content is determined by fire assay and Secondary Ion Mass Spectrometry (SIMS). Gold distribution in the sulphide minerals can also be determined by SIMS.
5.6 DIAMOND EXPLORATION SERVICES

5.6.1 Indicator Mineral Services

Materials processed for indicator minerals vary widely, ranging from till and alluvial samples, to beach sand and bedrock samples. As a result, there are a variety of flowsheets depending on the type of starting material. The basic flowsheet shown in Figure 5.1. It is designed to recover as wide a range of indicator minerals as possible, including diamonds and gold grains.

Typically, samples are wet screened after weighing. If analysis of the sample matrix is also required, all or part of the sample may be dried and screened to remove the -0.18mm material. This ensures the recovery of the clay-sized and finer material which can be critical hosts of mobile elements. Sample sizes can vary dramatically from a few hundred grams to 50-100kg in size. Often samples may have been pre-screened in the field to remove +2mm material to reduce transportation costs. An attrition mill may be used for sample disaggregation, particularly for clay-rich samples that may be indurated to some degree. Rock samples (usually 5-20kg) submitted for indicator mineral recovery are stage-crushed to -2mm. Stage crushing tends to yield a higher proportion of intact mineral grains. After screening, the sample is separated using heavy liquids.

Standard screen sizes for till samples are 0.85mm and 0.25mm. The screened -0.85+0.25mm fraction is dried and then fed to a Wilfley table fitted with a slurry pump which recirculates the tails. The table set-up parameters are adjusted to ensure that the complete heavy mineral portion of the sample is collected. If QC tests indicate inadequate heavy mineral recovery, the table tails will be processed through a Permroll magnet to recover any remaining magnetic minerals that might normally report to the heavy mineral concentrate. Most indicator mineral processing labs have access to an array of magnetic and electrostatic instruments that can be used for specific mineral separation processes.

The heavy mineral portion can then be acid washed prior to drying and processing in methylene iodide that has been diluted to a specific gravity (SG) of 3.1. Tetrabromoethane can be used if a lower specific gravity is preferred. After removal of ferromagnetic minerals with a hand magnet, the concentrate is divided into two fractions by screening at 0.5mm.
If the concentrate is large, 30g will be riffled out to speed processing. The remainder can be processed if needed or if the indicator mineral content is low.

A Frantz magnetic separator divides the sample into paramagnetic and non-magnetic mineral fractions. This helps indicator mineral picking as ilmenite and chromite are concentrated in the paramagnetic portion while the non-magnetic portion (also containing weakly paramagnetic grains) contains garnet, chrome diopside, olivine and other silicates. At each stage of the process, reject portions of the sample are dried, weighed and stored.

### 5.6.2 Indicator Mineral Selection

Mineral selection labs use high quality stereo microscopes with a variable 10 to 50 times zoom lens and daylight halogen fibre optic light sources. While recovery of the full suite of kimberlite indicator minerals, including diamond, is most common, some projects require recovery of a variety of minerals, including base metal indicator minerals, gold grains for morphological studies, zircon for mineral provenance studies, tourmaline from lamproite, and rutile from gold deposits. Occasionally fractions larger than 0.85mm or less than 0.25mm must be processed. Gold and PGE minerals can be concentrated by using a Superpanner to process silt sized (<0.063mm) fractions.
The surface textures of the kimberlite indicator minerals can be described. Descriptive parameters include mineral type, form, shape, lustre, clarity, surface texture and the degree of corrosion for chromites. Surface texture reports are often augmented by digital SEM images or photomicrographs.

Indicator mineral chemistry is determined by electron microprobe or QEMSCAN™ with calibrations based on well known standards (e.g. from the Smithsonian Institute & SPI) from a wide range of natural and synthetic minerals. Typically, it is recommended that 50-100 grains of key indicator minerals are analyzed per sampled lithology. Grain selection procedures include backscattered electron (BSE) imaging of altered diamond indicator mineral grains to analyze the non-altered core parts of chromite and ilmenite grains relevant to diamond-forming conditions.

5.6.3 Quality Assurance and Quality Control

The indicator mineral extraction process can be audited to the ISO/IEC 17025 standard by the Standards Council of Canada. Quality assurance procedures required include standard operating procedures for all aspects of the process and staff training. A Laboratory Information Management System can be used to provide detailed worksheets, batch and sample tracking including sub-sample weight, and labelling for all the products from each sample. Quality control procedures should include:

- Sample spiking with synthetic diamonds of SG 3.52
- Table tails audit with heavy liquids to verify complete heavy mineral recovery
- Balance and screen calibrations
- Quality control re-picking of 50% of samples
- Checking of picked indicator minerals by a mineralogist
- SEM-EDS checking of questionable grains (generally ilmenite).

5.6.4 Micro and Macro Diamond Extraction

Microdiamond recovery by caustic fusion is now a key part of diamond exploration programs. Minimum recommended sample sizes are 24 kg per specific lithological unit. Sample aliquots of 5-8 kg in size are dissolved in molten caustic soda in stainless steel fusion pots heated in kilns to 500 - 600°C. The molten mix is poured onto 0.105 mm screens and the residue is then washed and treated with acids. This leaves a small concentrate which is picked for diamonds. Microdiamond counts and weights should
be reported for each size class using a root-two progression of square mesh sieve sizes from 0.105mm up in accordance with CIM guidelines. Individual stones are measured (X, Y, Z dimensions) and described in terms of colour, clarity, percentage preservation and stone morphology. Key quality control procedures consist of spiking samples with synthetic diamonds and duplicate picking of the sample residues.

Kimberlite indicator minerals can be recovered from caustic fusion. The caustic fusion attack does not completely dissolve many refractory minerals such as picro-ilmenite, chromite, garnet, zircon and corundum and these can be picked for further study.

On a larger scale for mini-bulk samples, a dense media separation (DMS) plant is used, with either 1 t/hour or 10 t/hour capacity. These are used mainly for macro diamond extraction with a bottom screen size of 0.85mm or occasionally 0.5mm. DMS plants can also be used to extract gemstones such as ruby, sapphire or emerald.

5.7 MINERAL SANDS

A range of methods, including Wilfley tables, heavy liquid separations, Magstreams separators, and other magnetic separators are used to prepare heavy mineral concentrates. Microscopy plays a significant role in the evaluation of mineral sands. Grains are point-counted to determine the relative abundance of the economic minerals sought. Chemical analysis alone is not diagnostic because, for example, titanium could be present in at least four distinct mineral species.

The application of QEMSCAN™ technology to mineralogy methods has revolutionized the examination of mineral sands allowing rapid automated acquisition of identification, characterization and liberation data on a statistically valid number of grains.
6 SGS AUDIT POLICY - EXTERNAL 2ND PARTY AUDIT

6.1 POLICY SCOPE

This policy specifically applies to 2nd party audits, including reviews or inspections of SGS laboratories that “are conducted by parties having an interest in the organization, such as customers, or by other persons on their behalf” (ISO 19011)\(^5\). This policy has been written for the express purpose and guidance for SGS clients, their authorised representatives and SGS laboratory management. It details the practices as per ISO 19011 that are expected by SGS Minerals Services when clients and their representatives visit SGS facilities and people for the purpose of external review. SGS advocates transparency and accountability, and so encourages client review\(^5\), in accordance with ISO 19011. It is the responsibility of all SGS personnel to follow and adhere to this policy.

6.2 CONFIDENTIALITY

SGS requires that clients and their representatives to sign a confidentiality agreement prior to review. This must be signed by the SGS Minerals Services representative on-site. Refer to SGS Geochem Policy 2007-2.

6.3 AUDITOR IDENTIFICATION

Client representatives must provide documentation to support their identity and the client that they represent. A copy will be retained by SGS. ISO 19011 outlines in detail auditor competence. SGS is prepared to forsake this requirement if client representatives are able to identify affiliations with professional (geotechnical / scientific) bodies as an indication of their competence and qualification to conduct the review. Affiliations will be recorded by SGS.
6.4 PHOTOGRAPHS AND ACCESS

SGS allows photographs to be taken on the basis that no proprietary equipment, plant, systems, improvements and/or instructions are documented. Rulings will be made where necessary by the SGS Minerals Services representative. Photographs, as with all other documentation, must comply with ISO 19011 requirements for “fair representation”. SGS will allow unimpeded access to process and records only as they relate to a specific client. Auditors are to be escorted throughout the process by a senior representative of SGS Minerals Services.

6.5 HEALTH AND SAFETY

The auditor/client representative will be required to comply with all SGS OH&S requirements during the visit.

6.6 ADVANCE NOTICE

So that the auditor may be appropriately accompanied by a qualified senior representative of SGS Minerals Services, appropriate advance notice must be given of a review.

6.7 AUDIT OBJECTIVES, SCOPE AND CRITERIA

As per ISO 19011, an audit program/plan that specifies the objectives, scope and criteria of the audit is to be presented to SGS and discussed during an opening meeting. ISO 19011 also requires a closing meeting and a timely copy of the report. This report must reflect the advice and content provided so that SGS can understand the issues and, importantly, make appropriate corrective action. Upon receipt of an audit report, SGS will respond within 14 days.

6.8 AUDIT CONDUCT

The conduct of the audit ISO 19011 requires ethical conduct, fair presentation, due professional care, independence and an evidence-based approach.
7 CONCLUSION

Analytical information is vital at every stage of mineral development. Geoscientists need to work closely with geoanalysts to have a basic understanding of laboratory operations. We hope that this handbook has successfully provided a general introduction to geoanalysis and will stimulate further communication between the geoscientist and the analyst. The data generated by the analytical work will thus be fit-for-purpose and provide the reliability needed to make confident decisions throughout the life of a project.
8 ENDNOTES/REFERENCES


14 Ibid.

15 Ibid.


Paski, E., 2005 Canadian Mineral Analysts Annual General Meeting Workshop on Sampling


Ibid.


Ibid.


Figure courtesy of Lab Tech Essa, Australia, 2008.


40 Ibid.


51 The standard references are as follows:


ISO 19011:2002 – Guidelines for quality and / or environmental management encompasses audit and inspection.


Where review, here and throughout this policy, also encompasses audit and inspection.
## 9 APPENDICES

### 9.1 METAL OXIDE/METAL CONVERSION FACTORS

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9.3 FREQUENTLY REQUESTED EQUIVALENTS

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9.4 DRILL CORE SPECIFICATION

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9.5 GLOSSARY OF TERMS

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<tbody>
<tr>
<td>ADIS</td>
<td>Automated Digital Imaging System</td>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>ANU</td>
<td>Australian National University</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Minerals</td>
</tr>
<tr>
<td>BLEG</td>
<td>Bulk Leach Extractable Gold</td>
</tr>
<tr>
<td>BS</td>
<td>British Standard</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electron</td>
</tr>
<tr>
<td>CEM</td>
<td>Channel Electron Multiplier</td>
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<td>CHARGE</td>
<td>Sample Size</td>
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<tr>
<td>CIL</td>
<td>Carbon In Leach</td>
</tr>
<tr>
<td>CIM</td>
<td>Canadian Institute of Metalurgy</td>
</tr>
<tr>
<td>CIP</td>
<td>Carbon In Pulp</td>
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<tr>
<td>C/S</td>
<td>Counts Per Second</td>
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<tr>
<td>CV</td>
<td>Coefficient of Variance</td>
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<tr>
<td>DDH</td>
<td>Diamond Drill Hole</td>
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<tr>
<td>DIBK</td>
<td>Di-Isobutyl Ketone</td>
</tr>
<tr>
<td>DL</td>
<td>Detection Limit</td>
</tr>
<tr>
<td>DMG</td>
<td>Dimethylglyoxime</td>
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</table>
DMS Dense Media Separation
EDX Energy Dispersive X-ray Fluorescence
EDS Energy Dispersive Spectrometer
EDTA Ethylenediamine Tetraacetic Acid
FAAS Flame Atomic Absorption Spectrometry
FPD Flow Proportional Detector
GFAAS Graphite Furnace Atomic Absorption Spectrometry
GTA Graphite Tube Atomisation
HLS Heavy Liquid Separation
ICP Inductively Coupled Plasma
ICP-AES Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-OES Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS Inductively Coupled Plasma Mass Spectrometry
IEC International Electrical Commission
IMOA International Molybdenum Association
INAA Instrumental Neutron Activation Analysis
ISO International Standards Organisation
K Kelvin
LiF Lithium Fluoride
LIMS Laboratory Information Management System
LOI Loss on Ignition
MCA Multi-Channel Analyser
MIBK Methyl Isobutyl Ketone
MPD Mean Percentage Difference
NAA Neutron Activation Analysis
NATA National Association of Testing Authorities
PGE Platinum Group Elements
PTFE Polytetrafluoroethene (e.g. Teflon)
PVA Polyvinyl Alcohol
QA Quality Assurance
QC Quality Control
RAB Rotary Air Blast
RC Reverse Circulation
REE Rare Earth Elements
RF Radio Frequency
RNAA Radiochemical Neutron Activation Analysis
RSD Relative Standard Deviation
SD Standard Deviation
SEM Scanning Electron Microscope
TAP Thallium Acid Phthalate
TBE Tetrabromoethane
TMF Thallium Malonate Formate
UV Ultraviolet
XRD X-ray Diffraction
XRF X-ray Fluorescence
### 9.6 PERIODIC TABLE

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<td>Beryllium</td>
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<td>Sodium</td>
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### Lanthanide Series

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### Actinide Series

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<td>1.0971 ounces avoirdupois (av.)</td>
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<tr>
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<td>20 pennyweights (dwt.)</td>
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<tr>
<td>1 troy ounce</td>
<td>480 grains</td>
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<td>1 ounce (av.)</td>
<td>28.35 grams (g)</td>
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<td>1 pound (av.)</td>
<td>16 ounces (oz)</td>
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<tr>
<td>1 pound (av.)</td>
<td>453.59 grams (g)</td>
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<td>12 ounces (oz)</td>
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<td>1 pound (troy)</td>
<td>373.24 grams (g)</td>
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<td>29,166.6 troy ounces</td>
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<td>1 ton avoirdupois</td>
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<td>2000 pounds (av.)</td>
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<td>2240 pounds (av.)</td>
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<td>1000 kilograms (kg)</td>
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<td>0.001 milligrams per kilogram (mg/kg)</td>
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<tr>
<td>1 ppb</td>
<td>0.001 milligrams per litre (mg/L)</td>
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<tr>
<td>1 ppb</td>
<td>1000 parts per trillion (ppt)</td>
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### 9.8 THE ASSAY TON

1 ton avoirdupois = 29,166.6 troy ounces
1 mg: 1 assay ton = 1 ounce troy: 1 ton avoirdupois
1 ppm x 34.286 = 1 oz/ton

The term “assay ton” is derived from the historical assaying practice of weighing 29.166 g of sample for fusion during the fire assay process. Using this weight, a 1 mg bead of precious metal obtained at the end of the assay would correspond to one ounce per ton of that metal in the sample. This is because the ratio 1 mg : 29.166 g is the same as 1 ounce troy : 29,166 ounces troy. As shown in the table above, 29,166.6 ounces troy is 1 ton avoirdupois.
9.9 FIELD TESTS

There are some simple chemical field tests that can be used to test for different minerals.

- Dilute nitric acid can be used to test for sulfides. Drop some on a powdered specimen and watch for brown nitrous oxide fumes and/or the “rotten egg” smell of H₂S. This is a simple test to distinguish fool’s gold (pyrite or arsenopyrite) from gold.

- The presence of cobalt is indicated if a dilute nitric acid solution turns red or pink when placed on a powdered sample and brown with the addition of ammonia. The same treatment indicates copper if the nitric solution turns blue and then dark blue with the addition of ammonia.

- For a sample suspected to contain lead, treat with dilute nitric acid and then add dilute sulfuric or hydrochloric acid. The presence of lead is confirmed by a white precipitate.

- The “Zinc Zap” consists of two solutions, both poisonous (Reid 1969): Solution 1 (oxalic acid, diethylaniline, HCl) and Solution 2 (potassium ferriycanide) added in sequence on rock powder produce an orange to red coloured precipitate depending on zinc content. Copper produces an orange-brown precipitate. May be used as sprays on rock surfaces.

More complex tests can be performed for extractible metals (usually in silt or soil surveys). An acid extraction followed by the addition of a buffer solution such as ammonium citrate combined with hydroxylamine hydrochloride and dithizone or other complexing agent can result in a colour change. The colour is indicative of specific elements depending on the extraction, pH buffer and complexing agent conditions.