GEOCHEMICAL SAMPLING AND ANALYSES FOR ENVIRONMENTAL RISK ASSESSMENT USING THE WITS BASIN AS A CASE STUDY

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

Generally, and particularly in South Africa, there has been limited work done on the development of methodologies for determination of sample size and quantifying uncertainties in geochemical sampling and analyses. This, in turn may result in lack of confidence in the long-term predictions of geochemical modeling for Environmental Risk Assessment (ERA) and problems in obtaining approval of mining authorizations, water use licenses and mine closure plans.

This report addresses this deficiency in geochemical sampling and analyses and proposes two methodologies: (i) for quantifying uncertainties in geochemical sampling and analysis as a function of sample size and analysis and (ii) for determining the optimum sample size to ensure data quality.

The statistical analysis approach was adopted as the best method for sample size determination. The approach is based on the premise that “the size of the study sample is critical to producing meaningful results”. The size of the required samples depends on a number of factors including purpose of the study, available budget, variability of the population being sampled, acceptable error and required confidence level.

The methodology for estimating uncertainty is a fusion of existing methodologies for quantifying measurement uncertainty. The methodology takes a holistic view of the measurement process to include all the processes involved in obtaining measurement results as possible components / sources of uncertainty. Like the statistical analysis approach, the methodology employs basic statistical principles in estimating the size of uncertainty associated with a given measurement result. The approach identifies each component of uncertainty; estimates the size of each component and sums the contribution of each component in order to approximate the overall uncertainty value associated with a given measurement result.

The two methods were applied to Acid-Base Accounting (ABA) data derived from geochemical assessment for Environmental Risk Assessment of the West Wits and Vaal River tailings dams undertaken by Pulles and Howard de Lange Inc. on behalf of AngloGold Ltd. The study was aimed at assessing and evaluating the potential of tailings dams in the two mining areas to impact on water quality and implications of this impact in terms of mine closure and rehabilitation.

Findings from this study show that the number of samples needed is influenced by the purpose of the study, size of the target area, nature and type of material, budget, tolerable error and the confidence level required, among other factors. Acceptable error has an inverse relationship with sample size; confidence level and standard deviation have a positive correlation with sample size hence one can minimize error by increasing sample size. While a low value of acceptable error value and high confidence are always desirable, a trade-off among these competing factors must be found, given the fact that funds and time are normally limited.

The findings also demonstrated that uncertainties in geochemical sampling and analysis are unavoidable. They arise from the fact that only a small portion of the population rather than a census is used to derive conclusions about certain characteristics of the target population. This is further augmented by other influential quantities that affect the accuracy of the estimates. Effects such as poor sampling design, inadequate sample size, sample heterogeneity and other factors highly affect data quality and representivity, hence measurement uncertainty. Among these factors associated with sampling, heterogeneity was found to be the strongest contributing factor toward overall uncertainty. This implies an increased proportion of expenditure should be channelled toward sampling to minimize uncertainty.

Uncertainties can be reduced by adopting good sampling practices and increasing sample size, among other methods.

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Mr W Pulles	Pulles Howard & de Lange
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Mr B Mokgonyana	Water Research Commission (Co-ordinator)

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ABBREVIATIONS AND ACRONYMS

ABA	Acid-Base Accounting
AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
ANSI	American National Standards Institute
AP	Acid Potential
ARD	Acid Rock Drainage
ASTM	American Society for Testing and Materials
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
DBARD	Database for acid rock drainage
DQO	Data quality objectives
EPA	Environmental protection agency
ERA	Environmental risk assessment
EURACHEM	European chemistry
EUROLAB	European laboratories
GUM	The Guide to Expression of Uncertainty in Measurement
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ISO	International Organization of Standardization
IUPAC	International Union of Pure and Applied Chemistry
NAA	Neutron Activation Analysis
NAG	Net acid generation
NIST	National Institute of Standards and Technology
NNP	Net neutralizing potential
NP	Neutralizing potential
NPR	Neutralization potential ratio
QA/QC	Quality assurance and quality control
(R)ANOVA	Robust Analysis of Variance
SD	Standard Deviation
UKAS	United Kingdom Accreditation Service
VIM	International Vocabulary of Basic and General terms in Metrology
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1
INTRODUCTION

1.1 MOTIVATION

Quantification of the uncertainties associated with environmental geochemical prediction as a function of sample size and geochemical analyses are always a concern when performing an Environmental Risk Assessment (ERA). This is especially so when applying for mining authorization and/or closure and water use licenses. The difficulties in understanding and quantifying uncertainties are particularly critical when:

- Researchers and consultants compile proposals
- Mines compile their budgets or develop a terms of reference
- Regulators evaluate and or authorize permits, licenses and
- Referees and reviewers peer-review a paper or examine a report.

Generally, and particularly in South Africa, there has been limited work done on the development of methodologies for quantifying uncertainties in geochemical sampling, analyses and determination of sample size. Uncertainties in geochemical sampling and analyses affect the quality of data used in environmental studies and, as a result, the confidence that can be placed in the long-term predictions of geochemical modeling is questioned. This implies that results have to be validated by long duration monitoring programs thereby imposing an additional financial burden on the mining industry. This also leads to the slow approval of mining authorizations, water use licenses and mine closure plans.

The primary reason for this undesirable situation is a lack of nationally standardized and acceptable procedures for the analysis of uncertainty in geochemical investigations for ERA. This is further exacerbated by:

- Lack of knowledge and application of statistical methods
- Lack of understanding of the complexity of geological, soil and mining materials
- Lack of experience and knowledge of the significance/importance of data quality control
- Lack of easily understandable, operable and user-friendly methods specifically for geochemical sampling and analyses and
- Financial constraints, i.e. limited budgets.

From the above it is clear that there is a definite need for the development of a methodology/protocol that addresses geochemical sampling (sample sizing and representivity), analyses and data quality for application in geochemical predictions.

1.2 PROJECT AIMS

1.2.1 Primary aim

The primary aim of the project is to establish a methodology for quantification of the uncertainty associated with geochemical prediction for Environmental Risk Assessment (ERA) as a function of geochemical sample size and geochemical analysis for use by researchers, consultants, regulators and the mining industry.

1.2.2 Secondary aims

In addition to the primary aim stated above there are secondary aims which are to:

- Understand the geochemical sampling and analyses requirements for geochemical prediction for ERA.
- Establish a methodology for determining sample size (number and mass or volume) as well as sample representivity for ERA using a statistical method or formula.
- Apply and test the methodologies established for uncertainty quantification, sample optimization and data quality control for ERA using the Wits basin as a case study.

1.3 PROJECT METHODOLOGY

In order to achieve the above-mentioned objectives, the following tasks were performed:

- Conducting a comprehensive and extensive literature survey to review the available methodology for:
    - Quantifying uncertainties associated with geochemical prediction for ERA as a function of geochemical analyses; and
    - Determining geochemical sample size.
- Assessing the statistical theories, principles, concepts and their application for quantifying uncertainties associated with geochemical prediction as a function of sample size and geochemical analyses, sample size determination, analytical quality control, etc.
- Developing a statistical method or formula for the determination of geochemical sample size taking into account factors such as purpose of the ERA, level of confidence required, geological and geochemical principles, complexity of the prediction tools, financial constraints, etc.
- Converting the developed methodology into a simple, user-friendly tool that can be utilized to determine and or assess geochemical sampling size.
- Identification of parameters that can be applied to quantify uncertainties associated with prediction for ERA as a function of sample size and geochemical analyses and develop a methodology that can be converted into a user-friendly format for use by researchers, consultants, regulators and the mining industry.

The methodologies established will be tested using geochemical and mineralogical data from mining operations in the Wits Basin as a case study.

1.4 OVERVIEW OF THE CHAPTERS

Chapter 2 provides a detailed review of the literature on sample size and uncertainty in geochemical sampling and analysis for ERA. The chapter begins with an overview of geochemical sampling and analysis and quality assurance and quality control. This is then followed by an outline of the basic sampling theory, covering measures of the central tendency (mainly mean), measures of dispersion (variance, standard deviation and standard error of the mean), central limit theorem and confidence interval. A literature review on sample size determination and methodologies for quantifying uncertainty in geochemical sampling and analysis follows.

Chapter 3 presents the case study information based on the assessment of the potential of tailings dams and waste rock dumps in the Vaal River and West Wits mining areas to impact on water resources and implications of this in terms of mine closure and rehabilitation. The work was carried out by Pulles and Howard de Lange and Company for AngloGold Ashanti Gold.

Chapter 4 presents the methodology for sample size determination using the statistical analysis method. The effects of the various parameters that determine the calculation of sample size are discussed first. The parameters include standard deviation, standard error and confidence interval. A procedure for determining sample size is discussed and its application presented.

Chapter 5 presents the methodology for quantifying uncertainties in geochemical sampling and analysis as a function of sample size and analyses. The method is a synthesis of existing methods for estimating uncertainty including International Standards Organization (ISO), United Kingdom Accreditation Service (UKAS), European Chemistry (EURACHEM) (2000), GY's particulate sampling theory, and National Institute of Standards and Technology (NIST).

Chapter 6 presents the application of the methodology discussed in Chapter 5.

Chapter 7 covers the discussion, conclusions and recommendations for the study

1.5 GENERAL

Elizabeth Chihobvu was an MSc student in the Department of Geology, Faculty of Science, University of Fort Hare. She used this project as her MSc project and graduated on 8 May 2010.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

The main purpose of this chapter is to review literature on uncertainty as relates to sample size, sampling and analysis protocols order to meet the project requirements as outlined in Chapter one. The topics reviewed include:

- Sampling and analysis process;
- Quality assurance and quality control in geological investigations;
- Basic statistical theory;
- Methods for determining the sample size;
- Uncertainty and error;
- Uncertainty sources in geochemical sampling and analyses; and
- Theories for quantifying uncertainty.

The references used included:

- Published papers;
- Conference proceedings;
- Books;
- Research reports; and
- Internet web pages.

The chapter begins with an overview of geochemical sampling and analyses processes including quality assurance and quality control aspects followed by review of the basic concepts in statistics. Three methods for quantifying uncertainty: Quantifying Uncertainty in Analytical Measurement (QUAM) by the European Chemistry Board (EURACHEM), Pierre Gy's Particulate Sampling theory, and the Empirical method based on ANOVA by Dr Michael Ramsey are reviewed in detail. A comprehensive methodology for quantifying uncertainties is then developed from the reviewed theories. The method is discussed in detail in Chapter 6.

2.2 OVERVIEW OF GEOCHEMICAL SAMPLING AND ANALYSIS

In order to address the key issues stated above (data quality, uncertainty and sample representativeness), it is necessary to discuss the geochemical sampling and analysis measurement. While some examples of good sampling practices can now be found (Mason, 1992; Smith *et al*., 2004; Dominy and Petersen, 2005), the application of correct procedures is far from universal. Figure 2.1 illustrates the various stages involved in geochemical sampling and analysis.

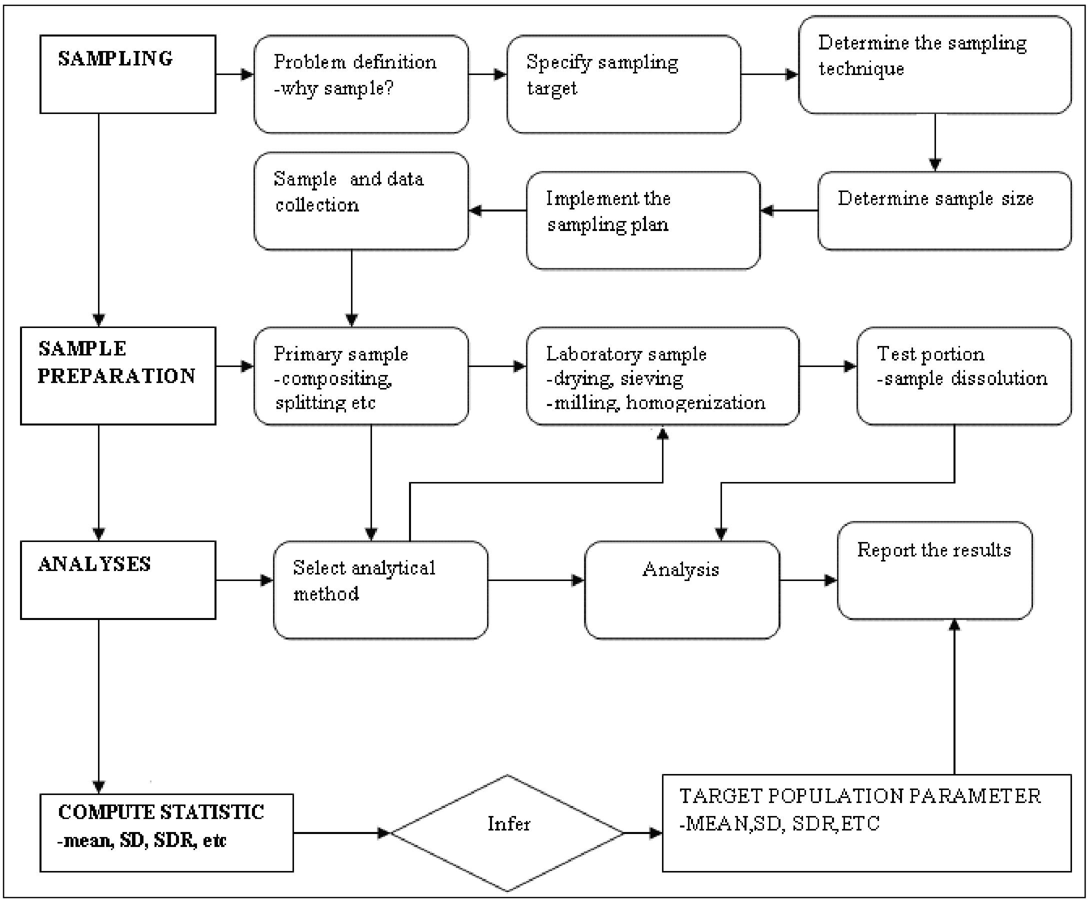


Figure 2.1: The measurement process in geochemical sampling and analysis

Geochemical sampling and analyses involves the processes of collecting and analysing geological materials such as borehole logs, ore samples, waste rock dumps and tailings disposal facilities in order to answer questions relating to a geological / geochemical scenario. Thus, to estimate the concentration of contaminants in mine waste material, an environmentalist collects several samples of waste material from the sampling target. Based on the contaminant concentration, the level of contamination of the whole population is estimated.

2.2.1 Stages in geochemical sampling and analytical processes

The process of geochemical sampling and analyses is multi-faceted with the four main processes being sampling, sample preparation, analysis and statistical interpretation. Each of these four main processes includes sub and intermediary processes such as transportation and sample preservation, etc., as shown in Figure 2.1.

2.2.2 Sampling

As depicted in Figure 2.1, the sampling process begins with definition of the project objectives, and a stage which requires the analyst to clearly explain why the study should be undertaken. Koerner (1996) also encourages a clear definition of sampling objectives in order to ensure that representative samples are collected. When undertaking geochemical investigations for Environmental Risk Assessment (ERA), the study may be carried out to either: (i) assess the impact of various mining features that include reactive material (such as sulphide minerals) on ground water quality and quantity (ii) monitor concentration changes of various contaminants over time (iii) applications for mine closure or (iv) compliance with regulations.

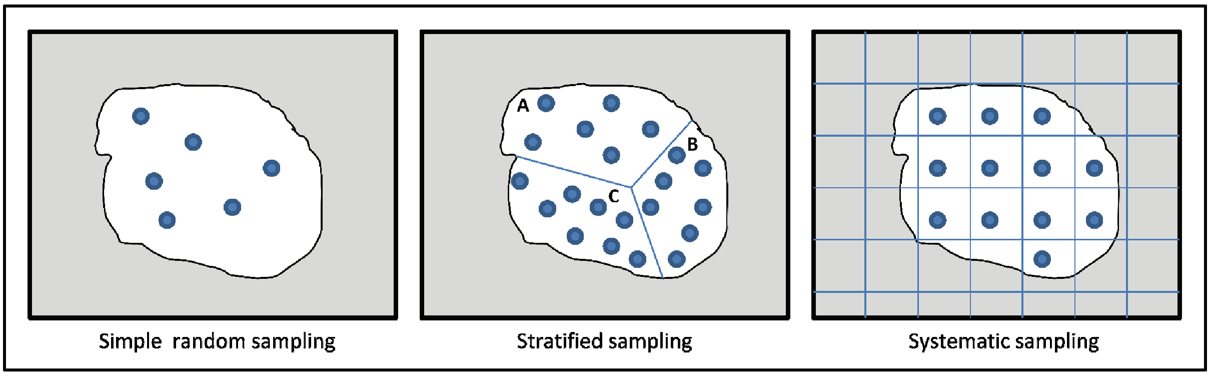
Once the problem that needs to be addressed has been clearly defined, it is possible to define a sampling target and a project objective that needs to be met with the particular investigation and sampling programme. A sampling target is the portion of material, at a particular time that the sample is intended to represent (EURACHEM / EUROLAB/CITAC / Nordtest, 2006). In terms of this, questions to be addressed include:

- What is to be sampled?
- How big is the sample target?
- Where is the sample target located?

Target definition is one of the major items that need to be elaborated on prior to designing a sampling programme. (EURACHEM/ EUROLAB/CITAC/ Nordtest, 2006). In geochemical investigations for ERA, a sampling target may be a waste rock dump, tailings disposal facility, temporary stockpile, opencast mine or underground mine.

As cited previously, sample representivity constitutes a fundamental part of the investigation process. Every sample is expected to reflect certain properties of the population it is drawn from. The ability to gather samples that are representative depends on a number of factors including sampling design.

Once the sampling target has been defined, it is necessary to design the sampling process which outlines how samples are to be collected from the target. Generally speaking, the more coverage the sampling technique has over the target, the higher the chances of collecting representative samples. The commonly used sampling designs are the probability sampling design (Back, 2001). These include simple random sampling, stratified sampling, cluster sampling and systematic sampling as shown in Figure 2.2. The choice of design depends upon the objectives of the study.


Simple random sampling

Stratified sampling

Systematic sampling

Figure 2.2: Sampling designs

Simple random sampling is a probability-based sampling design in which each sample occurring within the sampling target has equal chances of being selected. The main characteristic of this design is that the possibility of introducing bias is limited by the sampling design. Appropriate situations for using this sampling design approach include:

- Estimating the mean and totals for homogeneous population (Gilbert, 1987); and
- Cases where limited information is available about the sampling target.

Stratified sampling divides the target into non-overlapping homogeneous units or strata based on physical or chemical properties, knowledge of site history and or vertical and lateral distribution of the parameter of concern. As in a probability sampling design, samples are collected randomly from each stratum. The main aim of undertaking stratification is to minimize the effect of heterogeneity that highly affects precision of statistical calculations such as mean, standard deviation, etc. The number of samples within each stratum is proportional to the relative size of the site and stratum e.g. if the area of the stratum takes up 30% of the target population then 30% of the total samples would be taken from this stratum. One main advantage of the stratified random sampling is that the increased homogeneity in each strata, increases sampling precision (Back, 2001).

Stratified sampling design is not suitable for tracking peak values (MEND, 4.7.1-1, 1994). Simple random and stratified sampling designs are suitable for sampling of discreet units and they do not take into account spatial continuity and spatial correlation of the material properties (Mason, 1992). For this reason systematic grid sampling design is used in such situations. Systematic sampling is a statistically-based method of sampling in which the target is divided into a regular grid pattern before sample extraction. Sample locations are selected at regular intervals following one or more directions. Sample locations must be spaced widely enough. One drawback of the systematic sampling is the loss in precision when the population has a periodic trend that corresponds to the sampling interval (Back, 2001).

Selection of sampling strategy includes sample size determination. The decision regarding the number of samples required is determined by:

- the objectives of the study;
- accuracy required;
- sampling design;
- size of the sampling target; and
- sampling and project budget.

Sample size determination is further discussed in Section 2.4 of this chapter and in Chapter 4. As for sampling design, sample size affects sample representivity, thus the larger the sample size, the higher the representivity. However, caution must be exercised since collection of a large number of samples does not guarantee representivity.

Another critical step is the determination of an appropriate sampling technique to be used when collecting samples from the site. The technique selected depends on several factors including the type of material whether solid, liquid or gas, purpose of the investigation, budget and the sampling depth required. Other considerations include the texture of the material in the case of solid samples. A good sampling tool is one that preserves the integrity of the sample. Possible factors that may cause alteration of the sample from its original state include contamination from the shallow surface material as the sample is drawn from subsurface, contamination from the sampling tool itself and chemical reaction of the sample on exposure to the atmosphere.

A range of different sample collection techniques for different types of materials is listed in Table 2.1:

Table 2.1: Sampling techniques (MEND Report 4.5.1-1, 1994)

Technique	Phase	Depth	Degree of sample disturbance during collection
Hand auger	solid	on/near the surface	high
Trenching	solid	on/near the surface	moderate
Split spoon	solid	subsurface	low
Vibrating core drill	solid	subsurface	low
Shovel	solid	on or near the surface	moderate
Piezometers	liquid	subsurface	-
Bailers	liquid	subsurface	moderate
Surface grab	solid/liquid	on surface or submerged	-
Rotating drill	solid	subsurface	high
Suction lysimeter	liquid	subsurface	moderate
Syringe sampler	liquid	-	low

Samples collected for ERA play an important role in decision making and should be augmented by proper sample handling, preservation, and storage. The manner in which the samples are to be handled is determined by the type of sample and intended use. The samples should be handled so as to preserve their integrity and ensure that subsequent analyses measure parameters as they exist in the original sample target. Careful planning and selection of the container for holding the samples is important since these can be a significant source of sample contamination. Table 2.2 summarizes sample handling for water samples prior to analysis.

Table 2.2: Preservation methods for water analysis (Quevauviller, 2002)

Parameter	Sample container	Preservation method	Max. recommended storage
pH	Plastic or glass	Analyse immediately	Analyse immediately.
Sulphate	Plastic or glass	Refrigerate	28 days
Cyanide	Plastic or glass	Add NaOH to pH >12, refrigerate	14 days
Metals	Plastic or glass	Add HNO_3 to pH <2	6 months
Volatile organics	Glass	Add HCl to pH <2, refrigerate	Does not specify
Silica	Plastic	Refrigerate	28 days

2.2.3 Sample preparation

Sample preparation involves the physical and or chemical preparation processes carried out prior to analysis. It includes (i) sample homogenization; (ii) sieving and drying (iii) sample compositing (iv) milling and grinding and (v) riffle splitting and cone and quartering. A laboratory sample is drawn from the bulk field sample (primary sample). In most cases, the laboratory sample is not immediately fit for analysis and an additional preparation step is carried out to acquire a test portion (Geelhoed, 2005). The preparation method assumed relies on the analysis technique, type of material and objectives of the project. Sample dissolution is an example of one sample preparation technique that can be carried out before analysis.

Care must be practiced to avoid sample contamination from the equipment. For instance, it is not advisable to dry and sieve samples that are collected for the determination of volatile contaminants, as it alters the composition of the sample.

The choice of the preparation method adopted is a function of the objectives of the study, type of sample, budget, and analytical method, amongst other factors. For heterogeneous material or where the budget is limited, various increments may be composited to form a single composite sample. Elemental analysis of major rock elements by X- Ray Fluorescence (XRF) may require the preparation of a glass bead or pellets depending on what is to be determined. In the case of Inductively Coupled Plasma Mass Spectrometry (ICP MS) analysis a different preparation method is implemented. Sample dissolution by either acid digestion or water extraction may be employed in preparation of the test portion for ICP MS analysis.

Sample preparation for the test portion should be carried out under strict quality control conditions in order to minimize error. However, it is critical that analysts realize and remember that a measurement is only as good as the preparation that has preceded it (US EPA, 2004).

2.2.4 Analyses

After sample preparation, the sample is analyzed to determine the analyte(s). Numerous analytical methods are available to qualitatively/quantitatively measure the concentration of different analytes in geological investigations. The choice of the method is based on the material type, required accuracy, budget and most importantly, the project objectives. The analytical methods selected must be sufficiently sensitive to allow detection of a wide range of elements within the sample media at background levels. Examples of analytical techniques often adopted in geochemical studies for ERA include ICP MS which is used for multi-element analysis, XRF for the analysis of trace and major mineralogy, X-ray Diffraction (XRD) for mineralogy and many others. These methods and their application are summarized in Table 2.3.

Table 2.3: Analytical methods and their application

Methods	Application	Advantages	Limitations
Atomic adsorption spectrometry, AAS	For elemental analysis of solutions	-It is less sophisticated but provides quality results -fast analysis of an element	-low sensitivity to non metals -individual analysis of elements
ICP MS	Multi element analysis	Allow for rapid determination of many elements in a short period of time -high sensitivity -low detection limit	Elemental interferences Difficult to analyze non volatile samples
XRF	Elemental analysis (major and trace elements) for solids and non volatile liquids	-High sensitivity -minimum sample preparation	-Not sensitive to elements with atomic mass < Na -precision is limited by non uniformity of the sample -most suitable for major element analysis
XRD	Mineralogy of solids	Can distinguish polymorphs, isomers and conformers -less expensive -used for identification of secondary minerals	Detection and sensitivity depend on crystallite size
Microscopic study	Mineral forms, mineralogy	-provide information on mineral forms	
NAA	Elemental analysis of major and trace elements for solid and liquids	Very high sensitivity for many elements	Applicable to solid and liquids only

Each method that is selected has to be validated. The validation of an analytical method is a process that demonstrates that the results obtained by the method are reliable and reproducible (Quevauviller, 2002). Addition objectives of method validation are:

- Identify possible errors;
- Identify differences between methods; and
- Indicate if the method is acceptable for the intended purpose.

Method validation studies rely on the following key quantitative parameters: (CITAC/ EURACHEM, 2002)

PRECISION: This is the most vital of all the validation parameters. Precision is the agreement between a series of measurements obtained from multiple sampling of a homogeneous sample. Precision can be broken down into three classes:

- **Repeatability** which highlights variability observed under the same operating conditions over a short time.

- **Reproducibility** is the ability to reproduce data within predefined precision. It can be determined by the analysis of inter-laboratory results of the same sample.
- **Intermediate precision** is linked to the variation in results due to variation of one or more factors such as time, equipment, and analysts within a single laboratory. It can be expressed either as standard deviation or confidence interval.

Precision of an analytical procedure is usually expressed as the variance, standard deviation, or coefficient of variation of a series of measurements.

ACCURACY: This is the difference between the measured value and the true value. In most cases, the true value is unknown. Accuracy of a method can be assessed by the analysis of samples of known composition, a reference material (or a standard material). A comparison of results from analysis of standard reference materials with experimental results can be used to assess accuracy.

LINEARITY: The linearity of an analytical method is its ability, within a given range, to obtain results that are directly proportional to the concentration of analyte present in a sample. Linearity can be assessed by:

- Inspection of a plot of signal versus analyte concentration.
- Linear regression plots.

DETECTION LIMIT: The detection limit is the lowest amount of analyte concentration that can be detected above the noise level of the system. The detection limit may be determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level at which the analyte can be reliably detected.

SELECTIVITY: This parameter describes the ability of a method to accurately distinguish an analyte in a complex mixture with no interference from other components present in the mixture. Selectivity can be demonstrated by deliberately introducing known levels of impurities into a sample of known amounts of analyte of interest. When an analytical method is able to distinguish an analyte (s) from the impurities, the method is said to be selective.

BIAS: Bias of a method refers to the systematic errors which are introduced by the method or system. The bias of a method can be assessed by (i) use of primary or reference methods of known or small bias (ii) comparisons with a closely matched matrix (CRMs) (Ellison, Rosslein, and William, 2000)

ROBUSTNESS/RUGGEDNESS: The robustness of an analytical method is assessed by the introduction of small changes (e.g. temperature) to the analytical procedure which may or may not have a significant effect on method performance. The results obtained under such varying conditions are compared with precision under normal conditions.

2.2.5 Statistical inferences

The last step involves making some statistical inferences about the target population based on the sampling and analytical results. Such inferences are based on the application of statistical assessment and estimation to make reliable conclusions about the conditions existing in the sample target.

2.2.6 Reporting of analytical results

This is the last and crucial step of the analytical test work. It is through result reporting that the quality of measurements can be assessed by the information user. Reports must be prepared according to an agreed procedure and they must accurately reflect the findings of the study. In addition, the result must be expressed in an appropriate number of significant figures and should be accompanied by a statement of uncertainty. Uncertainty is dealt with in detail in Chapter 6.

2.2.7 Importance of geochemical sampling and analytical measurements

Accurate geochemical predictions for environmental impact depend on the collection of representative data, i.e. data reflecting the actual conditions on the ground. The accuracy of the other techniques employed during the predictions, such as geochemical modeling, depend on the accuracy of the sampling program. It is therefore important that good sampling and analysis protocols be put in place. Poor sampling and analytical techniques result in poor data and hence decision errors. Making decisions under significant and undefined uncertainty may lead to serious environmental consequences and heavy financial penalties.

2.3 QUALITY ASSURANCE AND QUALITY CONTROL

The value of geochemical measurements depends upon the level of confidence that can be placed in the results. Data quality objectives and quality assurance and quality control programs are critical to geochemical sampling and analyses for ERA. Since results obtained from sampling and analyses play a crucial role in decision making, emphasis should be placed on the quality of measurement results. The quality of a measurement result and the confidence placed on it depend on strict adherence to a well-structured QA/QC program.

2.3.1 Definitions

The following terms associated with a QA/QC program need to be defined:

Quality

Quality is “the totality of features and characteristics of a product or service that bear on its ability to satisfy stated or implied needs” (ISO 8402: 1986, pp. 3.1).

Quality Assurance

1) "All the planned and systematic activities implemented within the quality system and demonstrated as needed, to provide adequate confidence that an entity will fulfil requirements for quality." (ISO, 1993)
2) "A management system for assessing the qualitative and quantitative reliability of field and laboratory data and ensuring that all information and data are technically sound and properly documented."(Cavanagh *et al.*, 1998)

Quality Control

1) "It is the routine application of procedures for controlling the accuracy and precision of data measurements." Quality control programs consist of day to day activities such as the use of well maintained and properly calibrated equipment; adherence to written protocols; the regular use of quality control samples and diligent record keeping (Cavanagh *et al.*, 1998**).**
2) "The operational techniques and activities that are used to fulfil requirements for quality" (CITAC/EURACHEM, 2002))

2.3.2 Objectives of a Quality Assurance/Quality Control (QA/QC) program

The following objectives can be defined for a QA/QC program (Downing, and Mills, 2007):

- Document the procedures and methods of sample collection, preparation, and analysis.
- To give assurance that data generated are indicative of the study site characteristics
- To provide assurance as to the precision and accuracy of data.
- To provide assurance as to the accuracy from using recognized reference standards.
- To provide a chain of custody of samples.
- To help to ensure that results are valid and fit for purpose.
- To provide measurement of the uncertainty in the underlying data.
- To prevent the entry of large errors into the database used for geochemical modeling,

It is important for both laboratories and their customers to realize that QA cannot guarantee 100% reliable results due to errors which lead to measurement uncertainty (CITAC/EURACHEM, 2002). The QA/QC programs should be set up in the early planning stages of the investigation.

2.3.3 Crucial aspects for a QA/QC program

A quality assurance and quality control program for acid rock drainage (ARD) assessments should address the following aspects:

Sampling

- Qualification of the personnel;
- Quality control samples;
- Equipment calibration and decontamination;

- Sample preservation;
- Sampling record; and
- Chain of custody.

Analyses

- Laboratory selection;
- Laboratory accreditation;
- Staff qualification;
- Instrument calibration and servicing;
- Acceptable detection limits; and
- Laboratory quality control samples

Data management

- Documentation of records; and
- Reporting results.

2.3.3.1 Sampling

Sampling is one of the most vital components of an ARD assessment program. If the sampling work is not done properly, the errors associated with the collected samples will be carried over to the succeeding components of the ARD assessment program. Inconsistent and inappropriate sampling procedures should therefore be avoided. Factors to be considered under this are as follows:

(a) Qualifications of the personnel

One of the golden rules in sampling is that sampling should be carried out by qualified and experienced personnel. It is necessary to check and confirm that sampling personnel are fully trained in all the important elements that make up a successful sampling program and that they clearly understand the objectives of the sampling program.

(b) Quality control samples

It is generally recommended that 5 to 10% of the samples should be collected as quality control samples (duplicates, spikes etc) (Long, 2007). These are essential for checking and verifying the performance of the sampling and analytical procedures, possibility of contamination and precision. These quality control samples also aid in quantifying uncertainties linked to the sampling. The various field quality control samples and their purpose are listed in Table 2.4.

(c) Equipment calibration and decontamination

Sampling equipment should be decontaminated constantly to avoid sample contamination. This is especially vital when moving from one location to the next.

Table 2.4: Field quality control samples (Van Ee, Blum, and Starks, 1990)

TYPE	FUNCTION
Duplicate sample	Used to demonstrate the reproducibility of the sampling techniques and to test the precision of the overall analytical system (field and laboratory).
Field Blank	Used to check on potential sources of contamination resulting from exposure to the ambient air or from improperly cleaned sampling equipment.
Trip blank	Used to trace contamination introduced during shipment
Split Samples	Used to determine the precision of a laboratory analysis by allowing a comparison of analytical results for two parts of the same sample from the same location.
Spiked Sample	Used to provide a proficiency check on analyte recovery as a function of analyte loss during transport and storage of the collected samples and as a function of the analytical procedures and equipment.
Background Sample	Used to compare site conditions to the surrounding environment

(d) Sample record

A record for each sample should be kept and should include the following information:

- Sampler's name, i.e. the person who conducted sampling.
- Date and time the sample was collected.
- Location from which the sample was collected.
- Whether it is a composite sample or not.
- Any changes or modifications to the sample have to be recorded and the name of the person responsible should be recorded. This helps in establishing the chain of custody of the sample.

(e) Chain of custody

The chain of custody for samples allows one to track the history of a sample. A record should be kept for each sample collected. This record must contain:

- Date and time when the original sample was collected
- Sampling protocols
- Method and duration and location of any sample storage
- Detailed record of both physical and chemical sample preparation and preservation
- Details of the personnel who have handled the sample
- Records of any part of the sample that was disposed of.

The record should be updated constantly.

2.3.3.2 Analyses

Correct and reliable analysis relies on clear and adequate specification of the objectives of the study and strict adherence to good QA/QC practices. Without a clear understanding of the needs for analysis it is difficult to obtain useful results that clearly address the problem in question.

This section outlines some of the QA/QC measures that can be adopted during laboratory analysis. QA-QC programs are designed to monitor precision and quantify any possible biases – thus minimizing measurement errors.

(a) Laboratory

A certified laboratory, accredited by well known bodies such as the International Organization of Standardization ISO 25/International Electrotechnical Commission (IEC), ISO 9000/EN 29000 standards or other equivalent accreditation should be given first choice. Accreditation provides a standardized framework for the proper operation of testing laboratories. It is also recommended that an additional laboratory be selected to act as a check laboratory.

Example 1: Evaluating possible candidates using standard reference material

Table 2.5 displays results obtained when a standard of gold oxide certified at 1.49 gm/t was sent to four different laboratories for analysis.

Table 2.5: Example of evaluation of several laboratories 1.49 gm/t gold (Long, 2007)

								Ranking	
Lab	**Result 1**	**Result 2**	**Result 3**	**Result 4**	**Result 5**	**Mean**	**Standard deviation**	**Accuracy**	**Precision**
A	1.61	1.57	1.48	1.53	1.47	1.53	0.059	2	1
B	1.76	1.66	1.64	1.48	1.80	1.67	0.125	5	4
C	1.51	1.67	1.51	1.57	1.50	1.55	0.072	3	2
D	1.39	1.59	1.48	1.45	1.53	1.49	0.076	1	3
E	1.33	1.26	1.19	1.20	1.20	1.24	0.059	4	5

Based on the information presented above, the following conclusions can be drawn:

- Laboratory A results are both accurate and precise.
- Laboratory B results are inaccurate and imprecise.
- Laboratory C results are inaccurate but precise.
- Laboratory D results are accurate and imprecise.
- Laboratory E results are inaccurate and precise

Therefore, the results from laboratory A are the most acceptable. Based on similar procedures, the most desirable laboratory can be selected.

(b) Staff qualifications

It is generally recommended that analytical tasks be conducted by or under the supervision of qualified and experienced personnel. CITAC/EURACHEM (2002) and Long (2007) recommend that up-to-date records of each member of staff be maintained. These records should include academic qualifications, external and internal courses attended and relevant on-the-job training. The purpose of these records is to provide evidence that individual members of staff have the necessary qualifications and have adequate training to carry out particular analytical test work.

(c) Instrument calibration and servicing

An instrument service and calibration program should be put in place to ensure proper and accurate operation of all laboratory instruments. Calibration standards should be validated against standard reference materials. The calibration program should be well documented.

(d) Internal quality control

Sample analysis quality assurance relies heavily on the use of QC samples and certified reference standards for the determination of precision and accuracy. Field replicates provide the means by which sampling and natural variability can be measured. Analytical replicates are useful for assessing analytical precision. Quality control samples, listed in Table 2.6 should be analysed at the same time as original samples. In addition, standard reference materials should be inserted into every batch analysis. Table 2.6 lists laboratory quality control samples that may be used to assess quality in the laboratory.

Table 2.6: Laboratory quality control samples

TYPE	FUNCTION
Certified reference material (CRM)	Used for the calibration of an apparatus and assessment of a measurement method.
Laboratory replicate	Used to evaluate the method precision.
Matrix Spike	Used to establish if the method or procedure is appropriate for the analysis of a particular matrix.
Laboratory blanks	Assess contamination within the laboratory

An internal quality control program can be summarised as:

- At least one method blank should be analysed per set of 20 samples.
- Analyse one field blank per set of samples.
- A single duplicate of a sample chosen at random from each set of up to 20 samples should be analysed.
- Analyse one specimen that has been spiked with a known amount of the variable as a recovery check.

(e) External quality control

External quality control is a means of establishing the accuracy of the analytical method by inter-laboratory comparisons in which each participating laboratory uses the same test method on a set of identical samples. Results from the different laboratories are then compared and decisions are made on whether the method was accurate. Participating in an external quality control exercise is the only way to ensure that accuracy is independently monitored.

(f) Data management

Sampling and analytical programs will generate a considerable amount of data that will need to be properly managed to facilitate periodic review and revision of the sampling strategy. Data generated during a site investigation should be collated and presented in a logical form to enable the information to be assessed. A database provides a means by which the large volumes of data collected can be managed and maintained. A good database should contain all information needed to easily evaluate the quality of data, manage that data, and allow easy reference to hard copy (Long, 2007). There are various types of databases available but the main ones are flat file and relational databases.

Flat file style databases consist of one or more unrelated tables containing considerable records. They are usually ideal for small amounts of data. A well-known example is the spreadsheet such as Excel. Relational databases have a much more organized structure for storing data. The tables within the database are linked to one another – hence the term relational. Unlike most relational databases, the spreadsheet approach allows for more complex and detailed analysis and facilitates the comparison of calculation methods.

(g) Data analysis.

Data analysis procedures provide a platform by which errors and flaws within the measurement results can be identified. Data analysis involves all procedures such as statistical techniques and plots that are applied to describe, summarise, and compare data. It is recommended that all collected data should be analysed to determine any spurious results. Simple plots and statistical analysis may be carried out. As an example from an ARD assessment program where ABA results were obtained – it could be useful to plot inorganic carbonated NP against total NP to determine the possibility of correlation between carbonate content and total NP.

(h) Report analytical results

This is the last and crucial step of the analytical test work. It is through result reporting that the quality of measurements can be assessed by the information user. At least the following aspects should be incorporated in the results report:

- Sample ID and laboratory ID;
- Analysis date;
- Sample size;
- Sample (analyte)concentration units;
- Description of the analytical procedure adopted and calibration;
- Quantification and validation procedures;
- Quality control sample results; and
- Statement of uncertainty.

2.4 BASIC STATISTICAL THEORY

The main aim of undertaking geochemical sampling and analysis is to make some inference about the population from which a sample is drawn. It is through the application of basic statistical tools that inferences are made possible. This section covers basic statistics, including the following:

- Sampling distribution;
- Central limit theorem; and
- Confidence interval.

2.4.1 Sampling distribution

Sampling distributions are theoretical distributions that comprise of a finite number of sample statistics taken from a finite number of randomly selected samples of a specified sample size. Under this, the main question to be answered is "how close is the value of the statistic to the corresponding parameter of the entire population?" (Lenth, 2001). For example, if we have 60 elements analysed in a sample from a population and our sample mean $\bar{x}$ is 18.2, we would like to know how far this might be from the mean μ of the entire population. In most cases, given the difficulty of measuring the population parameters, we often infer the value of the mean μ, variance $\sigma^2$and standard deviation σ of the population from the sample mean $\bar{x}$, sample variance s^2, sample standard deviation σ, respectively. Thus the sampling distribution of the various sample statistics are used as estimates of the corresponding population parameter.

Although many distributions exist, the most popular and the important is that of the mean (Crépin and Johnson, 1993). The mean of the sampling distribution is equal to the sampled mean of the population:-

$$\bar{x} = \mu \qquad 2.1$$

Where

$\bar{x}$ is the sample mean and μ is the population mean.

The sample's mean $\bar{x}$ can be expressed by the equation below:

$$\bar{x} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad 2.2$$

Variance of sampling distribution of the mean indicates how the values are spread around the expected mean value. The sample variance can be expressed as:

$$S^2 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \bar{X}\ )^2 \qquad 2.3$$

Where n is the sample size.

Standard deviation (S) is the spread of values around the average in a single sample:

$$S = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_i - \bar{X})^2} \qquad 2.4$$

The standard deviation (S) value gives an indication of how the values spread within a given dataset. A large standard deviation (S) is an indication of data values that have high dispersion and wide spread of the numbers with a wide distribution of the values from their mean (µ). A small value of S shows that the individual data values are close to the mean of the data.

For a normally distributed dataset, there is a likelihood that approximately 68% of the scores are within one standard deviation of the mean (µ) and 95% of the scores are within two standard deviations of the mean µ. Further there is a 99.7% chance that individual measurements will fall within three standard deviations of the mean as shown in Figure 2.3 below.

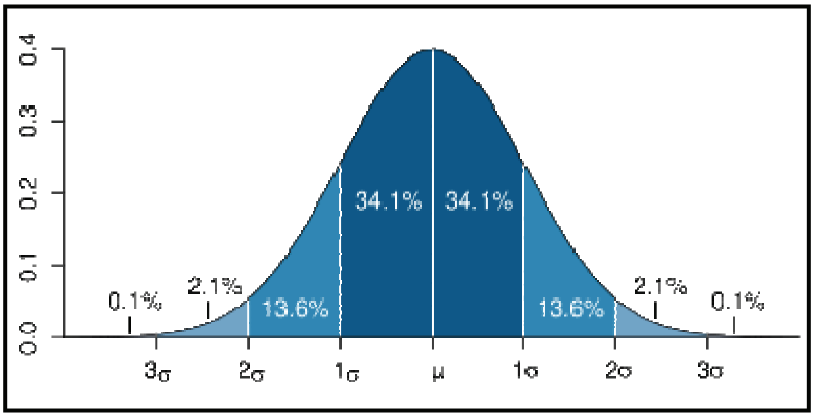


Figure 2.3: Standard deviation (Wikipedia, 2008).

Standard error of the mean: This is the standard deviation of the sampling distribution of the mean (Lane, 1993-2007). It therefore defines how the sample averages ($\bar{x}_i$) spread around the average (µ) of a population. It can be expressed as:

$$S_{\bar{x}} = \frac{S}{\sqrt{n}} \qquad 2.5$$

Standard error is also related to sample size (n). Equation 2.5 indicates that the standard error of the mean decreases proportionately with the square root of the sample size. Thus, the sampling distribution of $\bar{x}$ will be more concentrated the larger the sample size. Standard error is also one of the main measures of precision and uncertainty.

2.4.2 Central limit theorem

The basis of this theory is that, for a given distribution with a population mean μ and population variance σ^2, the sampling distribution of the mean approaches a normal distribution with a mean (μ) and a variance σ^2 as the sample size (n), increases (Lenth, 2001). But how large should the sample size before it is close to a normal distribution? Generally this is not an easy question to answer since there is not an exact point where it can be said that the sample size is large enough to warrant an assumption that the sampling distribution is normal. However, as a broad rule of thumb, a sample size of n = 30 is usually recommended as a cut-off point where it is assumed that a sampling distribution is approximately normal (Stockburger, 2002)

This concept is employed throughout the geochemical measurement process. For instance it is used in determining the number of samples and quality control situations where single measurements are erratic (Long, 2007). If more measurements are made, the average of the results is much more reliable for decision-making than when few measurements are made.

2.4.3 Confidence limits or levels

The confidence levels indicate the level of error or risk one is willing to accept. If n samples are drawn from a population with a mean μ and a standard deviation σ:

75% (α = 0.25) confidence limits for sample means = $\mu \pm 1.151*\sigma/\sqrt{n}$
95% (α = 0.05) confidence limits for sample means = $\mu \pm 1.960*\sigma/\sqrt{n}$
99% (α = 0.01) confidence limits for sample means = $\mu \pm 2.576*\sigma/\sqrt{n}$

2.5 SAMPLE SIZE

The objective of sampling is the collection of a representative sample that exhibits the true characteristics of the target population from which the sample is drawn. The collection of representative samples is dependent not only on good sampling design, but also on the collection of the right number of samples to satisfy the requirements of the study.

Sample size determination is a crucial part of the investigation procedure. Collection of too many samples is expensive and wasteful while too few samples may be unrepresentative (Reytblat, 2000). In scientific experiments involving human or animal subjects, sample size is a key issue for ethical reasons. An under-sized experiment exposes the subjects to potentially harmful treatments without advancing knowledge while in an over-sized experiment, an unnecessary number of subjects are exposed to a potentially harmful treatment, or are denied a potentially beneficial one (Lenth, 2001). It is therefore the investigator's responsibility to make sure that the optimum number of samples exhibiting the true characteristics of the population or area is collected.

2.5.1 Definition of sample size

Townend (2002) defines sample size as the number of measurements or observations made from each population.

2.5.2 Factors affecting sample size

Generally the factors that affect sample size are as follows:

(a) Purpose of the study is one of the major factors affecting sample size. For a small pilot study, prior to detailed sampling, a few samples may be collected to obtain a rough estimate of the conditions on the ground. For detailed studies, a minimum of 30 samples is recommended in order to capture the properties that exist within the material understudy. For the purpose of Acid Mine Drainage assessment of *in situ* rock, British Columbia Acid Mine Drainage Task Force (1989) recommends a minimum sample number based on the size of a geological unit (MEND, 4.5.1-1, 1994).

(b) Available information about the study target and statistical methods provide guides to the determination of optimum sample size (Germishuyse, Yibas and Pulles, 2002). In geological studies, such information includes: spatial distribution and geological properties of the material; geotechnical and physical properties and geochemical characteristics. If the sampling target was studied before, the previous information can be used to reduce required number of samples. Depending on the objectives of a study, the previously obtained mean and variance estimate values can be used to calculate sample size for the present study (Taylor and Kuyatt, 1994).

(c) Variability of the geological properties of the geological material to be studied: Basically the more heterogeneous a population is, the larger the sample size required to characterize the effect of variability. Conversely, a homogeneous population requires fewer samples.

(d) Size of the sampling target: If the sampling target is large, then more samples are required. On the other hand when the sampling unit is small, fewer samples are generally required.

e) Precision: Generally more samples are required to achieve greater precision.

(e) Cost: There is a direct relationship between cost and sample size. As the number of samples increase, the cost also increases. The relationship between cost and sample size can be demonstrated by the Figure 2.4, Myers (1997). When few samples are collected the cost is generally lower but the risk of collecting unrepresentative samples is high. When more samples are taken the sampling cost usually increases but errors and misclassification cost decrease (Back, 2001). Therefore a balance among competing factors should be sought.

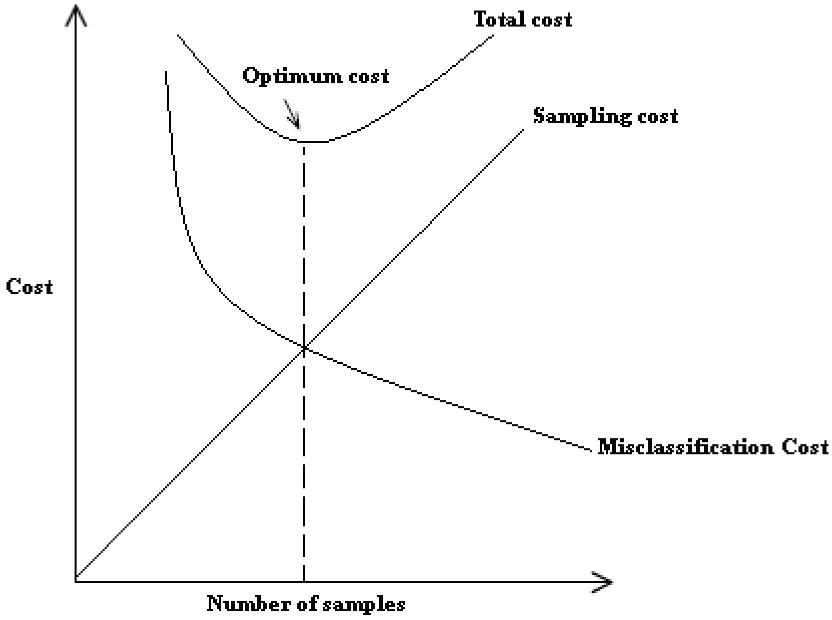


Figure 2.4: The relationship between cost and sample size (Myers, 1997)

2.5.3 Methods of determining sample size

There are numerous techniques for determining sample size. Some of the techniques are based on application of statistical or mathematical formulae while some are based on published tables and others on imitating the sample size from a previous similar study (Israel, 1992). For example, EPA tables for estimating the sample size required are listed in Appendix A. One major drawback of using such published tables is that they are mostly based on the assumption that the measured attributes are normally distributed, but when the data for the study do not follow this distribution; the use of the tables may lead to unreliable results. The use of sample size values from a previous similar study carries the risk of repeating errors that were made in the previous study.

The following sections review methodologies for determining sample size based on the application of statistical or mathematical formulae in determining sample size. The methods covered include:

- Statistical analysis method;
- Volume method; and
- Cost method.

(a) Statistical methods

A number of schools of thought have come up with different statistical formulas for calculating the number of samples required. Crépin and Johnson (1993) recommended the use of the statistical analysis method based on mean in determining the required sample size. The method can be expressed by the equation below:

$$n = \left(\frac{t_{\alpha/2} \times s}{d}\right)^2 \qquad 2.6$$

Where

n = the required number of samples

$t_{\alpha/2}$ = the Student´s t-value for a chosen level of precision, e.g. for a confidence level of 95% (α=0.05)

s = the standard deviation.

d = the variability in mean estimation we are willing to accept for the critical value, d^2 is the desired level of precision.

Barth *et al.* (1989) suggested a different approach in order to determine the minimum number of samples, n, required to achieve a specified precision and confidence level at a defined minimum detectable relative difference. The one-sided, one-sample t-test Equation 2.7, or one sided, two sample t- test, Equation 2.8 can be used.

$$n \geq \left[\frac{Z_a + Z_b}{D}\right]^2 + 0.5\, Z_a^2 \qquad 2.7$$

$$n \geq \left[\frac{Z_a + Z_b}{D}\right]^2 + 0.25\, Z_a^2 \qquad 2.8$$

Where:

n = number of samples

Z_a is the percentile of the standard normal distribution such that P ($Z \geq Z_a$) = infinity

Z_b is the percentile of the standard normal distribution such that P ($Z \geq Z_b$) = infinity

a = probability of a Type I error

b= probability of a Type II error

D= minimum relative detectable difference/CV

CV= coefficient of variation.

The parameter values are listed in Appendix B.

Huesemann (1994) and Back (2001) argue that to determine the number of the samples required, a small priori study area is necessary. From this, a rough estimate of the geochemical and analytical variance can be established, where after the necessary number of samples and number of analysis per sample to meet the specified objectives can be calculated. The statistical formula to calculate the sample size can be expressed as:

$$n = \frac{S_c^2}{S_x^2} \qquad 2.9$$

Where

n = number of samples

S_c and S_x are coefficients of variation (relative standard deviations).

For example, if the priori field study has given $S_c = 40\%$ and the sampling objective is $S_x \leq 10\%$, the approximate sample numbers required is 16.

(b) Volume method

The British Columbia Acid Mine Drainage Task Force 1991 developed a curve that can be used as a guideline to ascertain the minimum number of samples required to characterize each geological unit, Figure, 2.5. The curve was developed based on a limited number of sites within British Columbia, Canada as a function of the mass of the geologic unit being sampled (Downing, 2007). The recommended minimum number of samples is given below (MEND, 4.5.1-1, 1994):

$$n = 0.026M^{0.5} \qquad 2.10$$

Where

n = number of samples

M = mass of the geologic unit or lot in tons ($M>6*10^3$ ton).

For a 10^6 ton waste deposit, the minimum number of samples is 26 as shown in the diagram below.

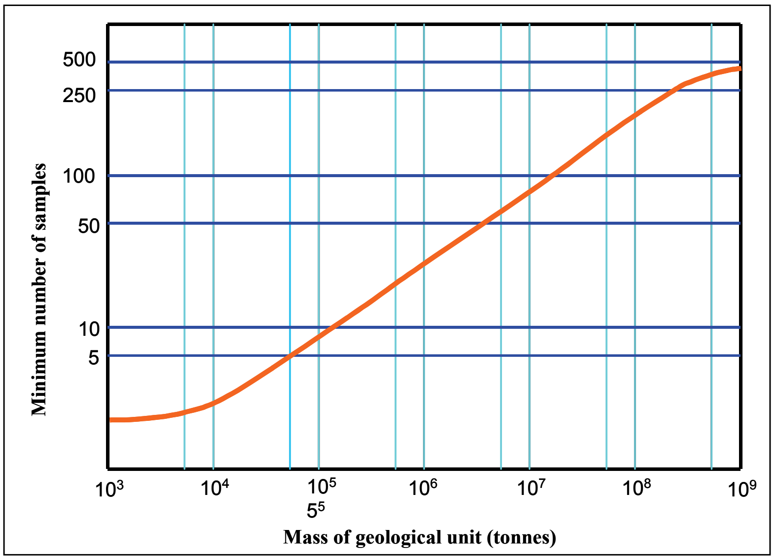


Figure 2.5: Sample size determination using the volume method (MEND, 4.5.1-1, 1994)

The sample volume required for a given study may be determined by using Gy's sampling which can be expressed by the following equation:

$$S^2 = \frac{Cd^3}{m} \qquad 2.11$$

Rearranging the equation in order to make **m** the subject of the formula would give (Yang, 2006):

$$\boldsymbol{m = \frac{Cd^3}{S^2}} \qquad \mathbf{2.12}$$

Where;
S is the standard deviation of the error
d is the size of the largest particle in the sample
C is a product of

- liberation factor,
- shape factor
- particle size distribution factor,
- composition factor.

The output of the equation is a mass needed to achieve a specified sampling error (Ramsey, 1998).

(c) Cost method

This method is based on ideas suggested by Peterson and Calvin (1965). There are many cases where the number of samples required by the previously discussed methods is not acceptable because of the cost of the sampling and analysis. The method seeks to establish a link between sample size, stipulated budget and the sampling and analytical cost. The relationship between the three factors can be expressed by the equation below:

$$\boldsymbol{n = \frac{C - C_o}{C_s + C_a}} \qquad \mathbf{2.13}$$

where *n* is number of samples , *C* is total cost, C_o is overhead cost or fixed cost, C_s is cost of sampling and C_a is cost of analysis.

This equation can be used in conjunction with previously discussed methods of determining sample size in order to arrive at the number of samples that will satisfy the budget and still have an identified precision. An example is given in Appendix B.

Example 2

Prior to sampling of the amount of lead in water, the geochemist obtained the following quotation from a consultancy firm:

Sampling = R200 per sample, analysis= R10 per sample, overhead cost = R12 000
The sampling and analytical budget was R40 000.
Therefore the numbers of samples that are required are:-

n= (R40 000-R15 000)/ (R200 +R30)
n =109

Therefore a sample size of 109 is required based on the stipulated budget and the costs for undertaking sampling and analysis.

Robertson, Robertson and Kristen (1990) discouraged the use of fixed sample numbers e.g. volume method. Instead they suggested a preliminary sampling plan for determining the best sampling strategy. The following strategies were recommended:

Replicate sampling: this involves extracting several samples at the same location. It can be adopted when the objective is determination of the mean of a given variable.
Sequential sampling: this can be used when the objective is to reduce variance between samples.
Exceedence driven sampling: the strategy is designed to identify outliers within a dataset. Croarkin (2003) defines an outlier as “an observation that lies an abnormal distance from other values in a random sample from a population”. When an outlier has been identified, sampling numbers are increased at locations where these outliers occur.
Markovian sampling strategy reflects the rise beyond a threshold level determined by previous sampling. The sample size is adjustable and based on "alert" levels. (Robertson, Robertson, and Kirsten, 1990)
Stratified sampling strategy divides the waste rock pile into homogeneous stratum. The strategy under its counterparts provides some statistical predictability.

2.5.4 Procedure for sample size determination

Croarkin (2003) proposed the following process for determining sample size:

- Determine the purpose or objectives of the study.
- Build up or find an equation that relates the desired precision to sample size.
- Use previous or prior information to estimate unknown parameters such as variance or mean.
- When a stratified sampling design is adopted, determine sample size for each stratum.
- The final sample size is scrutinized for practicality.

2.5.5 Summary

The determination of the sample size required is a function of the study objectives, cost, and variability. Each of the factors should be taken into account before deciding the number required. The method chosen should satisfy the needs at hand.

One major drawback associated with the use of statistical methods for determining sample size is the assumption that a simple random sample was drawn. This assumption brings in some complications especially when a different complex sampling design is adopted, for example-stratified sampling. The use of this design requires one to take into account the variances of sub-populations, strata, or clusters before an estimation of the variability in the population as a whole can be made (Israel, 1992).

In addition the use of statistical methods in sample size determination requires a good estimate of the standard deviation. However, more often than not, when the sample mean is unknown, the sample standard deviation is also unknown.

The mass methods are only applicable where solid materials are to be sampled. It cannot be applied where the sampling target is either a gas or fluid. Studies conducted by Smith and James (1981) have revealed that the mass techniques tend to give an "over-estimate" of mass. In addition, determination of the parameters linked to the calculation of the constant C is difficult.

The cost method, although important, does not take into account important aspects such as the required precision, confidence, and prior knowledge of the target. The aspects impact greatly on sample representivity and accuracy of the estimates.

Several methods of sample size determination were discussed in detail. Of all the methods, the method which satisfy the requirement of this study is the statistical analysis approach based on the formula $n=Z_{\alpha/2}^2*S^2/d^2$**.** One major advantage of the method is that some of the most important parameters that impact on sample size are directly incorporated in the formula for sample size determination. Such parameters include level of required accuracy, standard deviation which shows dispersion and confidence interval. The importance of this is that the user has control over the input and the output. These factors and their effect on sample size determination are further discussed in Chapter 4.

2.6 UNCERTAINTY

Uncertainty is inherent in all measurements including geochemical measurements and mathematical predictions, no matter how carefully they are made. In geochemical sampling and analyses, uncertainty arises from the fact that only a portion of the target is sampled instead of the whole population hence the obtained measurement value is one probable value out of a universe of possible values for the population understudy. What this implies is that if one were to repeat the same measurement several times it is likely that different results will be obtained. Variation between these repeated measurements is attributed to some influential factors resulting from inconsistency of the measurement process. The influential factors are referred to as uncertainty sources or components. Given the inherent variability of measurement, measurement results should be accompanied by an estimate of the uncertainty for the particular measurement result. (Adams, 2002)

2.6.1 Definitions

Uncertainty

International Standards Organization (ISO, 1995) defines uncertainty as “a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand”. The “measurand” is the quantity being measured (US EPA, *et al.*, 2004).The parameter may be, for example the experimental standard deviation of the arithmetic mean. Taylor (1996) defines uncertainty as a measure of the incompleteness of one´s knowledge or information about a quantity whose true value could be established with a perfect measuring device. Thus uncertainty can be summarised as a range of values in which the true value of the measurand is expected to lie with high probability. Related to the concept of measurement uncertainty are measurement error, precision and accuracy. ISO (1993) define accuracy as the closeness of agreement between a test result and the accepted reference value. Accuracy cannot be measured, it can only be surmised from secondary measures that reflect the likelihood that an analytical method is accurate (Mason, 1992).The precision is a measure (or an estimate) of the reproducibility (i.e. repeatability) of repeated measurements.

Error

Error is defined as the difference between the observed value and the true value of the measured quantity (ISO, 1993). It can be expressed by the equation below:

$$\boldsymbol{E = x_i - x} \qquad \mathbf{2.14}$$

Where E is error, x is the true value and x_i is the obtained or observed measurement value.

Pitard (2005) defines error as “variation in measurements, calculations, or observations of a quantity due to mistakes or to uncontrollable factors”.

Errors are not "mistakes" but refer to inevitable inaccuracies and imprecision of data resulting from limitations of selecting small representative samples from large volumes of material and from the sensitivity of analytical methods. As errors are cumulative, each step of sampling through to analysis can be identified as a source of error (Downing, 2007). Error consists of two components, i.e. systematic and random errors.

Systematic errors: these errors often lead to bias of the measurement, shifting all measurement in a systematic way so that measurement results vary in a predictable manner. For example, a balance may constantly read mass 0.001 g higher because it was poorly calibrated. These errors are consistent and can be difficult to identify and correct (Owen, and Jones, 1990). Systematic error can result in high precision but poor accuracy. Unlike random errors, they cannot be minimized by statistical analysis of repeated measurements. Systematic errors can be estimated using a certified reference material and may be reduced by calibration.

Random errors: these errors are variations between successive measurements made under identical experimental conditions due to limitations of the equipment or techniques used to make the measurement. Unlike, systematic errors, the errors cause measurements to vary in an unpredictable way hence the term "random error" (Owen, and Jones, 1990). Sources of random error include lack of sensitivity of the instrument, noise in the measurement and imprecise definition of object dimensions. In experimental measurements, random error can be reduced by taking a sufficient number of measurements (Morgan and Henrion, 1990).

2.6.2 Uncertainty vs. error

Although some scholars, for example Geelhoed (2005), use the two terms error and uncertainty interchangeably, these terms differ in a number of ways. Uncertainty takes a range of values in which the true value of the quantity being measured is expected to lie, while error is made up of an individual value reflecting how the measured value deviates from the true value, as shown in Figure 2.6. In most cases, the true value is unknown.

The likely errors for the measurement are estimated by prescribing a range/bound for these errors as illustrated in Figure 2.6. This collective range of errors is called uncertainty.

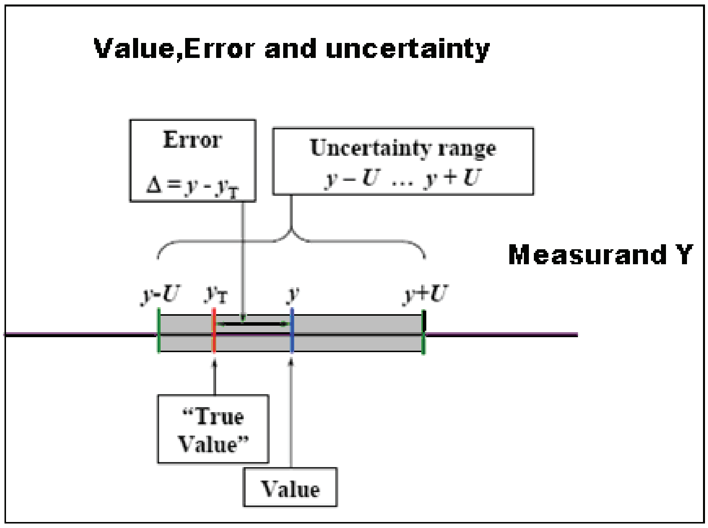


Figure 2.6: Relationship between value, error and uncertainty (Leito, 2004)

Example 1

For example an analyst from repeated measurement of mass reported the results below:

150.02	150.00	149.97	149.98	150.03

The mean of the measurement result is 150 g. The range of these values is 0.06 that is the difference between the maximum and the minimum value. This is an estimate of the possible range of errors. This can be written as:

Mass=150.00 g (mean) ± 0.06 g

This means that the analyst is confident that the true mass value lies between 149.97 and 150.03 g. Thus ± 0.06 g reflects uncertainty.

2.6.3 Need for evaluating uncertainty

Many world renowned organizations, American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories (ANSIN), ISO, EURACHEM, UKAS, and US EPA recommend that a statement of uncertainty accompany each measurement. Most of these bodies have released several reports and guidelines for evaluating and estimating measurement uncertainty. Thus one aim of reporting a result accompanied by an uncertainty value is to comply with regulations for reporting a scientific measurement result. For example, an estimation of the measurement uncertainty is required in ISO 17025 /9 (Magnusson, 2004). A proper acknowledgment of uncertainty associated with a given measurement result improves the credibility of the results. Further communication of uncertainty can lead to more informed decision-making, as the decision makers are able to carefully consider what may be possible and the consequences of such events (Huesemann, 1994).

2.6.4 Types of uncertainty

Uncertainty can be classified into two broad classes' namely sampling and analytical uncertainty. Sampling uncertainty refers to all possible sources of uncertainty, which may occur prior to analysis. In geochemical investigations, sampling uncertainty is often considered as the dominant source of uncertainty (Ramsey, 1998). This uncertainty is a result of many factors with the major source being heterogeneity. Other causes include improper sample handling and incomplete sampling equipment decontamination. Sampling uncertainty can be reduced by increasing the sample size.

Analytical uncertainty results from the limitations of analytical method used during analysis procedure. Common contributors include poor detection limits, analytical bias, lack of precision, and susceptibility to interferences. These factors create an uncertainty interval around the analytical result.

The Triad (2004) recognizes five types of uncertainty associated with measurements in hazardous waste site namely:

- Decision;
- Model;
- Analytical;
- Sampling; and
- Relational uncertainty.

Decision uncertainty is the total uncertainty contribution from political, economic, and public perception factors, alongside model, analytical, sampling, and relational uncertainties. Model uncertainty refers to the uncertainty associated with the inability of a model to accurately portray the key site features. Relational uncertainty is the uncertainty associated with the relationship between a parameter being measured and the true parameter of interest from a decision-making perspective (Triad, 2004). As for sampling and analytical uncertainty, the principles as discussed in the section above apply.

Haimes (1998) recognizes two types of uncertainty, namely knowledge and variability uncertainty. Variability uncertainty is linked to heterogeneity of the material being sampled. Knowledge uncertainty results from incomplete knowledge of the model that should be applied. The two are sometimes referred to as aleatory and epistemic uncertainty respectively. The two types are summarised in Figure 2.7.

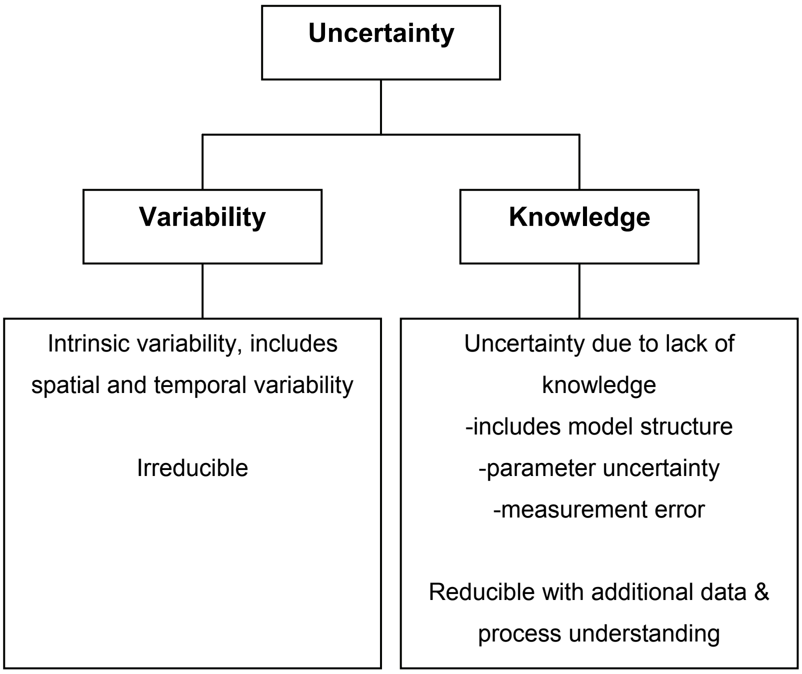


Figure 2.7: Types of uncertainty (Haimes, 1998).

This classification of uncertainty has the disadvantage of excluding other possible sources attributed to sampling and analysis. For instance instrument effects which are linked to analysis also contribute to measurement uncertainty.

Back (2001) divides uncertainty into three classes namely pre-sampling, sampling uncertainty, and post-sampling uncertainty. Pre-sampling uncertainty refers to uncertainty that occurs prior to sampling. Uncertainty is introduced during preliminary studies when prior information is used to estimate the value of some parameter. For example, use of standard deviation from previous studies to estimate the number of samples required for the present study. In this process it is inevitable that the estimated parameter will be associated with some uncertainty which is carried over to the present study.

Sampling uncertainty arises due to the fact that it is practically difficult to obtain samples that are reproducible and of highest quality. Generally field sampling uncertainty is much larger than uncertainty that is associated with post-sampling activities, such as sample preparation and chemical analysis (Crépin and Johnson, 1993). Post sampling uncertainty is uncertainty that occurs after sampling. Source of post sampling uncertainty include:

- Poor sample handling and transport,
- Contamination of the sample during preparation and sub-sampling, and
- Poor instrument calibration and human error.

Gy (1998) recognizes seven types of errors from both sampling and analyses. These are fundamental, grouping and segregation errors, periodic errors, increment delimitation error, increment extraction error, preparation errors and analytical errors. The most important of these is the fundamental error, which is associated with heterogeneity. This error unlike other errors cannot be eliminated but can be reduced by homogenising the sample.

2.6.5 Sources of uncertainty

For geochemical measurements, the identification of the possible sources of uncertainty is not a simple task. This is due to the complexity of the measurement process. In order to accurately identify the sources of uncertainty, it is advised to consider each process undertaken during the measurement process as a potential source of uncertainty.

(a) Sampling strategy

The sampling strategy defines how the samples are collected from a given sampling target and sources of uncertainty in this step could be:

- Only limited number of locations within the study population is selected.
- Few samples were collected.
- Strategy for sampling does not capture the extent of the variability that exists within the population being sampled.

(b) Sample preparation

All samples will undergo some form of preparation prior to analysis. The aim of sample preparation is to produce a manageable sample suitable for laboratory analysis. Sample preparation includes both chemical and physical processes such as acid digestion, drying and or sieving. These processes introduce uncertainty through the following (Pitard, 2005):

- Contamination of the sample.
- Loss of fines during crushing or fine particles may stick to the equipment due to electrostatic forces.
- Change in the physical, chemical, or mineralogical composition of the sample due for example to excessive drying.
- Poor handling of the sample and sample mix up.

(c) Analysis

The analytical method itself can be a major source of uncertainty for the measurement results. Geelhoed (2005) defines this uncertainty as the difference between the analysis result and the true value of the analyte concentration in the test portion. This variability component arises from imperfections of the analysis operation. It includes uncertainties associated with:

- Variations in the measurement conditions, for example, humidity changes affect results especially materials sensitive to humidity.
- Recovery of the analyte from a complex sample matrix.
- Reagent purity.
- Computational effects for example rounding off of figures can lead to inaccuracies in the final result.
- Human errors for example reading a meter or scale consistently high or low.
- Error that occurs during the publication of these data results.

(d) Heterogeneity

Heterogeneity expresses the variability inherent in the population or material being sampled in terms of the chemical and physical make up. This may be factors such as particulate size and levels of contamination. It includes both constitutional and distribution heterogeneity. Constitutional heterogeneity, describes the differences in composition, shape and density between the smallest individual and separable constituents. Distributional heterogeneity further describes the part of the overall heterogeneity stemming from spatial distributions at higher levels (Esbensen, 2005).

Heterogeneity has been identified as the major source of measurement uncertainty in geochemical sampling and uncertainty (Minkkinen, and Paakkunainen, 2005). Gy defines heterogeneity as:

$$\boldsymbol{h_i = a_i - \frac{a_L}{a_L} \times \frac{M_i}{\overline{M_\iota}}} \qquad \mathbf{2.15}$$

Where

h_i = heterogeneity,

a_i = value of the process variable in sample i,

a_L = mean value of the process variable in the lot,

M_i = the mass of the sample i and

$\bar{M}_i$ is the mean of the sample mass

A case in point is when uncertainty is introduced because increments from different locations in the target area will have different expected concentrations of analyte in a heterogeneous material concentration. For measurements subjected to averaging, sample-to-sample variation of the analyte concentration introduces uncertainty to the measurement result.

(e) Instrument

The instrument used for extraction of the sample from the target and analysis may present the weakest link in the measurement process. For most measuring instruments, uncertainty results from:

- Poor detection capabilities of some elements, for example XRF cannot detect minor elements with accuracy. The causes of such lack of capability are attributed to short counting time and high background interference and long decay time.
- Improper instrument calibration.
- Manufacturer specifications: most measurement instruments have an accompanying statement of accuracy or tolerance level specified by the manufacturer. This value should be incorporated in uncertainty measurements.

2.6.6 Methods for quantifying uncertainty

The section reviews some of the most popular methods for quantifying uncertainties in environmental studies. These include:

- Particulate sampling theory by Pierre Gy.
- EURACHEM method for quantifying uncertainty in analytical measurements.
- ANOVA (empirical approach) by Dr Michael Ramsey.

Parameters for expressing uncertainty

Table 2.7 highlights some of the parameters used in expressing uncertainty.

2.6.6.1 Top Down and Bottom up approach

Ramsey (1998) recognizes two broad approaches for quantifying measurement uncertainty, which are bottom up and top down approach. In the bottom up approach, each individual source of uncertainty is identified and quantified separately as standard uncertainty (its standard deviation). The overall uncertainty is found by combining the individual standard uncertainty values for each contributing uncertainty component. An example is the Particulate sampling theory by Gy. The bottom up approach uses already established methodology but requires that each source of uncertainty be identified which may be difficult to achieve. Gy’s method is discussed in detail in Section 2.5.6.2.

The top down approach estimates uncertainty from replicate samples or results obtained from inter-laboratory trials. (Ramsey and Argyraki, 1997). The scatter of these measurements is then used to estimate the uncertainty. An example is the empirical method that uses robust analysis of variance (ANOVA) to estimate uncertainty. Using this method, sources of uncertainty are grouped into two main classes- sampling and analytical uncertainty. One of its weaknesses is that it does not identify all the components contributing to uncertainty. The technique is further discussed in section 2.5.6.5.

Table 2.7: Parameters for expressing uncertainty

Parameter	Formula	
Variance	$S^2 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \bar{X})^2$	
Standard deviation	$S = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_i - \bar{X})^2}$	
Standard error	$S_{\bar{x}} = \frac{S}{\sqrt{n}}$	
Confidence interval	$\bar{X} \pm t_{\alpha/2}$	
Probability distributions	Rectangular	$a/\sqrt{3}$
	Triangular	$a/\sqrt{6}$
	Normal distribution	$a/\sqrt{2}$
		S

2.6.6.2 Particulate sampling theory, Pierre Gy

Uncertainty from both sampling and analysis can be quantified using Pierre Gy's sampling theory model.The theory is based upon the relationship that exists between the variability of the material, the particle sizes in the material, the distribution of the component of interest, and the size of sample taken (Mason, 1992).

According to Gy (1992);

"A sample is correct when all particles in a randomly chosen sampling unit have the same probability of being selected for inclusion in the sample."

Any deviations from correct sampling will result in sampling bias.

The theory classifies error into 10 classes (Figure 2.8). Some of these errors have a variance that can be estimated while others can give an idea whether the bias is positive or negative (Gustavsson, Lagerkvist, and Luthbom, 2005). Most sampling errors, except the preparation errors, are due to the material heterogeneity.

Global Estimation Error (GEE)

The Global Estimation Error (GEE) is the sum of the total sampling error (TSE) and the total analytical error (TAE) (Minkkinen, 2004). It can be expressed as follows:

$$GEE = TSE + TAE \qquad \mathbf{2.16}$$

Analytical Error (AE)

Analytical error is error resulting from the analytical technique used. These errors include instrumentation error, calibration error, operator errors, poor detection limits, analytical bias, and any other error linked to the analytical process. Unlike sampling errors, analytical errors are usually well-understood, and well-controlled by laboratory quality assurance and quality control procedures. Its contribution to GEE is usually small.

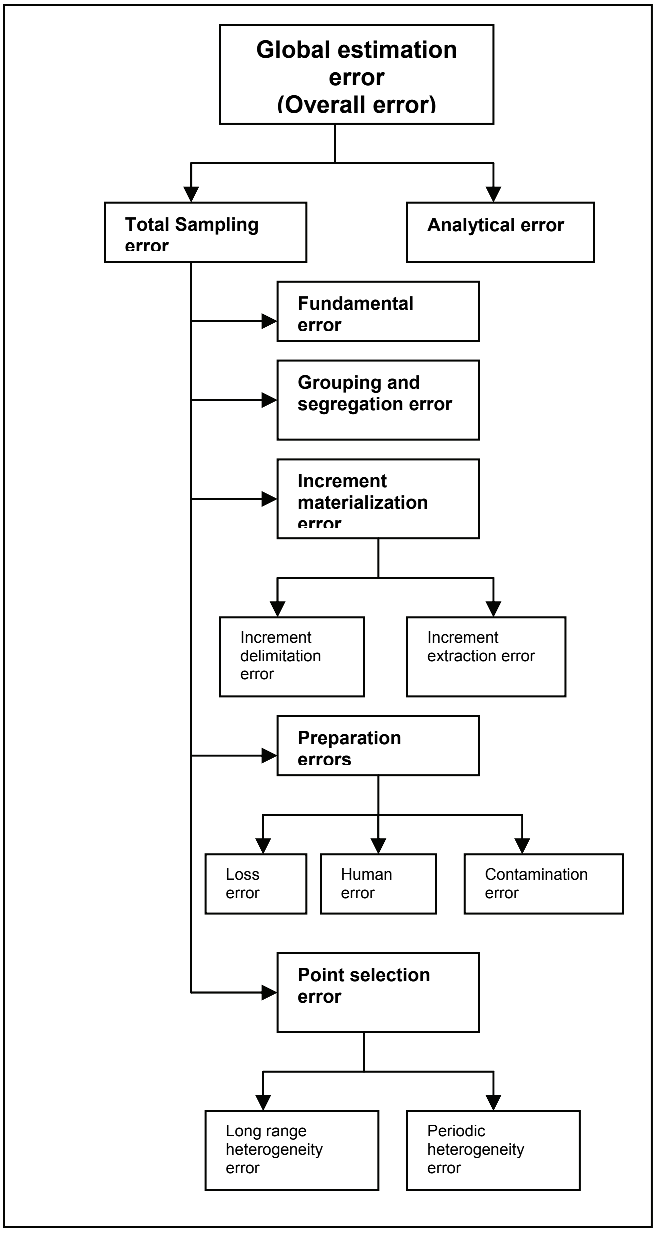


Figure 2-8: Classification of errors (Gy, 1992)

Total sampling error (TSE)

It is a combination of Preparation Errors (PE) and sampling or selection error (SE) (Mason, 1992). The selection or sampling error (SE) comprises of fundamental error, preparation error, increment extraction and delimitation error, periodic heterogeneity error, long range heterogeneity error and group and segregation error as shown in Figure 2-8.

This error can be expressed as follows:

$$\boldsymbol{TAE = PE + \sum(FE + GE + DE + EE + CE_2 + CE_3)} \qquad \mathbf{2.17}$$

Where

PE = Preparation error

FE = Fundamental Error

GE = Grouping and Segregation error

DE = Increment Delimitation Error

EE = Increment Extraction Error

CE_2 = Long Range Heterogeneity Fluctuation Error

CE_3 = Periodic Heterogeneity Fluctuation Error

Errors that contribute most to the total sampling error are fundamental error and grouping and segregation error.

Fundamental Error (FE)

Fundamental error is the main source of sampling error. The main cause of fundamental error is constitutional or compositional heterogeneity of the material being sampled. Sample heterogeneity may occur in terms of the particle size, particle weight, or particle shape. Fundamental error always exists and it is the only error that can be estimated beforehand, i.e. prior to performing sampling. Fundamental errors can be reduced by increasing the sample size or reducing the particle size of the material being sampled. The relationship between FE, mass, and particle size can be expressed as follows (Ramsey, 1998):

$$\boldsymbol{S^2 = \frac{Cd^3}{m}} \qquad \mathbf{2.18}$$

Where S is the standard deviation of the sampling error, m is the sample mass; d is the size of the largest particles in the sample and C, the constant, is a product of a number of factors.

It can be expressed as follow**s (**EURACHEM/ EUROLAB/CITAC/ Nordtest, 2006**)**:

$$\boldsymbol{C = f\, g\, \beta\, c} \qquad \mathbf{2.19}$$

Where *f* is the shape factor,

g is the size distribution factor (*g* =0.25 for wide size distribution and *g* =1 for uniform particle sizes,

β is the liberation factor for materials where the liberated particles are completely liberated, *β*= 1. For unliberated material an empirical equation, $\beta = (L/d)^x$

L – Diameter of the congregate

d – Single mineral diameter (librated single mineral)

Where values of *x* ranging from 0.5 to 1.5 have been suggested

c is the constitution factor and can be estimated if the necessary material properties are available by using (Minkkinen, 2004):

$$c = \frac{\left(1 - \frac{a_L}{\alpha}\right)}{\frac{a_L}{\alpha}} \rho_c + \left(1 - \frac{a_L}{\alpha}\right) \rho_m \qquad 2.20$$

Where

a_L is the average concentration of the lot

α – *the* concentration of the analyte in the critical particles,

ρ_c – *the* density of the critical particles

ρ_m – the density of the matrix.

The parameters are illustrated in Figure 2.9. From the equation it can be seen that doubling the sample mass will reduce variance by a factor of two and uncertainty by a factor of √2.

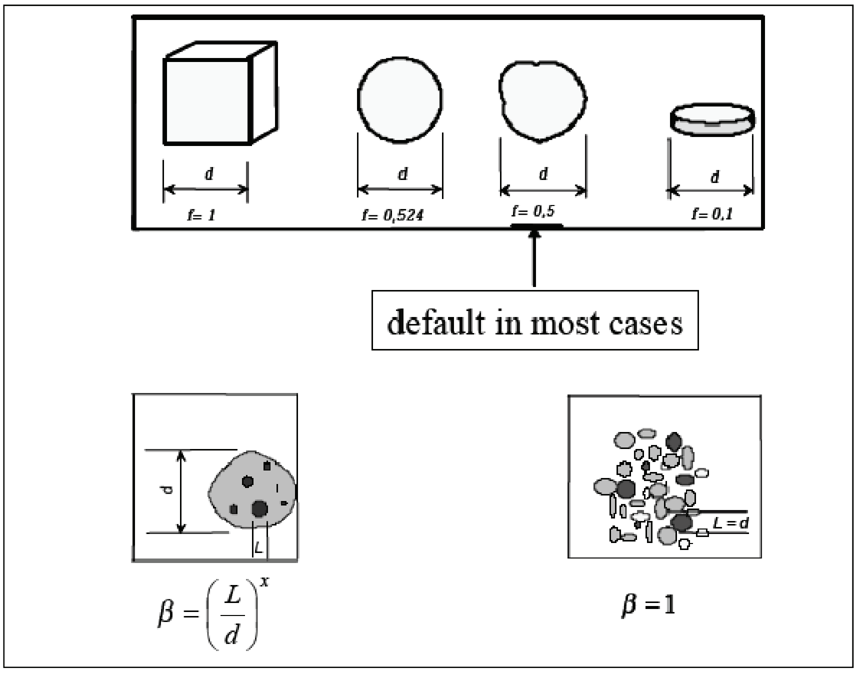


Figure 2.9: Estimation of factors for the estimation of the fundamental error [1]

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[1] Figure adapted from EURACHEM/ EUROLAB/CITAC/ Nordtest Guide, 2006.

Short summary

$C = fg\beta c = f*(1 \text{ to } 0.25)*(1 \text{ to } L/D)^{(0.5 \text{ to } 1.5)*}c$

where f is the shape factor, g is the size distribution factor (g =0.25 for wide size distribution and g =1 for uniform particle sizes, β is the liberation factor for materials where the liberated particles are completely liberated, β= 1.0 for unliberated material an empirical equation, β= (L/d)x where values of x ranging from 0.5 to 1.5 have been suggested and c is the constitution factor and can be estimated if the necessary material properties are available by using Equation 2.20 above.

Grouping and Segregation Error (GE)

This error results from distribution heterogeneity that occurs within the sample material. It results from non random segregation or grouping of sample elements. This is often attributed to the effects of gravity which causes for instance, high density particles with high levels of analyte to often drop to lower levels of the sample, causing subsamples from the top to be biased low and subsamples from the bottom to be biased high (Gerlach, *et al.*, 2004). The relationship between S^2 (FE) and S^2 (GSE) when taking N increments is expressed by (Gustavsson, Lagerkvist, and Luthbom, 2005).

$$S^2\,(GSE) \approx \frac{S^2\,(FE)}{N} \qquad 2.21$$

Where:
S^2 (GSE) = Variance of the grouping and segregation error
S^2 (FE) = Variance of the Fundamental Error
N = number of increments

Grouping and segregation errors can be minimized by collecting as many small increments as possible or by homogenization of the sample (USEPA, 1999)

Preparation error (PE)

These result from:

- Contamination due to improper procedures or contaminated equipment;
- Losses, e.g. fine particles are lost due to dusting or may stick to the sampling equipment due to electrostatic forces;
- A change in the physical, chemical or mineralogical composition of the sample;
- Human error, e.g. mixing up sample labels; and
- Sabotage and fraud, which although rare, may exist (Back, 2001)

These errors can be eliminated by using correct sampling practices and equipment, as well as operator training.

Increment extraction error (IXE)

This error occurs due to incorrect extraction of an increment. The extraction is said to be correct if the particles with their centre of mass inside the defined sample volume get into the sample. Thus a correct sampling tool should include materials that should be part of the sample and exclude those that should not be part of the sample (Mason, 1992). This error can be reduced by using the correct equipment.

Increment delimitation error (IDE)

This error occurs when the sampler or sampling device delimits portions of material to be sampled. This results in a non uniform probability of each particle to be collected**.** The expected bias from delimitation error is given in Equation 2.22 (Gustavsson, Luthbom and Lagerkvist, 2005):

$$\boldsymbol{E[B] = E[C_s - E\;[C_c]} \qquad \mathbf{2.22}$$

Where

E [B] is the expected bias,

E [C_S] expected mean concentration in extracted sample, and

E [C_C] is the expected mean concentration in the sample.

This error can be eliminated by using a proper sampling device.

Periodic Heterogeneity Fluctuation Error (CE_3)

This is a non random and cyclic error resulting from the fluctuations in the material to be sampled. These periodic fluctuations can be both spatial and temporal. For example variations in rainfall patterns from one season to another may result in a cyclic pattern of pollutant concentrations found in the vadose zone (Back, 2001). This error can be minimized by compositing samples correctly (USEPA, 1999)

Long – range Heterogeneity Fluctuation Error (CE_2)

This error is generated by the heterogeneity resulting from local trends (Mason, 1992). The error is non-random. Variance of this error can be quantified using variograms (Back, 2001). This error can be reduced by taking many increments to form the sample.

Advantages of this approach

- Largest source of uncertainty can be easily identified.
- It gives a transparent method showing which components of uncertainty have been considered in the summation of uncertainty.The theory is applicable to the sampling of particulate materials and fluids (Borgman *et al.*, 1996). The theory is generally comprehensive in that it takes into account all sources of error resulting from the process of sampling and analyses. Other theories only cover a small part of the sampling problem but Gy´s theory is the only theory of sampling of particulate material that is accepted and undisputed world-wide (Pitard, 1993).

- Where prior information is available, the approaches can be less costly than extensive experimental studies (EURACHEM /EUROLAB/ CITAC/ Nordtest Guide, 2006)

Limitations of this approach

- The method is very theoretical and therefore difficult to implement. May require detailed prior measurements of the mineralogy, grain size and analyte speciation of the material to be sampled (e.g. soil) and how these vary across the target.
- The theory is not appropriate where the sampling target consist of volatile or semi volatile chemicals.
- The estimates for C (constant) are difficult to determine.
- Gy has presented his work in a number of French and English publications but the high complexity has restricted the use of his sampling theory by engineers and scientists. In cases where Gy's published works are encountered, they are difficult to understand even if one is able to translate from French into English.

2.6.6.3 Quantifying uncertainty in analytical measurements (EURACHEM/ CITAC Guide CG4)

The EURACHEM guide offers guidance for the evaluation of measurement uncertainty, particularly that arising from chemical analysis. The guide operates within the ISO framework based on "Guide to the expression of Uncertainty in Measurement" (GUM). According to the guide, the process of estimating uncertainty for a given measurement result can be broken down into four steps which are:

Step 1: Specify the measurand
Step 2: Identify the uncertainty sources
Step 3: Quantify the uncertainty components
Step 4: Calculate the combined uncertainty

Step 1: Specify the measurand.

Measurand is defined by ISO (1993) as the particular quantity subject to measurement. This step requires the analyst to clearly give a detailed statement regarding the measurand including its relationship to the input quantities upon which it depends, i.e. provide a quantitative expression relating the value of the measurand to the parameters on which it depends. These parameters may be other measurands, quantities which are not directly measured, or constants. Basically the required level of detail for the specification of the measurand depends on a number of factors including the required level of accuracy of the measurement and the available information (Adams, 2002)

Step 2: Identify uncertainty sources

Following the definition of the measurand is the identification of uncertainty sources. This step requires that a comprehensive list of all possible sources of uncertainty be compiled. In preparing the list it is crucial to start with the basic expression used to calculate the measurand. A cause and effect diagram[2] may the used in order to avoid double counting of sources. Figure 2.10 illustrates a cause and effect diagram. Possible sources of uncertainty that may result during sampling and analyses are listed in Figure 2.12.

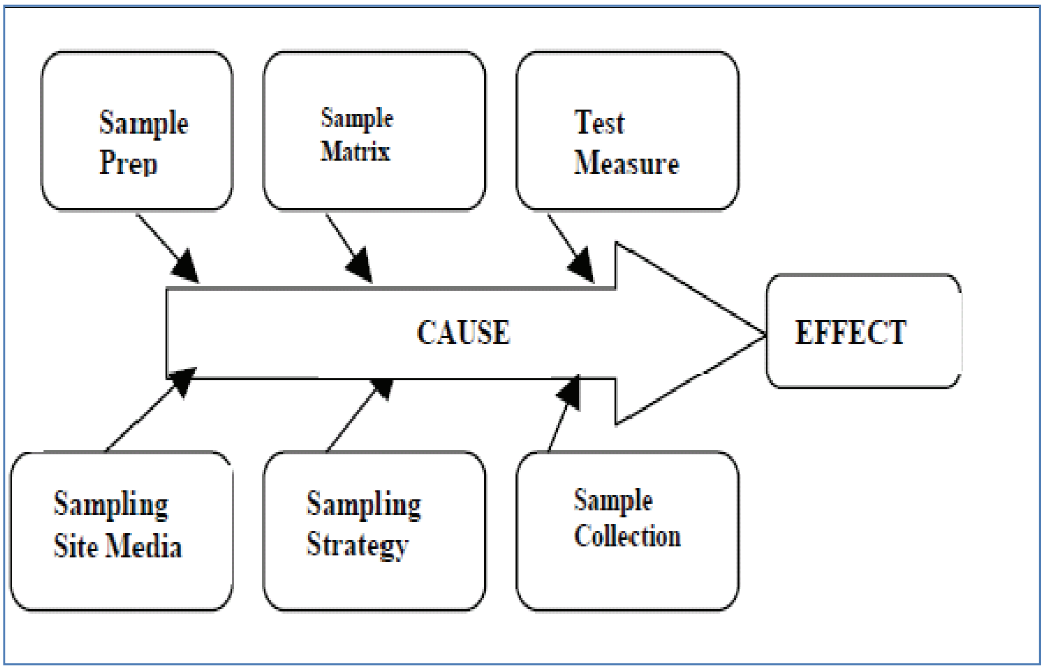

Figure 2.10: Field sample uncertainty sources

Step 3: Quantifying uncertainty

After sources of uncertainty are identified, an estimate of the likely size of these sources is made**.** Prior to quantifying the various sources it is important to first reconcile the information requirements with the available data. If there is not enough data, a plan should be made to obtain the further data requirements

- Uncertainty arising from the various sources can be quantified by determining the combined contribution to the uncertainty on the results from some or all of these sources using method performance data. Performance data is data derived from method validation studies of the analysis method used.

OR

- Evaluating the uncertainty arising from each individual source and then combining them using the laws of uncertainty propagation (Equations 2.23 or 2.24)

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[2] Cause and effect diagram is a graphical representation of the component uncertainty effects that cause measurement uncertainty.(Ingersoll, 2001)

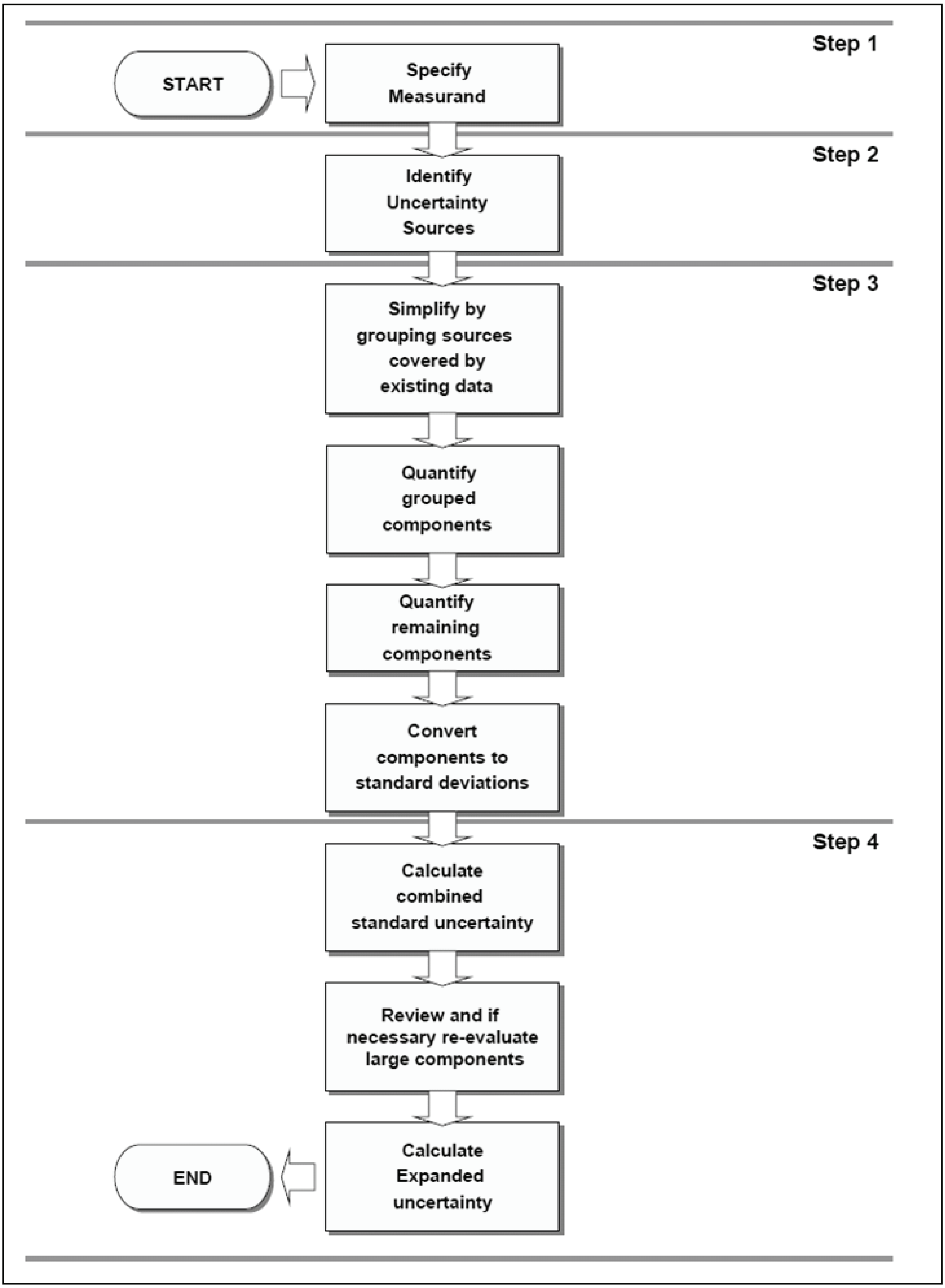

Figure 2.11: Uncertainty estimation process (Ellison, Rosslein and William, 2000)

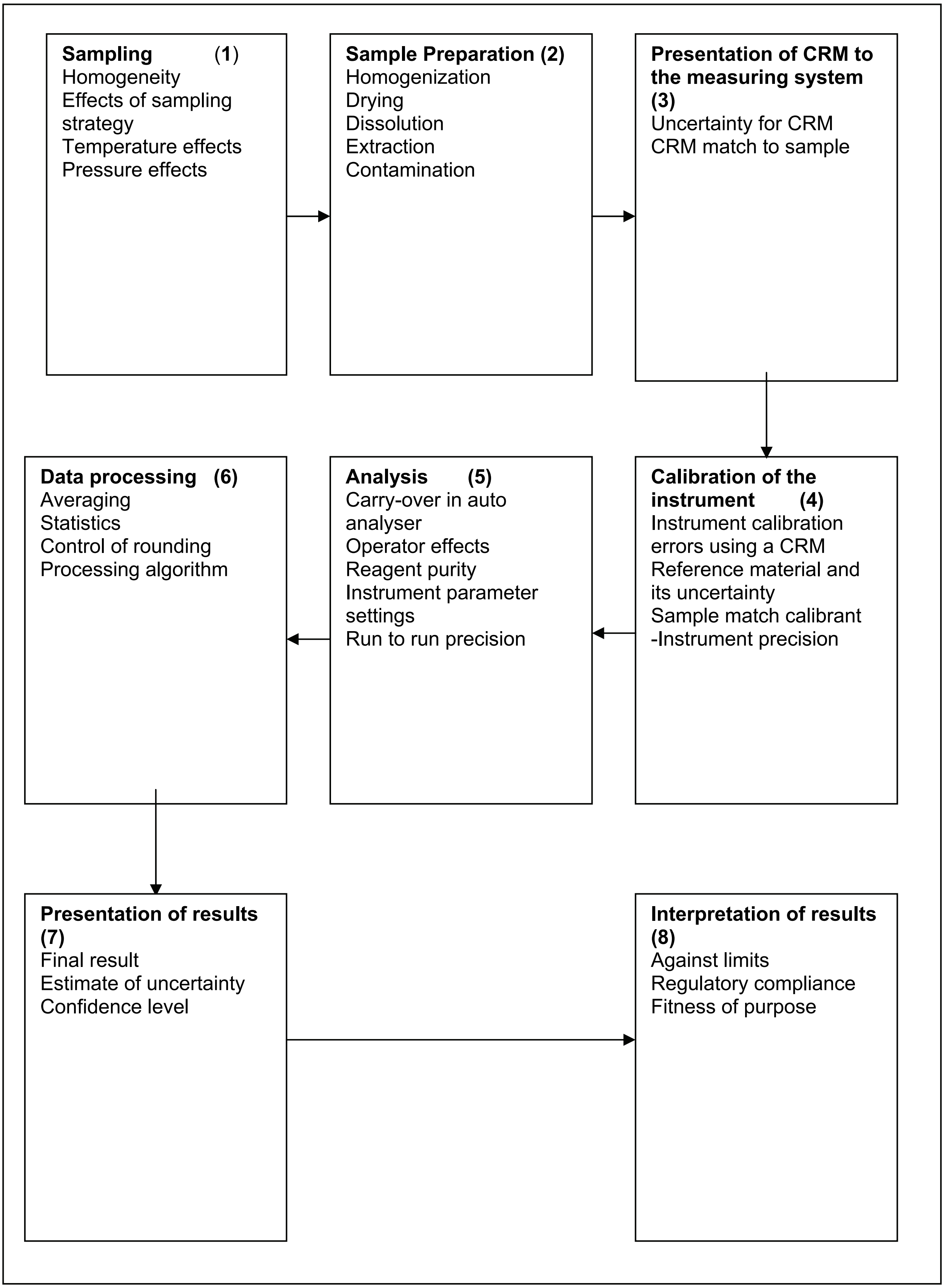

Figure 2.12: Flow chart for processes involved in sampling and analysis (Ellison, Rosslein and William, 2000).

Uncertainty estimation based on performance data

The guide presents several ways of estimating uncertainty based on performance data. Only one of these methods will be considered, uncertainty estimation using in house development and validation studies.

Uncertainty estimation using in house development and validation studies

Method validation parameters such as precision, bias, linearity, detection limit, robustness and specificity can be used as means of estimating measurement uncertainty. According to Ellison, Rosslein, and William (2000) uncertainty estimation from these parameters uses the best available estimate precision which can be obtained from calculating the standard deviation of an overall bias and its uncertainty. A good estimate of precision can be obtained from taking the standard deviation value of replicate analyses performed on the study of several samples. Bias can be estimated by repeated analysis of a relevant CRM.

Quantification of individual components.

When method performance data is unavailable it is recommended that uncertainty sources be evaluated individually. The components can be derived from:

Experimental variation of input variables – the uncertainty associated with variables often arises from random effects which cause variation of results when the experiment is repeated. In this case uncertainty is quantified in terms of the standard deviation of the values.

From standing data **–** standing data such as calibration certificates often provide information regarding uncertainty.

By modeling from theoretical principles **–** physical theories which provide good models for effects on result exist. One well known example is the effect of temperature on volume. By establishing the relationship between the two, uncertainties can be calculated (Ellison, Rosslein, and William, 2000).

Using judgment – Not all sources of uncertainty make a significant contribution to measurement uncertainty. Prior to combining uncertainty, the contributing uncertainties must be expressed as standard uncertainties (the standard deviations).

Each source of uncertainty is converted to standard deviation. When an uncertainty component is expressed as a standard deviation it is referred to as standard uncertainty. (ISO, 1993)

Rules for converting uncertainty components to standard deviation:

- Where uncertainty components were evaluated experimentally from the dispersion of repeated measurements, the standard deviation of the results is the standard uncertainty
- In the case of contribution to uncertainty in single measurements, the standard uncertainty is the standard deviation.
- For results subjected to averaging, the standard uncertainty is the standard error of the mean.

Step 4. Combining standard uncertainty

There are two main rules that can be followed when combining uncertainty. These rules are based on laws of error propagation (Taylor, 1996).

Rule 1

For models involving a sum or difference of quantities, combined standard uncertainty $u_c(y)$ is:

$$\boldsymbol{u_c\left(y(p,q\,\ldots\ldots)\right) = \sqrt{u(p)^2} + u(q)^2 + \cdots} \quad \mathbf{2.23}$$

Rule 2

For models that involve a product or quotient, combined uncertainty is given by:

$$\boldsymbol{u_c(y) = y\sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + \ldots..}} \quad \mathbf{2.24}$$

Calculating expanded uncertainty

The combined uncertainty is multiplied by the coverage factor (k) in order to obtain the expanded uncertainty. Expanded uncertainty provides an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand (ISO, 1993). It can be expressed as:

$$\boldsymbol{U = k * u_c} \qquad \mathbf{2.25}$$

Where U is the expanded uncertainty and k is the coverage factor.

In choosing the coverage factor (k), there are a number of aspects that have to be considered:

- The level of confidence required;
- Knowledge of the underlying distribution; and
- Knowledge of the number of values used to estimate random effects.

Reporting uncertainty

Information required when reporting uncertainty includes:

- Method used to calculate the measurand and the standard uncertainty
- The values and all sources of all corrections for both the calculation and uncertainty analysis.
- List of all the components of uncertainty with full documentation on how each was evaluated.

The procedure below is used for reporting combined standard uncertainty

Results: x (units) e.g. Total lead: 4.37%w/w

Standard uncertainty: 0.005%w/w

Expanded uncertainty is reported as
Result: (x ±U) units e.g. Total lead: (4.37±0.05)%w/w

Advantages of the method

- The method is based on existing techniques which makes it easy to apply.
- It also allows the analyst to see which component is contributing more to uncertainty hence the analyst can see where an adjustment in the sampling or analytical process is required in order to minimize uncertainty.

Limitations of the technique

- The definition of the element that is being measured is usually problematic. This is the case with geochemical sampling and analyses where a number of measurements and procedures are carried out.
- Some components of uncertainty are not readily quantifiable.
- More emphasis is placed on the contribution from analyses toward measurement uncertainty. As illustrated in Figure 2.1, the measurement process begins by sampling and hence it should also be taken into account when quantifying measurement uncertainty.

2.6.6.4 Analysis of Variance (ANOVA)

The classical statistical method ANOVA (analysis of variance) can be used to disaggregate the sampling uncertainty, analytical uncertainty and geochemical variability. The ANOVA, approach also known as the Empirical approach for quantifying uncertainty is based on the broad class; top down approach (EURACHEM/ EUROLAB/CITAC/ Nordtest, 2006). Unlike Pierre Gy's Sampling theory, one does not have to identify various sources of uncertainty individually. The uncertainty sources are classed into two broad classes, those associated with random components, and those associated with the systematic component of uncertainty. These are further subdivided depending on whether they arise from the sampling or analytical process.

To be able to estimate uncertainty, the analyst has to estimate the sizes of errors (random and systematic) caused by sampling and analysis first. Random errors are expressed as the precision of the method using the standard deviation in units of concentration, or as precision relative to the mean value as a percentage, at 95 % confidence. Systematic error is expressed as the bias of the method and is the difference between the mean of a number of measurements by a method and the certified value[3] obtained from certified reference material. The bias is expressed in the units of concentration, or again relative to the mean as a percentage.

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[3] This value is used since the true concentration is unknown.

Sources of uncertainty

There are four main sources of uncertainty. These sources are summarised in Table 2.8.

Table 2.8: Uncertainty contributions in the empirical approach

Process	Random (Precision)	Systematic (Bias)
Analysis	Analytical variability (combined contribution of random effect)	Analytical bias(combined effect of bias sources)
Sampling	Sampling variability (dominated by heterogeneity and operator variations)	Sampling bias (combined effect of selection bias, operator bias etc.)

Source: EURACHEM/ EUROLAB/CITAC/ Nordtest (2006)

Statistical models for estimating uncertainty

In order to design experimental methods to estimate uncertainty using this approach, a statistical model describing the relationship between the measured and true values of analyte concentration is required. If the sources of variation are independent, the measurement variance σ^2_{meas} is given by:

$$\sigma^2_{measurement} = \sigma^2_{sampling} + \sigma^2_{analytical} \qquad \mathbf{2.26}$$

Where $\sigma^2_{sampling}$ is the between-sample variance on one target (largely due to analyte heterogeneity) and $\sigma^2_{analytical}$ is the between-analysis variance on one sample.

If statistical estimates of variance (s^2) are used to approximate these parameters, we get

$$s^2_{measurement} = s^2_{sampling} + s^2_{analytical} \qquad \mathbf{2.27}$$

The standard uncertainty (*u*) can be estimated using s_{meas} , which is therefore given by

$$s^2_{measurement} = \sqrt{s^2_{sampling} + s^2_{analytical}} \qquad \mathbf{2.28}$$

Estimating uncertainty

According to Ramsey, there are four methods that can be used to estimate uncertainty. These vary in terms of the number of samplers[4] and the number of protocols. These are:

(a) Using single sampler and single protocol
(b) Using single sampler and multiple protocols
(c) Using multiple samplers and single protocol
(d) Using multiple samplers and multiple protocols

---

[4] Sampler is the sampling personnel ,that is, a person conducting the sampling

These can be summarised in Table 2.9 below:

Table 2.9: Four empirical methods for estimating combined uncertainty

Method number	**Method Description**	**Samplers (persons)**	**Protocols**	**Component estimated**			
				P_{samp}	**B_{samp}**	**P_{anal}**	**B_{analy}**
1	Duplicates	Single	Single	Yes	No	Yes	No
2	Protocols	Single	Multiple	Between protocols		Yes	No
3	CTS	Multiple	Single	Between samplers		Yes	Yes
4	SPT	Multiple	Multiple	Between protocols -between samplers		Yes	Yes

Four methods for estimating uncertainty in measurements (P_{anal} = precision of analytical method, B_{samp} = bias of sampling method, CTS = Collaborative Trial in Sampling, and SPT = Sampling Proficiency Test).

In this document focus will be placed on the first method.

Method 1: Single sampler and single protocols

The basis of the method is that the sampling precision and analytical precision can be estimated by taking duplicate samples for some proportion of the sample increments. The duplicate samples are not taken at exactly the same place, but separated by a distance that reflects the separation that might have occurred by a totally independent interpretation of the sampling protocol. Duplicate chemical analyses are then made on these duplicate samples as shown in the balanced experimental design below (Figure 2.13).

Calculating uncertainty and its components

Analysis of variance ANOVA is used to estimate the sampling and analytical precision. Analysis of variance (ANOVA) is a statistical technique for testing differences among group means. The purpose of analysis of variance model ANOVA is to identify the sources of variation and construct the proper tests to compare them. Estimation of the uncertainty derived from the systematic components of both the sampling and analytical process, analytical and sampling bias are done separately.

The classical ANOVA method is sensitive to outliers in the data set (Back, 2001) hence the Robust ANOVA method is used calculate uncertainty from the random component. Robust ANOVA allows the separation of sampling and analytical variances from the total variance. It is not affected by outlier values which makes it give reliable results compared to the classical ANOVA method (EURACHEM/ EUROLAB/CITAC/ Nordtest, 2006).

Robust ANOVA is implemented using ROBOCOOP4.EXE program which is a compiled FORTRAN program. ANOVA is not only restricted to this program, there are other statistical packages that are available

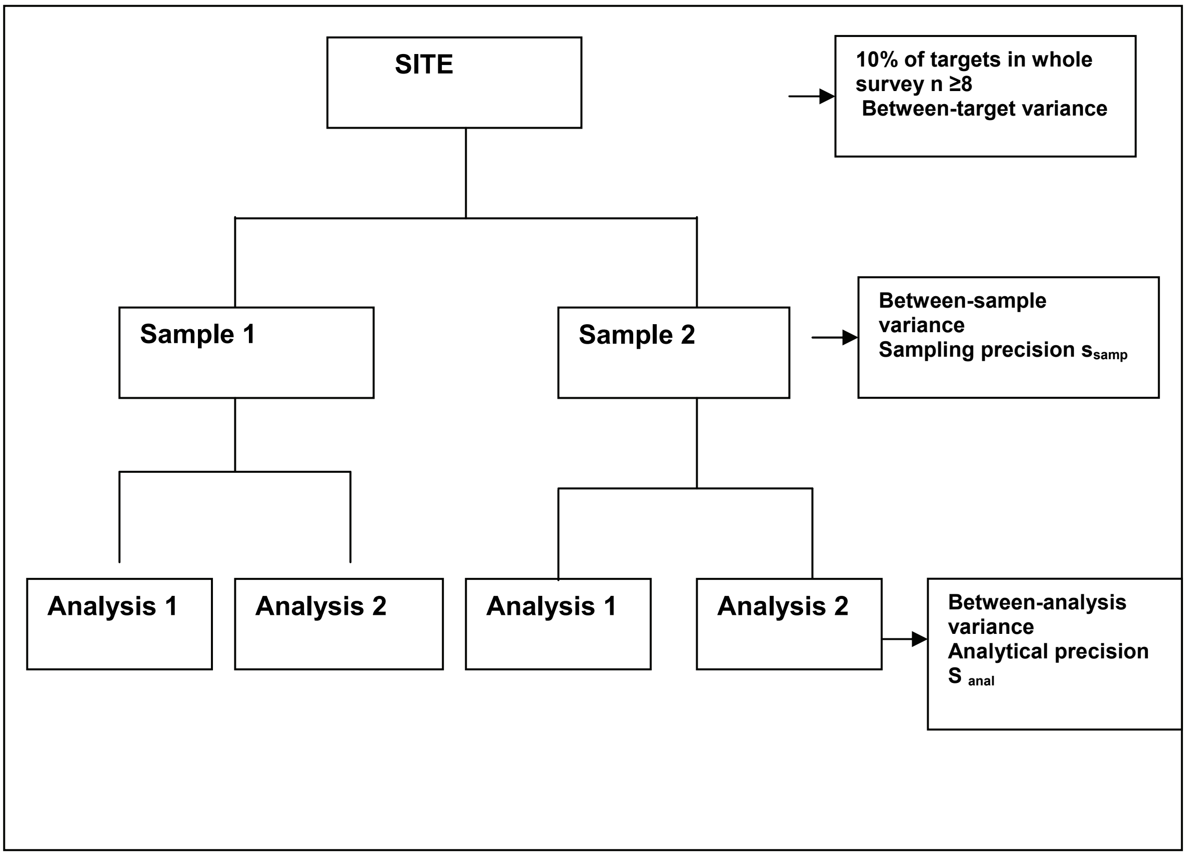


Figure 2.13: Balanced design

Output

The output from the ROBOCOOP.EXE4 program for ANOVA consists of three components of variability for robust analysis of variance. The first 5 lines of results are for classic ANOVA and the last five are for robust ANOVA as shown in Table 2.10. From the table showing the output, it can be seen that 4 parameters have been calculated for robust ANOVA. These are mean, sigma values, percent variance, and sigma total.

Table 2.10: Output of ROBCOOP4.EXE program (Ramsey, 1998**)**

```
CLASSICAL ANOVA RESULTS

Mean = 317.79999
Standard Deviation (Total) = 240.19238
                        Between-target          Sampling        Analysis
Sums of Squares         173 8031.9              370075.5        6473.0
Standard Deviation           197.5                 135.4          18.0
Percentage Variance          67.6                   31.8           0.6
ROBUST ANOVA RESULTS:
Mean = 297.30884
Standard Deviation (Total) = 218.48763
                        Between-target   Sampling      Analysis     Measurement
Standard Deviation        179.674         123.814        11.144       124.314
Percentage Variance       67.626           32.114         0.260        32.373
Relative Uncertainty        -              83.290         7.497       83.626
(% at 95% confidence)
```

The robust ANOVA results are used for the calculation of uncertainty. Classical ANOVA results are available for comparison purposes.

Interpretation of the results

- The mean value is the mean of the input data in the same units as input data.
- The sigma value represents estimates of standard deviation for three sources of variance.
- The percent variance expresses each of the three variances as a percentage of the total variance.

The sampling standard deviation $S_{sampling}$ =123.8 and analysis standard deviation $S_{analysis}$ =11.14.

The combined uncertainty ***u*** is a function of two independent variances and can be expressed as:

$$u_{measurement} = \sqrt{S^2_{analysis} + S^2_{sampling}} = 124.3$$

Note: the results in the output of ROBOCOOP 4 above are not linked to any calculations.
Its expanded uncertainty is:

$$\boldsymbol{U = u \times k} \qquad \mathbf{2.29}$$

Where k is the coverage factor and the value is 1.96 which gives a 95% confidence interval for the uncertainty.

“The calculated value of the uncertainty applies to measurements made on single samples taken in the survey. If n multiple samples are taken at any individual location within the site, the uncertainty on the average for that location is the value given by calculating the relative uncertainty divided by √n. This is equal to the standard error on the mean value (s/√n)”, Equation 1.5 (Ramsey, 1998, pg 101).

Estimation of sampling and analytical systematic error (bias)

- Estimation of analytical bias can be done through using repeated measurements of the certified reference material (CRM). If the systematic error found using this procedure is insignificant, the uncertainty associated with the systematic error is simply the combination of the standard uncertainty on the CRM value with the standard deviation associated with the systematic error.
- Estimation of sampling systematic error (sampling bias):
  (i) Can be done using sampling proficiency test. The procedure enables laboratories to monitor their measurement capability both by comparison to peer laboratories, and over time within their own laboratory.

(ii) Can be done by collecting paired samples for various targets. After chemical analysis of the two samples, the difference between a pair of results is an estimate of the bias for that target. Repeating the procedure for many distinct targets improves the precision of the estimate.

There are no hard and fast rules concerning how the bias estimates can be incorporated into the uncertainty measurements. The estimate for bias can be expressed as standard uncertainty and then incorporated into the measurement uncertainty.

Limitations

- The method only estimates the uncertainty resulting from random components and does not include those resulting from systematic errors.
- If fewer duplication samples are used there will be large uncertainties on the estimates of variances.
- If large quantities of dataset are involved the process may be tedious and time consuming.
- The method’s approach to sampling bias excludes bias introduced by the sampling equipment and bias inherent in the sample according to Pierre Gy´s sampling theory (Back, 2001).

2.7 SUMMARY

Reporting uncertainty of a measurement result provides the means for assessing the reliability of a measurement result. Measurement uncertainty prescribes a range in which the true value of the measurand is expected to lie. As results from sampling and analysis play an important role in decision making, it is crucial that uncertainty in sampling and analyses be evaluated and be part of result reporting. Unreliable results lead to poor decisions and potentially serious consequences. Every procedure undertaken from sampling, sample collection and preparation, analysis and the interpretation of the results should be recognized as potential sources of uncertainty.

As indicated above, three methods of quantifying measurement uncertainty were reviewed in detail. Although the methods vary, one assumption common to all the models is that measurement uncertainty can be defined statistically and expressions are derived for estimating and combining uncertainties from the various uncertainty components. The commonly used parameter is the standard deviation which defines how values spread.

Both Particulate Sampling Theory and EURACHEM methods are based on the bottom up approach in which one has to identify uncertainty sources, quantify them individually and combine them using some statistical model to obtain the overall uncertainty. This concept is contrary to the ANOVA model as suggested by Dr Michael Ramsey in which the overall uncertainty is determined without necessarily identifying the individual uncertainty components.

The method proposed by EURACHEM provides easy to follow steps for quantifying uncertainty but unlike the Particulate Sampling Theory which is comprehensive, the method emphasizes the effect of analyses. As seen above, the geochemical measurement process is a multi-tier process including sampling, sample preparation and analyses and these factors should be considered as potential sources of uncertainty.

ANOVA on the other hand, places more emphasis on the uncertainty components associated with random error and does not give a clear explanation on how uncertainty associated with systematic error is determined. Due to this lack of clarity regarding quantification of effects associated with systematic error, it is mostly likely that systematic effects are neglected hence an underestimate of the uncertainty value is provided. In addition, the fact that samples have to be accompanied by duplicates make the method expensive to implement especially taking into account that most projects normally work on a limited budget.

The Particulate Sampling theory as well as ANOVA have been applied in the field of environmental geochemistry, for example in estimating concentration of Cadmium and Phosphorous in topsoil (EURACHEM/EUROLAB/CITAC/Nordtest Guide, 2006 pg34-83). One disadvantage associated with ANOVA is that although the model is simple to use, it requires independent estimates of uncertainty contribution from sampling and analysis bias while some components of the Particulate Sampling Theory for example estimates of the four factors within Gy's constant C may be difficult to determine with any degree of certainty.

From the reviewed methods it can be seen that there is a definite need for a more user friendly method which can be applied in geochemical studies as stated in the objectives of this study. A new methodology for quantifying uncertainty in geochemical sampling and analyses was developed and it can be summarised as follows:

- Definition of the objectives of the investigation.
- Definition of the sampling target.
- Specification of the measurand
- Description of the sampling and analysis protocol.
- Identification of the sources of uncertainty.
- Quantification of the sources of uncertainty.
- Calculating the combined implications of the uncertainty components.
- Calculating the expanded uncertainty

This new method, akin to the previously discussed method, is based on the application of statistics in quantifying uncertainty in geochemical sampling and analysis. The method uses basic statistical parameters which are easy to understand. It is based on simple and straight forward steps which can be easily followed. Where complex sampling or analytical procedures have been used, the method is easily altered to suit the need at hand. The method is further discussed in Chapter 6.

CHAPTER 3
CASE STUDY INFORMATION

3.1 BACKGROUND

The case study is based on a geochemical assessment of tailings dams and waste rock carried out by Pulles Howard and De Lange (PHD) for AngloGold Ashanti Gold Mines Environmental Management. The objective of the assessment was to evaluate the potential of tailings dams and waste rock dumps in the Vaal River and West Wits mining areas to impact on water resources and implications of this in terms of mine closure and rehabilitation.

Gold mining waste is known to contain large quantities of heavy metals found in the host ore and chemical elements used in the extraction process such as cyanide. Under favourable conditions, in the presence of water and oxygen, metals and sulphur react with water and oxygen to produce discharges which are highly acidic. These, if discharged into the environment, may result in the contamination of water resources making the water unsafe for human and animal consumption

3.2 METHODOLOGY

In order to fully address the problem in question, PHD developed an in house geochemical assessment programme for ERA. The methodology adopted in undertaking geochemical assessment of tailings dams and waste rock can be summarised by Figure 3.1.

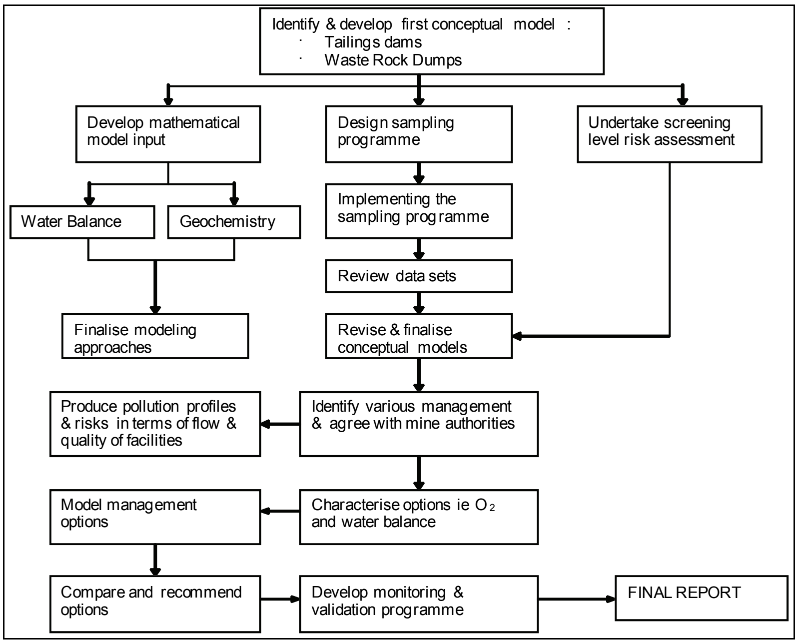


Figure 3.1: Methodology followed during the project (Pulles*, et al.*, 2003)

Although all procedures illustrated in Figure 3.1 are of importance, for the purpose of this study, the main focus will be on the sampling and analyses procedure.

3.3 SAMPLING TARGET

The sampling targets were tailings dams situated in the West Wits and Vaal River mining area owned by AngloGold Ashanti, as shown in Figure 3.2.

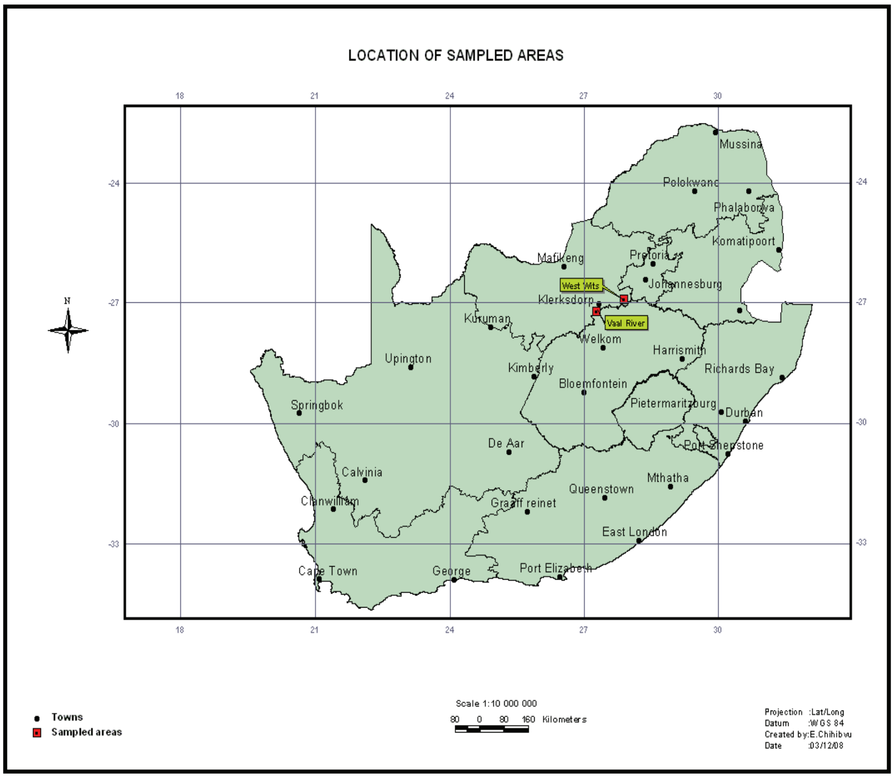


Figure 3.2: Location of Sampled areas; Vaal River and West Wits

3.3.1 West Wits Mine (Ashanti Gold)

The West Wits tailings consist of three complexes namely:

(a) The Old North Tailings Complex with tailings covering an area of 108 ha and containing approximately 24.12 × 10^6 m^3 of tailings.

(b) The New North tailings complex occupying an area of 237 ha and consisting of four dams: 5A, 5B, 7A and 7B.

(c) The South Tailings complex has an estimated tailings volume of 11.12 × 10^6 m^3 and consists of two dams including an upper dam with an area of 55.1 ha and a lower dam with 73.3 ha Figure 3.3.

3.3.2 Vaal River Mine (Ashanti Gold)

In the case of the Vaal River area, two tailing dams were sampled. The West tailings complex occupy as area of 450 ha while the West extension tailings dam has an area of 150 ha. The areas are illustrated in Figure 3.4 below.

3.4 SAMPLING PROTOCOL

The section gives an outline of the procedures adopted in sampling the tailings dams.

3.4.1 Sampling tool

Dutch Augers were used for sampling of tailings.

3.4.2 Sample collection

- Sample positions were planned at 1 sample point per 10 hectares.
- Positions were marked on a plan and a Global Positioning System (GPS) was used to locate each point.
- Samples were collected using a Dutch auger at 50 cm depth intervals.
- At shallow sample sites, samples were taken to a depth of 2.5 m and deep holes to a depth of 10 meters. Due to the presence of a saturated zone, very little was recovered and therefore no deep holes were drilled.
- Collected samples were labeled with each sample labeled three times.
- For some proposed sampling points, the positions were changed due to inaccessibility.

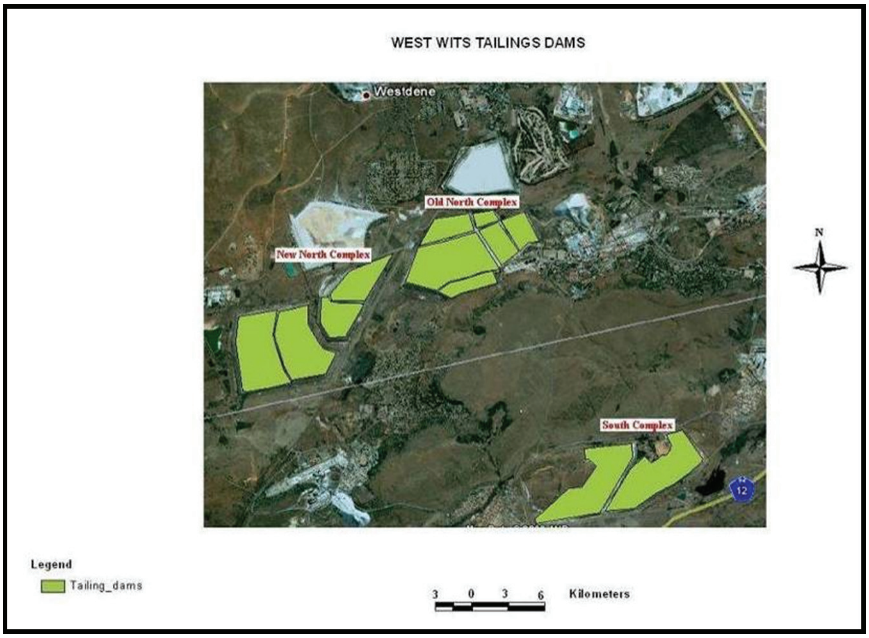


Figure 3.3: West Wits tailings dams (Google Earth, 2007)

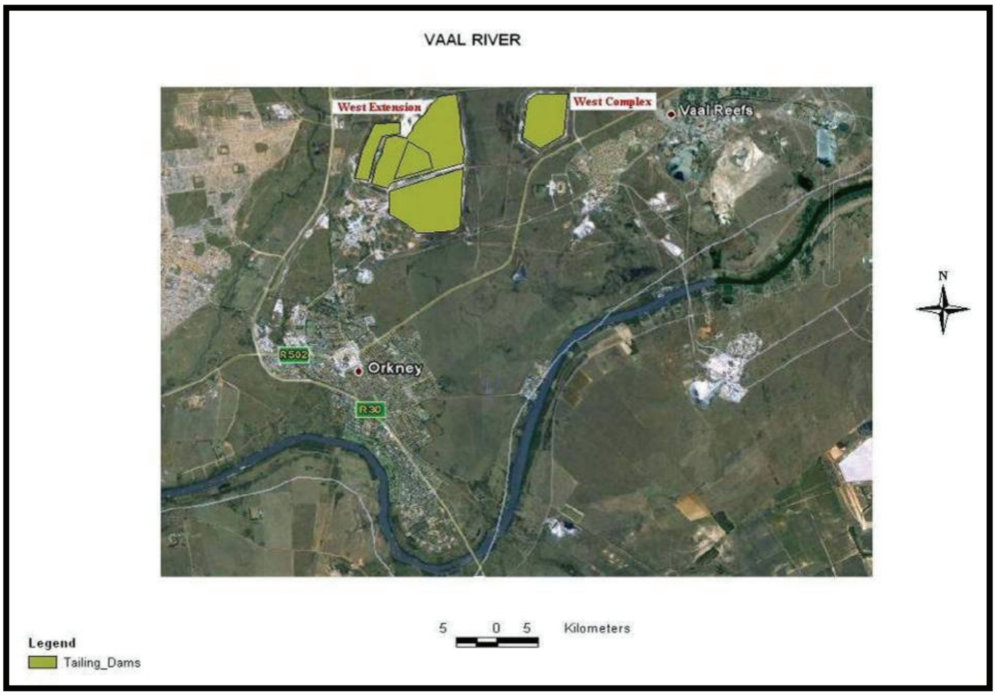


Figure 3.4: Vaal River tailings dams (Goggle Earth, 2007)

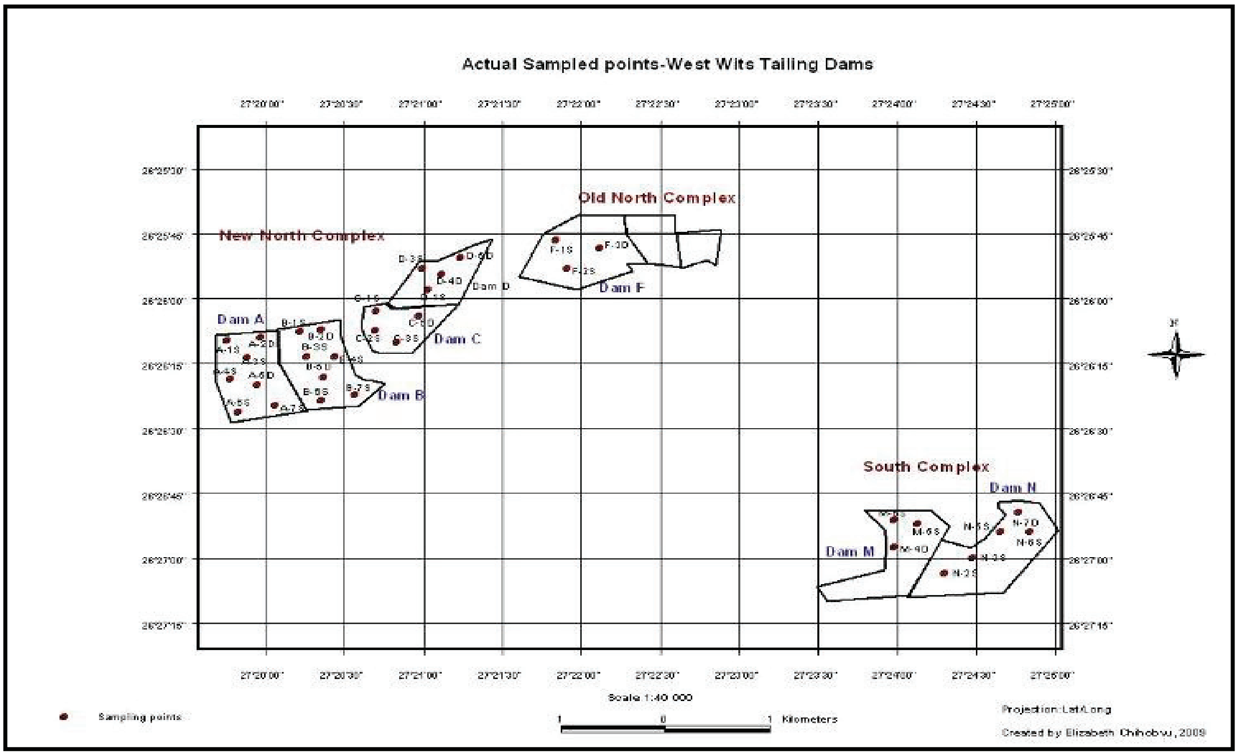


Figure 3.5: Sampled points, West Wits tailing dams

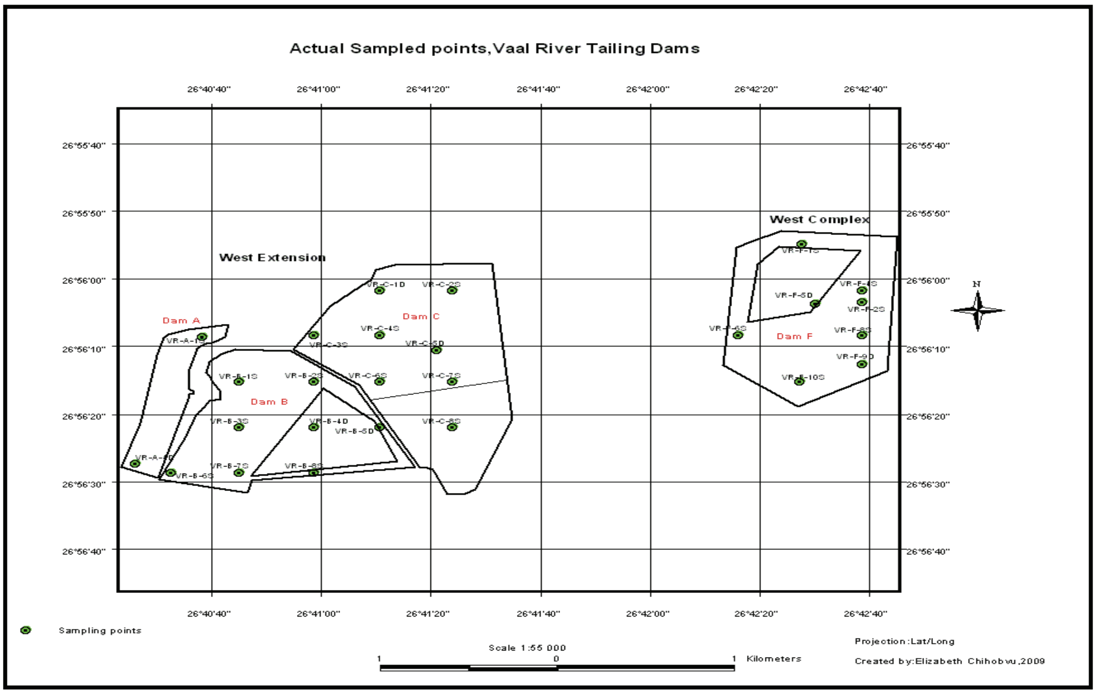


Figure 3.6: Sampled points, Vaal River tailing dams

3.5 ANALYTICAL PROTOCOLS USED

3.5.1 Sample Compositing

Samples were composited prior to analyses. All primary samples collected were composited into two composite groups. Composite samples from each shallow hole were made for ABA and moisture content analyses. Where there was no significant differences in paste pH, samples from each deep hole were made into one composite. Composite samples were further analysed for X Ray Diffraction (XRD), X Ray Fluorescence (XRF), water extraction Inductive Coupled Plasma Mass Spectrometry (ICPMS), Aqua Regia ICP MS, particle size distribution and microscopic studies, Table 3.1:

Table 3.1: Static tests conducted

Parameter	**Analysis technique (s)**
Acid Base Accounting (ABA)	Sobek Method
pH	pH meter
Particle size	wet and dry sieving
Mineralogy	X ray diffraction(XRD) Microscope
Major and trace minerals	X ray fluorescence (XRF)
Multi-element analysis	Inductively Coupled Plasma Mass Spectrometry (ICP MS)

For the purpose of this discussion, only Acid Base Accounting (ABA) data will be considered. Other methods are discussed in detail in the main report prepared for AngloGold, Ashanti Mines. All results obtained have been archived in a geochemical database.

3.5.2 Acid Base Accounting (ABA)

Acid base accounting (ABA) is the balance between acid production and acid consumption properties of mine waste (Fey, 2003). The potential for a given rock to generate and neutralize acid is determined by its mineralogical composition. This includes not only the quantitative mineralogical composition, but also individual mineral grain size, shape, texture and spatial relationship with other mineral grains (Mills, 1995).

Components of the ABA analysis include:

- Total sulphur
- Paste pH
- Acid potential (AP)
- Neutralization potential (NP)
- Net Neutralization potential (NNP)
- Neutralization potential ratio (NPR)
- It is usually the first step for determining AMD potential of mine waste.

Acid Base Accounting was carried out for the first batch of composite samples as illustrated in Appendix D.

Total sulphur

Total sulphur content is used to predict acid generation potential from geological material if all the sulphur (S) present reacts (Kania, 1998). The most common sulphide minerals that weather to produce AMD include pyrite (FeS_2), marcasite (FeS_2), chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS). The total sulphur (%) was measured using a Leco analyser. The resultant values were used to calculate acid potential.

Acid Potential (AP)

Acid potential is calculated from the product of total sulphur and 31.25kg/t of calcium carbonate (Sobek *et al.,* 1978). The relationship can be expressed by the equation below:

$$\boldsymbol{AP = Total\,Sulphur}\ (\%)\ \times \boldsymbol{31.25\ kg/t\ CaCO_3} \qquad \boldsymbol{3.1}$$

Neutralization Potential (NP)

The procedure used is based on the Fizz test by Sobek *et al.*, 1978. NP is expressed as:

$$\boldsymbol{NP = \frac{50a\left[x\left(\frac{b}{a}\right)y\right]}{c}} \qquad \boldsymbol{3.2}$$

Where

a is the normality of HCl added in digestion,
b is the normality of NaOH used in the titration,
c is the mass of sample in grams,
x is the volume of HCl added in ml; and
y is the volume of NaOH added in titration.

Paste pH

The pH was determined using a pH meter. Further discussion is presented in Chapter 6.

Net Neutralization Potential (NNP)

Net Neutralization Potential refers to the calculated difference between NP and AP

$$NNP = NP - AP \qquad 3.3$$

According to the total sulphur (%) and the ratio between NP and AP the material was classified as shown in Table 3.2.

Table 3.2: Rock type classification (Pulles et al., 2003**)**

TYPE I	Potentially acidic forming	Total S (%)>0.25% and NP:AP ratio 1:1 or less
TYPE II	Intermediate	Total S(%)>0.25% and NP:AP ratio 1:1 to 3:1
TYPE III	Non Acid forming	Total S(%)<0.25%and NP:AP ratio 3:1 or greater

3.6 RESULTS

All analytical results have been stored in a geochemical database accompanying this report. The database in Excel spreadsheet format consists of several worksheets highlighting the various analytical procedures carried out. The basic unit of all the sheets is an individual sample or sample composite. The structure of the database is as discussed below.

Common fields

- Location: Large locality for example West Wits mining area
- Small locality e.g. Dam A
- Coordinates: Latitude and Longitude in Decimal degrees
- Sample ID ; e.g. A-3S

Specific Fields

❖ Mineralogy worksheet:

Quartz	Hematite	Calcite	Dolomite	Gypsum	Plagioclase	K-feldspar	Amphibole	Mica	Prophyllite	Chlorite

❖ Acid Base Accounting (ABA) worksheet

Paste pH	Total S (%)	AP (kg/t)	NP:AP ratio	C-NP (kg/t)	C-NNP (kg/t)	Rock Type total S	Rock type AP:NP	Sampling depth	Composite	Latitude (Decimal degrees)	Longitude (Decimal Degrees)

❖ Grain Size worksheet

Sample weight (g)	750 um (g)	150 um (g)	75um (g)	>75 um (g)	Total (g)	Accuracy (%)	Error (%)	Material type

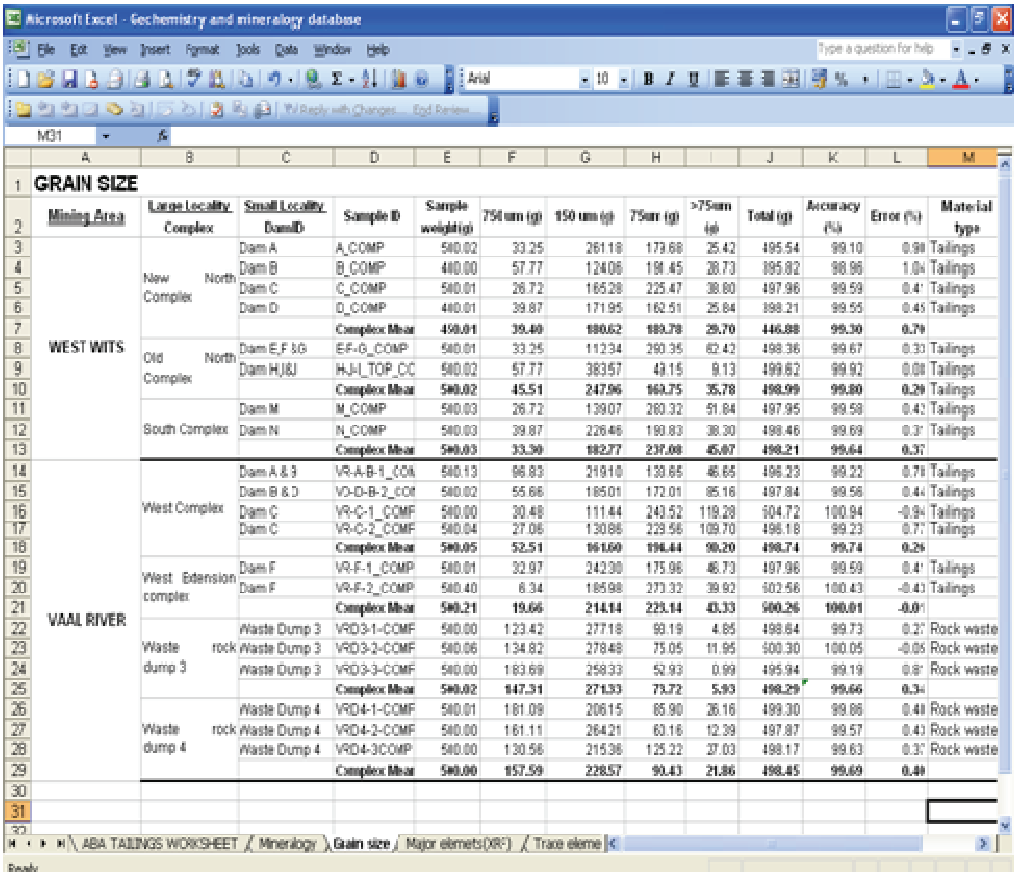
❖ Major Elements worksheet

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3	L.O.I	Material Type

❖ Trace elements

As	Ba	Ce	Co	Cr	Cu	Ga	Hf	Mo	Nb	Ni	Pb	Rb	Sc	Sr	Ta	Th	U	V	W	Y	Zn	Zr	Material type

Figure 3.7 below illustrates an example of the structure of the worksheets.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	GRAIN SIZE												
2	Mining Area	Large Locality Complex	Small Locality DamID	Sample ID	Sample weight(g)	750 um (g)	150 um (g)	75um (g)	>75um (g)	Total (g)	Accuracy (%)	Error (%)	Material type
3	WEST WITS	New North Complex	Dam A	A_COMP	500.02	33.25	261.18	173.68	25.42	495.54	99.10	0.90	Tailings
4			Dam B	B_COMP	400.00	57.77	124.06	191.45	28.73	395.82	98.96	1.04	Tailings
5			Dam C	C_COMP	500.01	26.72	165.28	225.47	38.80	497.96	99.59	0.41	Tailings
6			Dam D	D_COMP	400.01	39.87	171.95	162.51	25.84	398.21	99.55	0.45	Tailings
7				Complex Mean	450.01	39.40	180.62	189.78	29.70	446.88	99.30	0.79	
8		Old North Complex	Dam E,F &G	E-F-G_COMP	500.01	33.25	112.34	290.35	62.42	498.36	99.67	0.33	Tailings
9			Dam H,I&J	H-J-I_TOP_CC	500.02	57.77	383.57	49.15	9.13	499.62	99.92	0.08	Tailings
10				Complex Mean	500.02	45.51	247.96	169.75	35.78	498.99	99.80	0.29	Tailings
11		South Complex	Dam M	M_COMP	500.03	26.72	139.07	280.32	51.84	497.95	99.58	0.42	Tailings
12			Dam N	N_COMP	500.03	39.87	226.46	190.83	38.30	498.46	99.69	0.31	Tailings
13				Complex Mean	500.03	33.30	182.77	237.08	45.07	498.21	99.64	0.37	
14	VAAL RIVER	West Complex	Dam A & B	VR-A-B-1_COM	500.13	96.83	219.10	133.65	46.65	496.23	99.22	0.78	Tailings
15			Dam B & D	VO-D-B-2_COM	500.02	55.66	185.01	172.01	85.16	497.84	99.56	0.44	Tailings
16			Dam C	VR-C-1_COMP	500.00	30.48	111.44	243.52	119.28	504.72	100.94	-0.94	Tailings
17			Dam C	VR-C-2_COMP	500.04	27.06	130.86	229.56	109.70	496.18	99.23	0.77	Tailings
18				Complex Mean	500.05	52.51	161.60	196.44	90.20	498.74	99.74	0.26	
19		West Extension complex	Dam F	VR-F-1_COMP	500.01	32.97	242.30	175.96	46.73	497.96	99.59	0.41	Tailings
20			Dam F	VR-F-2_COMP	500.40	6.34	185.98	273.32	39.92	502.56	100.43	-0.43	Tailings
21				Complex Mean	500.21	19.66	214.14	224.14	43.33	500.26	100.01	-0.01	
22		Waste rock dump 3	Waste Dump 3	VRD3-1-COMP	500.00	123.42	277.18	93.19	4.85	498.64	99.73	0.27	Rock waste
23			Waste Dump 3	VRD3-2-COMP	500.06	134.82	278.48	75.05	11.95	500.30	100.05	-0.05	Rock waste
24			Waste Dump 3	VRD3-3-COMP	500.00	183.69	258.33	52.93	0.99	495.94	99.19	0.81	Rock waste
25				Complex Mean	500.02	147.31	271.33	73.72	5.93	498.29	99.66	0.34	
26		Waste rock dump 4	Waste Dump 4	VRD4-1-COMP	500.01	181.09	206.15	85.90	26.16	499.30	99.86	0.14	Rock waste
27			Waste Dump 4	VRD4-2-COMP	500.00	161.11	264.21	60.16	12.39	497.87	99.57	0.43	Rock waste
28			Waste Dump 4	VRD4-3COMP	500.00	130.56	215.36	125.22	27.03	498.17	99.63	0.37	Rock waste
29				Complex Mean	500.00	157.59	228.57	90.43	21.86	498.45	99.69	0.31	

Figure 3.7: An example of the structure of the worksheet

CHAPTER 4
DETERMINATION OF SAMPLE SIZE

4.1 INTRODUCTION

Sample size determination is one of the most crucial and difficult steps in the geochemical investigation process. Studies of geological materials have revealed that variability exists in terms of mineralization, chemical composition and alteration. Under such conditions, it is essential that an adequate sample size that accurately characterizes the variability be collected.

This chapter provides a detailed discussion of sample size determination using a statistical analysis approach. In order to successfully determine optimum sample size needed to satisfy the objectives of a study, several factors need to be considered. These include: the purpose of the investigation, type of material to be sampled, cost of sampling, variability of the material and available site information. Additional considerations are the required level of acceptable error, confidence interval and standard deviation. These factors and their effects are explored in detail in the following sections.

4.2 OVERVIEW OF THE STATISTICAL METHOD

If a sample size n with the values (x_1, x_2,…x_n) is drawn from a starting population that has a mean "μ" and a standard deviation "σ", then the sample mean "$\bar{x}$" is given by :

$$\bar{\boldsymbol{x}} = \frac{\sum_{i=1}^{n} \boldsymbol{X}_i}{\boldsymbol{n}} \qquad \mathbf{4.1}$$

Where $\bar{x}$ (sample mean) is assumed to present the best estimate of μ, and therefore $\mu = \bar{x}$.

The difference between μ and $\bar{x}$ is estimation error (d). With a given confidence level, the sample mean estimate and estimation error are often reported as follows:

$$\bar{x} \pm \mathbf{d}$$

The estimation error **(d)** equals:

$$\boldsymbol{d} = \boldsymbol{T}_{\propto/2} \times \frac{\boldsymbol{\sigma}}{\sqrt{\boldsymbol{n}}} \qquad \mathbf{4.2}$$

Tα represents the function of T distribution, which is only related to sample numbers and confidence levels as shown in Table 4.1.

Table 4.1: T values for different sample numbers and confidence levels

Sample numbers	Confidence levels			
	80%	90%	95%	99%
5	1.533	2.132	2.776	4.604
10	1.383	1.833	2.262	3.250
25	1.318	1.711	2.064	2.797
30	1.311	1.699	2.045	2.756
40	1.303	1.684	2.021	2.704
60	1.296	1.671	2.00	2.660
120	1.289	1.658	1.980	2.617
>120	1.282	1.645	1.96	2.576

Based on the Central Limit Theorem, as long as the sample numbers are reasonably large (usually greater than 30), the sample mean will tend to be normally distributed. Therefore, the estimation error (d) can be expressed as follows:

$$\boldsymbol{d = Z_{\propto/2} \times \frac{\sigma}{\sqrt{n}}} \qquad \mathbf{4.3}$$

Where

$Z_{\alpha/2}$ represents the function of normal distribution which related to confidence levels, Table 4.2.

Table 4.2: Z values for different confidence levels

Confidence levels	75%	85%	95%	99%
Z values	1.15	1.44	1.96	2.57

From the Equation (4.3), it can be seen that for a given confidence level, the estimation error is dictated by the standard deviation of the population and the sample numbers. On the other hand, the wider the population spreads, the larger the estimation error is. The bigger the sample size, the smaller the estimation error is. For a given confidence level, the estimation error is determined by the sample size. If there is a desire to reduce the error, sample size should be increased. However, increasing sample numbers means spending more money. So a balance been competing factors should be sought. Rearranging Equation (4.3), we get the following formula:

$$\boldsymbol{n = \left(\frac{Z_{\alpha/2} \times \sigma}{d}\right)^2} \qquad \mathbf{4.4}$$

This is the basic model for determination of sample size. Usually the population standard deviation “σ,” is unknown but it can be estimated by taking sample standard deviation “S” and equation 4.4 then becomes:

$$\boldsymbol{n = \left(\frac{Z_{\alpha/2} \times s}{d}\right)^2} \qquad \mathbf{4.5}$$

The formula is a more convenient way for estimating the sample size for continuous data.

4.3 PARAMETERS THAT AFFECT SAMPLE SIZE

In order to illustrate the factors that influence sample size determination, randomly chosen pH results for West Wits tailings dams were used as shown in Table 4.3.

Table 4.3: pH data (Pulles *et al.,* 2002)

9.00	8.80	8.10	7.60	8.20
9.00	8.30	8.40	8.10	8.10
8.10	8.40	8.70	8.50	8.20
8.30	8.30	8.60	8.20	8.30
8.20	8.30	8.50	8.20	8.10
8.30	7.90	7.60	8.40	8.50
8.30	8.40	7.50	8.00	8.40
8.30	8.40	8.40	8.50	8.60
7.80	8.30	8.20	7.70	8.90
8.20	8.30	8.10	8.50	8.70
8.20	8.20	8.60	8.80	8.40
8.20	8.40	8.50	8.00	8.50
8.10	8.30	8.50	8.60	8.70
8.00	8.30	8.40	8.70	8.60
8.20	8.30	8.40	8.60	9.00
8.30	8.20	8.20	8.70	8.60
7.50	8.50	7.80	8.40	8.80
7.70	8.50	8.20	8.20	8.60
8.20	8.40	8.30	8.30	8.60
8.40	8.40	7.50	8.40	8.60
8.20	8.30	7.90	8.50	8.10
8.00	8.50	7.90	8.30	9.10
7.60	8.70	8.20	8.50	8.50
8.10	8.50	8.10	8.50	8.50
8.60	8.50	8.30	8.60	8.40
8.70	8.60	8.30	8.50	8.70
8.40	8.40	8.30	8.20	8.80
8.20	8.50	8.30	8.10	8.40
8.50	8.50	8.40	8.20	8.40
8.60	8.60	8.40	8.20	8.70
8.30	8.40	8.40	8.30	8.50
8.20	8.50	8.20	8.00	8.40
8.90	8.50	8.10	8.30	8.30
8.70	8.40	8.30	8.60	8.10
8.50	8.10	8.70	8.60	8.80
8.80	8.40	8.90	8.30	8.50
8.30	8.50	7.20	7.80	8.70
8.50	8.60	8.60	7.70	8.50
8.00	8.00	7.90	8.20	8.20
8.60	8.30	8.20	8.60	8.40
Parameter	Sample numbers	Mean	Variance	Standard deviation
Value	200	8.35	0.09	0.30

4.3.1 Confidence level

Confidence level as discussed in Chapter 2 specifies how confident one is that the parameter (mean) lies in the specified interval or range. Based on Equation 4.4, an increase in required confidence level means more samples will be required. This relationship can be illustrated using the dataset from Table 4.3.

The mean ($\bar{x}$) of the data set is 8.35. This is the estimate of population mean (true mean). If it is necessary to know with 75% confidence level and standard error of 0.02 that 75 out of 100 samples are within the true population mean of 8.35±0.02, sample size (n) required is:

$$n = \left(\frac{\mathbf{1.152 \times 0.302}}{\mathbf{0.022}}\right)^{\mathbf{2}} \approx \mathbf{298}$$

Therefore the required sample size is 298.

BUT

If the confidence level is increased to 95%, the required samples are:

$$\boldsymbol{n} = \left(\frac{\mathbf{1.962 \times 0.302}}{\mathbf{0.022}}\right)^{\mathbf{2}} \approx \mathbf{866}$$

The calculated results show that if it is necessary to increase the confidence level, it becomes necessary to increase the sample numbers. However, the relationship is not linear, as doubling the sample size does not halve the confidence interval (Israel, 1992). This relationship is shown in Table 4.4.

Table 4.4: Sample numbers for different confidence levels

Confidence levels	75%	80%	85%	90%	95%	99%
Sample numbers	298	369	467	605	866	1486

4.3.2 Standard deviation or population spread

Standard deviation defines how the population is spread. This parameter, like standard error and confidence level also affects sample size. Essentially the wider the population spreads, the larger the number of samples needed. The relationship can be demonstrated by the example below. The sample standard deviation of the dataset in Table 4.3:

s = 0.30

Given a 95% confidence and the standard error of 0.02, the sample size for dataset (Table 4.3) can be calculated as follows:

$$\boldsymbol{n = \left(\frac{1.962 \times 0.302}{0.022}\right)^{2} \approx 866}$$

If the standard deviation is increased to 0.40 with 95% confidence level and standard error of 0.02, the required sample size is:

$$\boldsymbol{n = \left(\frac{1.962 \times 0.40}{0.022}\right)^{2} \approx 1539}$$

From the results, it is clear that the standard deviation of the population affects sample size, with an increased standard deviation requiring more samples to obtain the same confidence levels.

4.3.3 Standard Error

Equation 4.4 shows that a relationship exists between sample size and the standard error. This relationship is exponential and an increase in sample size is followed by a decrease in standard error. The data in Table 4.5 illustrates this relationship. Using the data values in Table 4.3, s =0.30, C.I = 95% and standard error (a) = 0.02; and (b) = 0.04, then the required sample size n is:

$$\boldsymbol{a)\ n = \left(\frac{1.962 \times 0.302}{0.022}\right)^{2} \approx 866}$$

$$\boldsymbol{b)\ n = \left(\frac{1.962 \times 0.302}{0.040}\right)^{2} \approx 219}$$

Table 4.5: Sample numbers for different standard error (d)

Standard error	0.01	0.02	0.03	0.04	0.05
Sample numbers	3 511	866	385	219	140

The results above indicate that a small standard error value is associated with a large sample size. In addition the formula shows that to halve the error, the sample size needs to be quadrupled.

4.3.4 Cost of taking the samples

Financial issues assist in determining how precise the estimates should be. If the decision to be made will incur significant financial outlay, then more samples should be collected in order to have increased confidence in the decision. However, a large sample size means a higher sampling budget and this needs to be balanced against the financial consequences of making a wrong decision based on data with lower confidence levels.

4.4 PROCEDURE FOR DETERMINING SAMPLE SIZE

A step-wise procedure for determining sample size is shown in Figure 4.1 below.

4.4.1 Specify the sampling objectives

In order to correctly determine sample size, it is essential to clarify the objectives of the investigation. One should ask the question “what do I want to know?” and “what information do I expect to gain?” Only when these questions are addressed can one decide on the number of samples to collect. Study objectives vary and hence sample sizes vary as well. In a geochemical investigation, the nature of the questions that need to be answered will determine the type of assessment tool to be used and consequently the data requirements for that assessment tool. Generally speaking, geochemical assessments undertaken in support of mine closure applications will require the highest level of confidence in the results and will require the more extensive sampling programs. It is important to discuss and agree on acceptable confidence levels with key stakeholders prior to designing the sampling program in order to ensure that sufficient samples are taken to support the decisions to be made.

Similarly, decisions relating to placement and design of waste material facilities such as waste rock dumps, tailings disposal facilities, in-pit disposal systems, etc require a very high level of confidence as decisions relating to these facilities cannot easily be changed at a later date.

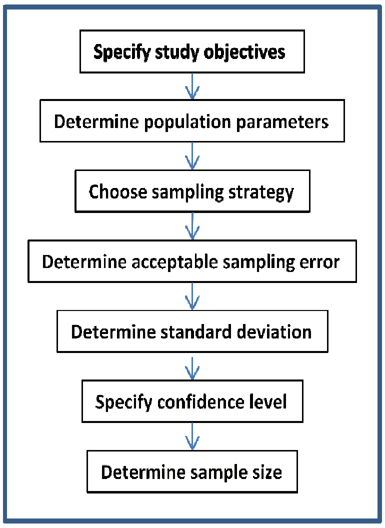


Figure 4.1: Procedure for determining sample size

4.4.2 Determine the population parameters

Determination of the population parameters is the next step after definition of the study objectives. In this process the following questions should be investigated:

- Is the population homogeneous?
- What are the statistical properties of the sample target in terms of mean, standard deviation, median, etc?
- What is the spatial distribution and physical size of the sample target?

The critical parameters such as mean, standard deviation, acceptable error can potentially be acquired from various sources of information such as:

- Previous publications and documents;
- Similar previous studies; and

- Pilot sampling study of the sample target.

4.4.3 Choose the sampling strategy

Once the above information has been gathered, the next step is to select a sampling strategy. Care must be taken when choosing the sampling strategy. The analyst should take into account such aspects as spatial continuity, correlation of the geological properties, cost and variability. If the sample material is homogeneous, a random sampling strategy may be adopted. If the sample area is heterogeneous, stratified or systematic sampling strategies are preferable. With a stratified sampling strategy, the area is divided into several subpopulations and random samples are collected from each stratum and the sample size of each subpopulation is calculated separately. In addition, stratified design is more economical in that the number of samples is reduced since the target area is divided into different stratum with each stratum having similar properties. The advantage of the systematic grid method is that it takes spatial continuity into account (US EPA, 1999).

4.4.4 Determination of the acceptable standard error

In order to calculate the sample size, it is necessary to define the study standard error. This is the acceptable error that the stakeholders are willing to accept. The following guidelines can be used to decide on the specific value of the standard error (Yang, 2006):

- The value should be greater than the analysis error
- The value can be calculated as 5% of the sample mean
- The value can be taken as the maximum allowable value for the ERA purpose.

This value can be obtained by referring to previous data or consulting secondary sources of information such as, journals. As stated in previous sections, the use of historical data from other studies should be done with caution. Only when it can be demonstrated that the project from which previous data is derived was successful can one confidently use the data. It should also be borne in mind that geological situations and geological materials vary considerably. It is considered more appropriate to conduct a small pilot study on the sample target and use the obtained estimates to determine acceptable standard error rather than to use data from previous studies. It is critical that the agreed project standard error be accepted by all stakeholders prior to initiating the sampling program.

4.4.5 Determine standard deviation

Standard deviation is a critical component of the sample size formula. Although the analyst has less control over variance, it must be incorporated into the design. Methods that can be used to estimate the standard deviation value as an input for sample size determination, include use of a pilot study, use of data from previous studies of similar populations, estimates assisted by some logical mathematical results (Bartlett, Kotrlik, and Haggins, 2001). A more detailed discussion of some of these methods is provided under section 4.6.

4.4.6 Specify confidence level

Confidence interval provides a range of values that has a specified probability of containing the parameter being estimated. The frequently used and recommended confidence level is 95% and its alpha value is 0.01 (Yang and Zhao, 2005). The z value associated with this confidence level is 1.96. This value can be obtained from standard normal distribution tables. If a 95% confidence level has been chosen it simply means that it is believed that the population mean lies within this range 95% of the time.

One major factor affecting the choice of confidence level is the purpose of the study or investigation. Higher confidence levels for example 99% confidence level are often employed in cases where decisions based on the assessment are critical and errors may cause substantial harm (Bartlett, Kotrlik, and Haggins, 2001). Lower confidence levels for example 75% may be used for instance when identifying trivial differences or other statistical phenomena as an antecedent to further studies.

4.4.7 Determine the sample size

When the various parameters necessary to determine sample size have been estimated, the parameters are combined using the formula below:

$$\boldsymbol{n} = \left(\frac{\boldsymbol{Z_{\alpha/2}} \times \boldsymbol{s}}{\boldsymbol{d}}\right)^{2} \qquad \mathbf{4.4}$$

There are two types of sample sizes to be decided on (Yang, 2006):

(1) **Minimum sample size**: When we use the formula to calculate the sample size we assume that the samples are normally distributed, although based on the Central Limit Theorem, the assumption is correct only when the sample numbers are reasonably large. In statistics, 30-50 samples can be taken as reasonably large. Considering the costs of the sampling 30 is considered as a reasonable minimum sample size.

(2) **Maximum sample size**: The sample size calculated based on the formula can be taken as the maximum sample size because it assumes all samples as random and independent and gives each sample an equal weight.

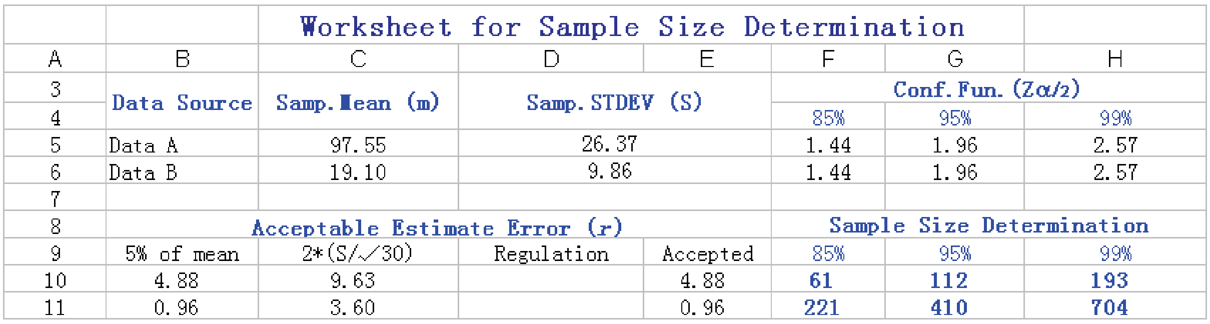
4.4.8 Limitations

- One disadvantage associated with the method is that a "good" estimate of the population standard deviation is necessary. Often this value is unknown.
- The approach is based on the assumption that data is normally distributed.
- The method assumes that a simple random sampling scheme is the method of choice and does not apply when other sampling schemes are chosen.

4 .5 SPREADSHEET FORMAT FOR SAMPLE SIZE DETERMINATION

This section outlines the spreadsheet method of calculating sample size based on the statistical analysis approach.

Table 4.6: Worksheet for sample size determination



		Worksheet for Sample Size Determination					
A	B	C	D	E	F	G	H
3	Data Source	Samp.Mean (m)	Samp.STDEV (S)		Conf.Fun.(Zα/2)		
4					85%	95%	99%
5	Data A	97.55	26.37		1.44	1.96	2.57
6	Data B	19.10	9.86		1.44	1.96	2.57
7							
8	Acceptable Estimate Error (r)				Sample Size Determination		
9	5% of mean	2*(S/√30)	Regulation	Accepted	85%	95%	99%
10	4.88	9.63		4.88	61	112	193
11	0.96	3.60		0.96	221	410	704

The procedure for determining sample size in spreadsheet format is based on the following steps:

Step 1: Calculate the sample mean (m) and the sample standard deviation.

For the sample mean (m), the formula is:

"= AVERAGE (Xij: Ynm)"

Where Xij represents the beginning cell of the data matrix and Ynm the end cell of the data matrix.

For the sample standard deviation (S), the formula is:

"= STDEV (Xij: Ynm)",

Where Xij represents the beginning cell of the data matrix and Ynm the end cell of the data matrix.

Step 2: Determine the acceptable standard error

If the related regulation or protocol presents the guideline for the error, use the guideline; otherwise, choose the lesser between "5% of mean" and "2xS/√30". The formula is:

"=IF (D10=0, MIN (B10, C10), D10)" (for Date A) or

"=IF (D11=0, MIN (B11, C11), D11)" (for Data B)

Step 3: Calculate the required sample number

For the confidence level of 85%, the formula is:

"=IF [(D5^2*F5^2/E10^2)>30, D5^2*F5^2/E10^2, 30]" (for Date A) or

"=IF [(D6^2*F6^2/E11^2)>30, D6^2*F6^2/E11^2, 30)]" (for Data B)

For the confidence level of 95%, the formula is:

"=IF [(D5^2*G5^2/E10^2)>30, D5^2*G5^2/E10^2, 30]" (for Date A) or
"=IF [(D6^2*G6^2/E11^2)>30, D6^2*G6^2/E11^2, 30]" (for Data B)

For the confidence level of 99%, the formula is:

"=IF [(D5^2*H5^2/E10^2)>30,D5^2*H5^2/E10^2,30]"(for Date A) or
"=IF [(D6^2*H6^2/E11^2)>30,D6^2*H6^2/E11^2,30]" (for Data B)

4.6 APPLICATION: SAMPLE SIZE DETERMINATION

This section serves to illustrate how the proposed methodology can be applied. It also serves to assess if the number of samples collected during the case study were enough for ERA. As such, ABA results for Vaal River dam 3 and West Wits dam N will be used to demonstrate the applicability of the method. The data for the two dams is presented in Table 4.7. Key parameters for acid rock drainage (ARD) study are the acid potential (AP) and the neutralising potential (NP). These parameters are used to illustrate how the proper sample size can be determined.

Table 4.7: ABA data from the Wits Basin (Pulles *et al.*, 2003)

Location	Sample ID	Total S (wt %)	Calcite (kg/t)	AP (kg/t)	NP (kg/t)
Vaal River	VRD3 A1	0.130	8.75	4.06	8.75
	VRD3 A2	0.277	0.25	8.66	0.25
	VRD3 A3	0.326	0.00	10.19	0.00
	VRD3 A4	0.310	0.75	9.69	0.75
	VRD3 A5	0.207	2.00	6.47	2.00
	VRD3 A6	0.320	0.25	10.00	0.25
	VRD3 P1	0.070	2.00	2.19	2.00
	VRD3 P2	0.125	0.00	3.91	0.00
	VRD3 P3	0.283	0.00	8.84	0.00
	VRD3 P4	0.127	0.75	3.97	0.75
	VRD3 P7	0.188	0.00	5.88	0.00
	VRD3 P10	0.247	0.00	7.72	0.00
West Wits	N-1S	0.789	2.75	24.66	2.75
	N-2S	0.656	7.50	20.50	7.50
	N-3D	0.691	9.75	21.59	9.75
	N-5S	0.764	7.50	23.88	7.50
	N-6S	0.716	7.00	22.38	7.00
	N-7D	0.652	9.75	20.38	9.75

The dataset in the table above was derived from results obtained from the case study of Vaal River and West Wits tailing dams as discussed in Chapter 3. The dataset is only a small portion of the results that were obtained from the study. Population A represents 12 samples taken from Vaal River

ABA results and Population B represents 6 samples extracted from ABA results for West Wits mining area.

For the population A, The sample means ($m_{AP (A)}, m_{NP (A)}$) and the sample standard deviations ($S_{AP(A)}, S_{NP(A)}$) are calculated as follows:

$$\mathbf{m_{AP (A)} = 1/12 \sum x_i = 6.80}$$

$$\mathbf{m_{NP(A)} = 1/12 \sum x_j = 1.23}$$

$$\mathbf{S_{AP(A)} = SQRT\ [(1/11)*\sum(x_i - 6.80)^2] = 2.77}$$

$$\mathbf{S_{NP(A)} = SQRT\ [(1/11)*\sum(x_j - 1.23)^2] = 2.48}$$

For the population B, the sample means ($m_{AP(B)}, m_{NP(B)},$) and the sample standard deviations ($S_{AP(B)}, S_{NP(B)}$) are calculated as follows:

$$\mathbf{m_{AP(B)} = 1/6 \sum x_i = 22.23}$$

$$\mathbf{m_{NP(B)} = 1/6 \sum x_j = 7.38}$$

$$\mathbf{S_{AP(B)} = SQRT\ [(1/5)*\sum(x_i - 22.23)^2] = 1.758}$$

$$\mathbf{S_{NP(B)} = SQRT\ [(1/5)*\sum(x_j - 7.38)^2] = 2.563}$$

Here we set that the acceptable sampling error (*r*) of AP and NP equals 1(kg/t) and the required confidence level equals 95%.

Based on the information above, the sample sizes can be calculated as follows:

$$\begin{aligned}\mathbf{n_{AP(A)}} &= \mathbf{Z_{\alpha/2}{}^2 S_{AP(A)}{}^2 / r^2} \\ &= \mathbf{1.96^2 * 2.77^2 / 1^2} \\ &= \mathbf{30} \\ \mathbf{n_{NP(A)}} &= \mathbf{Z_{\alpha/2}{}^2 S_{NP(A)}{}^2 / r^2} \\ &= \mathbf{1.96^2 * 2.48^2 / 1^2} \\ &= \mathbf{24} \\ \mathbf{n_{AP(B)}} &= \mathbf{Z_{\alpha/2}{}^2 S_{AP(B)}{}^2 / r^2} \\ &= \mathbf{1.96^2 * 1.758^2 / 1^2} \\ &= \mathbf{12} \\ \mathbf{n_{NP(B)}} &= \mathbf{Z_{\alpha/2}{}^2 S_{NP(B)}{}^2 / r^2} \\ &= \mathbf{1.96^2 * 2.563^2 / 1^2} \\ &= \mathbf{25}\end{aligned}$$

4.7 SUMMARY

Sample size determination is a crucial step in the statistical design of the project sampling program. An adequate sample size helps ensures that the study will yield reliable information which is critical for decision making. Studies involving human subjects should be designed with a large enough sample size so that the risk of making wrong decisions is eliminated.

Performing a valid sample size calculation requires estimates of the variability in the data, as well as an agreement on the confidence level and acceptable sampling error that will be acceptable for the project. Standard deviation, the most often used measure of variability, and acceptable sampling error is mostly unknown. These parameters can be estimated from historic data from projects of a similar nature or preferably from a pilot sampling study. The main risk of using data from previous studies in estimating sample size is the possibility of error propagation. Errors made in the previous study may be carried over to the present study and care is therefore required when using such data.

There is an exponential relationship between sample size and acceptable sampling error. In order to reduce error by a factor of two, the sample size has to be quadrupled. For any given confidence level, the larger the sample size, the smaller the confidence interval.

In the case of variability, the more heterogeneous a population, the larger the sample size required to obtain a given level of precision. The more homogeneous a population, the smaller the sample size required.

Although the determination of sample size presents a difficult task, the hurdles can be overcome by drafting a proper sampling plan. It is of great importance that the sampler understands the purpose and uses of the sampling data prior to deciding the number of samples required. As sample size affects representivity and decision making and may have significant cost implications, it is essential that the right sample size be specified.

CHAPTER 5
METHODOLOGY FOR QUANTIFYING UNCERTAINTY IN GEOCHEMICAL SAMPLING AND ANALYSES AS A FUNCTION OF SAMPLE SIZE

5.1 INTRODUCTION

The results of a measurement are incomplete without an accompanying statement of uncertainty. Measurement uncertainty is one of the main factors that fundamentally impacts data quality and therefore decision-making. In the case of geochemical investigations for ERA, decision-making under uncertainty may lead to serious consequences which may result in the loss of public trust and confidence and significant financial losses.

This chapter presents a methodology for quantifying uncertainties in geochemical sampling and analysis as a function of sample size and analytical methods. While many existing methods for estimating uncertainty focus on analysis as the main contributing factor to uncertainty, the method presented here also recognizes the effect and contributions from sampling and sample preparation towards measurement uncertainty. This stems from the fact that the measurement process is a multi-faceted process comprising of sampling, sample preparation, and analysis; hence the importance of considering the uncertainty contributions from all procedures involved. The resulting value will be a more realistic estimate of uncertainty than that derived from considering the influence and effect of a single factor only.

The methodology for quantifying uncertainty is based on nine steps which are:

- Definition of the objectives of the study.
- Definition of the sampling target.
- Specification of the measurand.
- Description of the sampling and analysis protocol.
- Identification of the sources of uncertainty.
- Quantification of the sources of uncertainty.
- Calculating the combined implications of the uncertainty components.
- Calculating the expanded uncertainty.
- Reporting the result.

Various uncertainty components are grouped into two categories, Category A and Category B- based on the method used to evaluate them. Category A encompasses all sources of uncertainty that can be evaluated using statistical methods while Category B evaluates uncertainty components that cannot be evaluated using statistical methods.

The standard uncertainties are combined to reach a total or overall uncertainty using the laws of error propagation. An expanded uncertainty is calculated to define an interval about the result of a measurement that is expected to encompass a specified fraction of the possible values for the measurand.

5.2 THE IMPORTANCE OF QUANTIFYING AND REPORTING UNCERTAINTY ASSOCIATED WITH A MEASURAND RESULT

The following points summarise the importance of evaluating and reporting the measurement uncertainty:

- A statement of the uncertainty associated with a result conveys to the customer the ‘quality’ of the result (CITAC/EURACHEM, 2002);
- Providing the value of uncertainty instils confidence in the result of a measurement and shows the data users that the result can be relied on;
- It leads to better-informed decision-making;
- It allows for the comparison of two measurement results; and
- Information is obtained for improving the method.

5.3 PROCEDURES FOR QUANTIFYING UNCERTAINTY

The results of geochemical assessments depend on the collection of good quality and representative samples. However, no matter how careful one is in selecting, preparing and analyzing the sample, the results always contain uncertainty. In other words, measurement uncertainty is unavoidable. This section provides a detailed discussion of the steps that may be adopted when quantifying uncertainties in the geochemical sampling and analyses process. The steps are summarised in Figure 5.1 below.

5.3.1 Step 1: Define the objectives of the study

Definition of the study objectives or purpose is the most important and critical step in quantifying uncertainty. It is difficult to arrive at a meaningful estimate of uncertainty without clearly understanding what the objectives of the measurements are. A clear description of the purpose of the investigation provides background on the actual issues addressed by the study. It is therefore crucial that the objectives of the measurement are clearly understood prior to undertaking geochemical measurements for ERA. The objectives of the assessment will also dictate the assessment tools that will need to be used and these tools, in turn, will have specific data requirements that need to be addressed through the sampling and analytical campaign.

An example of a sampling objective would be to estimate the mean concentration levels of the element lead in water or detecting soil mercury contamination.

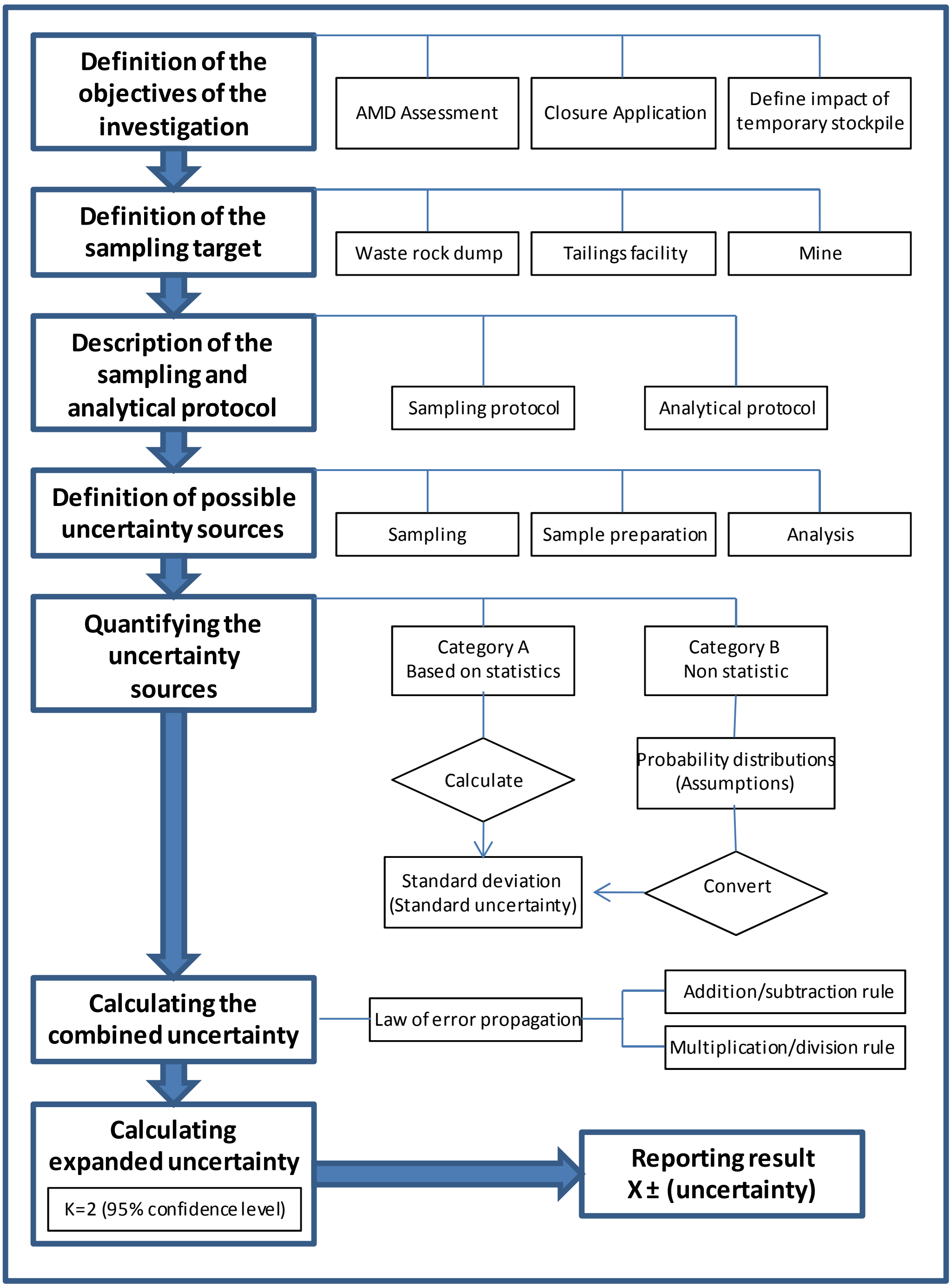


Figure 5.1: Steps in quantifying uncertainty

5.3.2 Step 2: Definition of the sampling target

A sampling target is an area or a portion of material that the sample represents at a particular time. The target may be defined in terms of space (geographic boundaries) or time – that is when, where and which portion of the whole is to be sampled? Thus for a 10 ha waste rock dump, one may decide to sample only 3 ha. The 3 ha would then be the sampling target.

Questions that should be addressed by the target definition include:

- What type of material is present in the target area?
- Is the material heterogeneous or homogeneous?
- What are its variables? (mean, standard deviation for key parameters of concern)

Information relating to the sampling target can be obtained from geological reports, historic information and conducting a preliminary study. Whichever method is adopted, the definition should reflect the purpose of study.

5.3.3 Step 3: Definition of the measurand

This step requires the analyst to give a clear and detailed statement of the quantity being measured. This quantity may be a directly measured variable (value), or indirectly determined relying on input of other variables to determine the measurand in question. The latter is often associated with a mathematical model which relates the input variables ($X_{1,}$ $X_{2\ldots\ldots\ldots\ldots}X_N$) to the measurand (output), Y (EAL Task Force, 1999). Most measurements, specifically in geochemistry, are associated with the latter in which the measurand is determined through the measurement of other variables and the relationship can therefore be generalized as Y= f($X_{1,}$ $X_{2\ldots\ldots\ldots\ldots}X_N$). Such measurements are referred to as multivariate measurements and they call for the development of a mathematical expression which relates the measurand Y to the variables X_1, $X_{2\ldots\ldots}$ on which it depends. The value of developing such mathematical models lies in their ability to precisely describe how the value of the output quantity depends on the values of the inputs.

The step can be summarized as:

- Determine what variables need to be measured to estimate the measurand Y, i.e. the input quantities if the measurand cannot be determined directly.
- Transcribe the actual relationship between the measurand and the inputs or develop the mathematical model outlining how the measurand Y relates to the input parameters X_1, $X_{2\ldots\ldots\ldots\ldots}X_N$ on which it depends.

Example I – measuring Acid Potential (AP) of gold waste dump material

The measurand can be defined as assessment of Acid Potential (AP) of gold mine waste material which depends on the input variables: total sulphur content, molecular weight of Calcium Carbonate ($CaCO_3$) and atomic weight of sulphur.

This relationship between the measurand and the input parameters on which it depends can be expressed as:

$$\boldsymbol{AP = Total\ Sulphur}\ (\%)\ \times \boldsymbol{31.25kg\ CaCO_3} \qquad \boldsymbol{5.1}$$

5.3.4 Step 4: Description of the sampling and analysis protocols followed

This step requires the user to give a detailed outline of the sampling and analytical protocols adopted during the investigation. Sampling and analytical protocols provide details of all the measurement processes that were carried out in order to obtain the measurand. The importance of this step is that the protocol followed would be used as reference especially when determining the source of uncertainty

Sampling protocol

Under sampling protocol, the following aspects should be highlighted:

- The sampling method used and whether it was a stratified or random method of sampling. Any modifications or changes made to the technique should be included.
- The number of samples collected.
- The sampling tool used and spacing or interval.
- Sample labelling and preservation.
- QA/QC used in order to ensure quality.

Many samples get contaminated during this stage hence the manner in which the samples were handled should be highlighted.

Analyses protocols

This step encompasses all steps carried out from preparation of the test portion to the analysis itself. These procedures should be stated in detail and the list should include:

- Instrument(s) used;
- Specifications of the analysis methodology;
- Specifications of reagents used;
- How sample(s) were handled;
- Any calculations that were undertaken prior to and after analysis; and
- QA/QC program adopted to ensure quality.

A write up of the sample preparation procedure should be included in this step.

5.3.5 Step 5: Identifying sources of uncertainty

Following the specification of the procedure used, it is necessary to compile a list of the possible sources of uncertainty in the measurement process. Since some sources contribute more to uncertainty than others, it is important to start with major sources, the quantities that have the largest influence on the measurement.

As stated at the beginning of this chapter, most methods of quantifying uncertainty emphasise the contribution of laboratory analysis towards measurement uncertainty. However, studies by Ramsey (1998) revealed that of all primary procedures undertaken during geochemical investigations, primary sampling contributes more to measurement uncertainty than analysis, Figure 5.2 (Schwedt, 1997). As such, it is crucial that all processes involved in the multi-tiered measurement process be considered as potential sources of uncertainty.

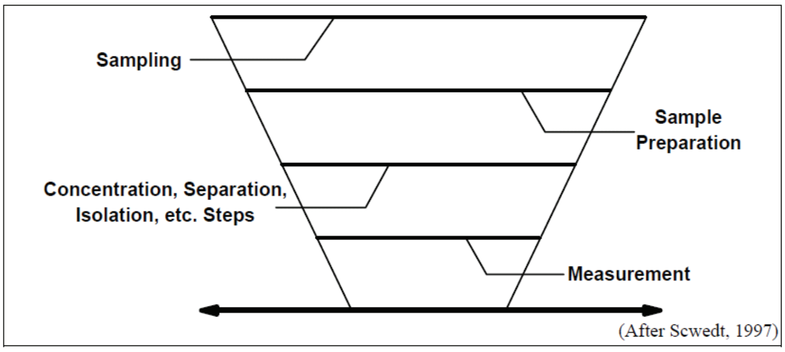


Figure 5.2: Degree of error in laboratory sample preparation relative to other activities (US EPA *e.al*, 2004)

Common sources of uncertainty in geochemical investigations

The following sections discuss common sources of uncertainty in geochemical sampling for ERA. It is crucial to begin with the input quantities used in determining the measurand in drawing up the list of the sources of uncertainty (USEPA *et al*., 2004). Secondary sources of information such as journals, manufacturer’s specifications, manuals, and books may be consulted for additional information regarding potential uncertainty sources.

SAMPLING

As stated in the previous section, the sampling process, like all processes involved in geochemical measurement, contributes towards the uncertainty associated with the value of the measurand in several ways including:

- **Heterogeneity (variability):** This is one of the major sources of uncertainty in geochemical sampling and analysis. For most geological materials, for example waste rock dumps, heterogeneity exists in terms of the particle size distribution, mineralisation and alteration and analyte concentrations. The effect of this source of uncertainty can be displayed by variations in terms of the observable analyte concentration among samples collected from different points of the sampling target (the random effect). Most scholars, including Pitard (1993), argue that heterogeneity remains the largest uncertainty source contributing towards the overall uncertainty in geochemical sampling and analyses measurements. This uncertainty source can be minimized by taking many increments or reducing particle size of the sample material.

- **Sampling design:** Sampling design introduces uncertainty when a limited number of locations are sampled and the strategy fails to capture the complete extent of the inherent variability which exists within the target.
- **Incorrect sampling**: Error is introduced when the size and geometry of the sampling tool used violates the fundamental principle of sampling. According to the principle, a selected sample is structurally accurate when all the units within the lot have equal probability of being selected. Any deviation from this principle would result in bias.
- **Sample handling:** The container or equipment used for holding the sample during transport from the field to the laboratory may affect the analyte recovery. Bias is introduced when the walls of the container absorb the analyte of interest or contaminate the sample (or allows the analyte to escape in the case of volatile elements such as mercury and arsenic.
- **Limited sample mass:** The mass of the sample analysed may not be enough to actually capture the actual conditions existing within the sampling target

SAMPLE PREPARATION

Sample preparation is another dominant source of uncertainty in geochemical investigations, with uncertainty arising from:

- Sample homogenisation,
- Incomplete extraction of the analyte from the sample,
- Loss of analyte due to over drying of the sample
- Loss of volatiles due to excessive drying or crushing, and
- Sample contamination.

ENVIRONMENTAL FACTORS

Environmental factors such as vibrations, changes in humidity, changes in temperature, and electronic noise, or other effects may affect the measurement process thereby contributing to uncertainty. These factors may affect the functionality of the instrument used to take the measurements, introducing errors as a result. Mass, pH and volume measurements are examples of measurements that are highly influenced by the environment.

INSTRUMENT EFFECTS

The instrument used for analysis may present the weakest link in the measurement process. Under instrument effects, uncertainty is introduced by:

- **Poor detection capabilities of the analytical instrument**: The uncertainty associated with the sensitivity of an analytical device consists of a contribution from the standards used for instrument calibration, a contribution from the curve fitting process and a contribution from the model used to describe the response. For example, XRFs generally fail to detect minor elements with accuracy.

Causes of such incapability are linked to short counting time, high back ground interference and long decay time. This source of uncertainty can be minimized by using more sensitive techniques.

- **Improper instrument calibration**: The uncertainty component associated with the calibration will include an uncertainty contribution from the reference materials and an uncertainty contribution from the calibration line fitting.
- **Instrumental drift:** Electronic instruments have readings that drift over time. This source of uncertainty can be significant and should be considered.
- **Manufacturer specifications:** Most measurement instruments have an accompanying statement of accuracy or tolerance level specified by the manufacturer. This value should be incorporated in uncertainty measurements.

ANALYTICAL ERROR

For most methods of estimating uncertainty, the assumption is that bias has been corrected and it is negligible. However, even if the bias is zero, it has to be estimated and treated as an uncertainty component. Method bias can be assessed and estimated through the inter-laboratory comparisons, certified reference material (CRM), recovery tests, and comparison to results from reference methods[5].

Common sources of uncertainty in the laboratory results from:

- Incorrect identification of samples.
- Misinterpretation of the analytical method.
- Sample contamination.
- Inaccuracy of sample weights, or volumes for example constantly reading a meter or scale consistently high or low.
- Inappropriate sample dissolution/treatment.
- Improper or inappropriate instrumentation /inaccurate measurement.
- Calculation errors.
- Data mix up and incorrect reporting.

These sources are closed associated with human error.

Cause and effect diagrams (fish bone) may be used as convenient and effective means for analysing uncertainty sources. The diagram assists in identifying, exploring, and displaying relevant uncertainty sources and highlights their effect on the measurement result. The procedures for constructing cause and effect diagrams can be summarised as follows:

- When the result is based on a mathematical equation, it is recommended to use the parameters in the equation as the main branches for the diagram. If the parameters are unknown, one would

---

[5] Note that the list stated and the potential sources of uncertainty stated are not exhaustive. Other methods for estimating method bias exist.

consider the main procedures of the measurement process (i.e. sampling, sample preparation and analysis).

- The next step is to consider additional factors that form sub-branches for the main effects (main branches).

When all the sources have been identified, it is necessary to remove any duplication and group causes that are related. Figure 5.3 illustrates a cause and effect diagram for uncertainty sources associated with sampling.

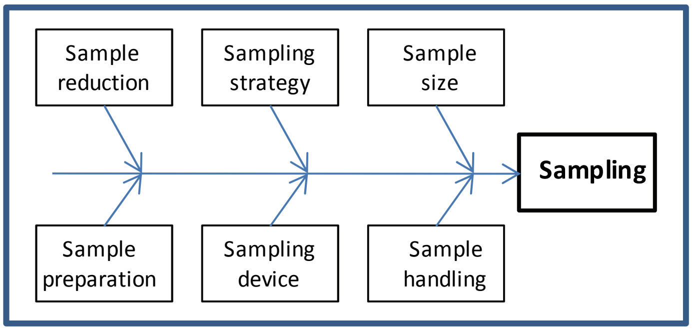


Figure 5.3: Cause and effect diagram for uncertainties in sampling process

Example II

Common sources of uncertainty in ICP-MS measurements include:

- Incomplete dissolution of the analyte.
- Spectral interferences including isobaric interference, molecular interferences and doubly charged ion interference.
- Space charge effects.
- Trace elements such as Be, As and Hg have a high first ionization potential with the result that low temperature plasma will give reduced signal for these elements.
- The presence of salts such as NaCl leads to reduced sensitivity.

Example III

Potential sources of uncertainty in X-Ray Fluorescence (XRF) analysis results include:

- Calibration of the spectrometer: once a measurement device is selected it must be calibrated. Failure to adjust the instrument to the required standard yields incorrect results.
- Sample non-homogeneity.
- Sample preparation: The sample is liable to contamination during homogenization, grinding, milling, and polishing. Two commonly used polishing agents – Silicon Carbide (SiC) and Aluminum Oxide (Al_2O_3) – contain elements that are often measured as silicon (Si) and aluminum (Al).
- Enhancement effect due to matrix effects.
- Counting errors.
- Spectral overlaps.

In the case of trace element determination, the uncertainty of the x-ray's peak intensity is also an important factor.

5.3.6 Step 6: Quantify the uncertainty components[6]

Once the sources of uncertainty have been identified they need to be quantified. For this methodology each contributing source is broken down into its constituent components and the size of the uncertainty component estimated. Each of these separate contributions to uncertainty is referred to as an uncertainty component (Ellison, Rosslein and William, 2000). The uncertainty components are then expressed as standard deviation. Standard uncertainty denoted as $u_{(s)}$ is the term used when an uncertainty component is expressed as a standard deviation.

One major setback presented by trying to identify each uncertainty component and quantifying them is that some of the components are difficult to quantify – for example the effect of the sampling strategy. As important as the factor is as a potential source of uncertainty, assigning uncertainty contribution in a quantitative way can be a complex task. Such problems are curbed by seeking additional information from literature, conducting additional experiments, or using judgment based on experience in order to effectively model the uncertainty component.

EVALUATING UNCERTAINTY COMPONENTS

After identification of the possible sources of uncertainty, the next step is to assess the uncertainty sources that are accounted for by the available data prior to estimating the size of each contributing component. Additional sources of information may be consulted to gather information about uncertainty components which are not adequately represented by existing information. In cases where data is absent, it may be necessary to conduct experiments to obtain additional information regarding a particular source of uncertainty.

Basically there are two main categories for evaluating standard uncertainty – category A and B, based on the method used to estimate their numerical values. **Category A**[7] is used to calculate standard uncertainty for estimates obtained by statistical analysis, for example uncertainty components arising from repeated measurements. **Category B** is used to evaluate standard uncertainty for uncertainty components obtained by non-statistical means, for example uncertainty stated by the manufacturer. Expressing uncertainty components quantitatively to standard uncertainty enables all estimates to be in an equivalent form facilitating combination of all uncertainties.

---

[6] **NOTE**: Not all sources of uncertainty can be quantified. It is also important to recognize that not all of the components of uncertainty will make a significant contribution to combined uncertainty. A preliminary estimate of the contribution of each component or combination of components to the uncertainty should be made and those that are not significant eliminated.(Ellison, Rosslein and William, 2000, pg 4)

[7] Category A refers to the method by which the uncertainty estimate was obtained not the nature of the uncertainty contributor itself (Adams, 2002). This is also the case with category B.

Category A Uncertainty

The Category A approach to uncertainty estimation assumes that statistical methods can provide reasonable estimates of the measurement uncertainty (Adams, 2002). Sources that can be evaluated using this method are often associated with random error, i.e. experiment measurement results which vary when the measurement is repeated.

An example of a Category A evaluation involves making a series of n independent measurements of a quantity, ***Qi*** and calculating the arithmetic mean and the experimental standard deviation of the mean. The arithmetic mean is regarded as the best estimate of the measurand and standard deviation of the mean provides a good approximation of the uncertainty associated with the mean measurement.

Procedure for estimating Category A uncertainty

1. Identifying and removing outliers from the dataset. Outliers negatively affect the statistical parameters such as mean and standard deviation. Presence of outliers increases the calculated parameter value especially standard deviation and therefore should be discarded. It is recommended that an inquiry be made regarding the presence of outliers prior to their rejection. The analyst should at least try to understand why they appeared.

   Several methods of detecting outliers exist including Grubb's test and Chauvenet's criterion. The procedure for detecting outlier based on the Chauvenet's criterion can be summarised as below (Wikipedia, 2007):

   - Calculate the mean and standard deviation.
   - Determine the probability that a given data point will be at the value of the suspect data point. Using the normal distribution function
   - Multiply this probability by the number of data points taken
   - Remove the point if the result is less than 0.5

2. The measurement results are summed and divided by the number of samples to get the mean.

$$\bar{x} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad 5.2$$

3. Determination of the standard deviation (Equation 5.3) of the measurements, which characterizes the variability, or spread, of the observed values.

$$S = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (X_i - \bar{X}\ )^2} \qquad 5.3$$

4. Determination of the standard error of the mean (Equation 5.4) which is the standard uncertainty of the measurement:

$$\boldsymbol{u_{\bar{x}} = \frac{s}{\sqrt{n}}} \qquad \mathbf{5.4}$$

Where $u_{\bar{x}}$ is the standard uncertainty.

Example IV
Seven pH measurements for waste rock yielded the following results:

8.12	8.52	8.4	8.28
8.15	8.44	8.32	
Mean	Standard Deviation	Standard Error	
8.32	0.15	0.06	

The arithmetic mean $\bar{P}$ for these results:

$$\mathbf{\bar{P} = 8.32} \qquad 5.5$$

The standard uncertainty of P is

$$\mathbf{u_p = 0.06} \qquad 5.6$$

The procedure for determining standard uncertainty mentioned above is true for multiple measurements. In the case of single measurements, the uncertainty associated with the results is determined by taking the standard deviation of the measurement. The advantage of using the standard uncertainty based on the standard error is that it relates the uncertainty to the sample size hence uncertainty can be reduced by increasing the sample size.

Category B Uncertainty

A Category B evaluation is used to estimate the standard uncertainty value for uncertainty sources which cannot be evaluated by statistical analysis as is the case with Category A. The successful identification and evaluation of these contributions depends heavily on a detailed knowledge of the measurement process and the experience of the person making the measurements.

Uncertainty components that can be evaluated by category B are chiefly derived from (EAL Task Force, 1999):

- Specifications of the manufacturer, for example the reported calibration uncertainty assigned to reference standards;
- Previous measurement data;
- Data provided in calibration and other certificates;
- The effects of environmental conditions;

- Uncertainties assigned to reference data taken from handbooks, e.g. uncertainties associated with atomic weight; and
- Experience with behaviour and properties of instruments.

The manner in which the uncertainty components which can be evaluated by this category are transformed to standard uncertainty primarily depends on available information regarding the uncertainty component. In some instances, conversions to standard uncertainty solely rely on the knowledge, judgment or experience of the analyst.

The following section discusses some of the possible methods that can be employed in assessing and converting Category B uncertainty components to standard uncertainty.

Method 1: This method calls for the conversion of the stated uncertainty to standard uncertainty by dividing the stated uncertainty by the multiplier (Taylor and Kuyatt, 2004).

Example V

A calibration certificate for a weight reference standard provides a value of 15 000.005 g with an associated expanded uncertainty[8] of 45 mg (coverage factor of k=1.96) the standard uncertainty contribution from calibration is:

$u_{(m)}$ is 45 mg (stated uncertainty)/1.96 (coverage factor which is the multiplier)
= 22.95 mg

Method 2: If there are specifications that contain an uncertainty bound for an input quantity at a stated confidence interval, the standard uncertainty is calculated by dividing the stated uncertainty by an appropriate factor for the confidence interval.

Example VI

For a given Certified Reference Material (CRM), with a certified value of 14.21 ± 0.2 and a 95% confidence level, the standard uncertainty for the CRM is

$(u_{crm}) = 0.2/1.96 = 0.10$

Method 3: Probability Distributions:

A probability distribution is a mathematical function giving the probability that a random variable takes any given value or else belongs to a set of values (UKAS, 2007). There are many probability distributions that can be assumed but in this section, only three distributions are considered-rectangular, triangular, and normal distribution.

---

[8] Expanded uncertainty = uncertainty*coverage factor (k).(commonly used value for k=1.96 which is equivalent to 95% confidence interval)

1. Rectangular/uniform distribution

Rectangular distribution is assumed when the only information available about the input quantity x are the upper and lower limits ± x and no other information is available. Assuming this probability denotes that the true value for the quantity lies anywhere within the specified bound as shown in Figure 5.4.

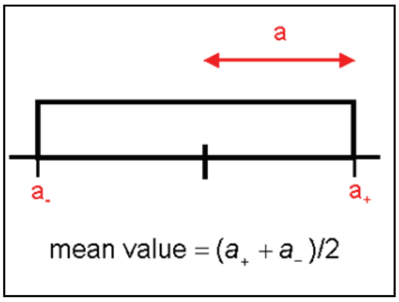


Figure 5.4: Rectangular distribution (Vetter, 2001)

The standard deviation for this distribution is given as:

$$u(a) = s = \frac{a}{\sqrt{3}} \qquad 5.7$$

Conditions for assuming this probability distribution are as follows:

1. Uniform probability – that is all values between and including the limits have equal probabilities of occurring.
2. There is a zero chance of the uncertainty contributor occurring outside of the limits of the distribution.

Example VII

A 50 ml Grade A volumetric flask is certified to within ±0.25 ml. The standard uncertainty (standard deviation) associated with using the flask is calculated by dividing the given limit (uncertainty) with the rectangular distribution.

$$\mathbf{u_{(vol)} = 0.25/\sqrt{3}}$$
$$\mathbf{= \pm\ 0.14\ ml.}$$

Where $\mathbf{u_{(vol)}}$ is the standard uncertainty associated with volume measurement.

Given a reading of 23.5 g on an analytical balance with a manufacturer's specified tolerance of 0.1 g the standard uncertainty for the reading is:

$$\mathbf{u_{(mass)} = 0.1/\sqrt{3}}$$
$$\mathbf{= 0.1}$$

Therefore the true value of the measurand lies somewhere between 23.4 and 23.6 g.

2. Triangular Distribution

This distribution is assumed when the information available about the input quantity x is the upper and lower limit ± *a*, and there is high probability that the quantity x values close to the centre of the limits are more probable than values near the limits.

The standard uncertainty of this distribution is given as:

$$\boldsymbol{u(a) = s = \frac{a}{\sqrt{6}}} \tag{5.8}$$

Where:

u (*a*) is the standard uncertainty associated with quantity *a*

S is the standard deviation.

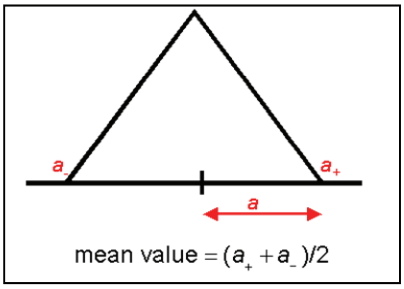


Figure 5.5: Triangular distribution (Vetter, 2001)

3. Normal distribution

The adoption of a normal distribution is valid for several situations. Firstly, the distribution is assumed when estimates are made from repeated measurements of a randomly varying process where standard uncertainty (u_x) equals the standard deviation (s) of the repeated measurements:

$$\boldsymbol{u_x = s} \tag{5.9}$$

Secondly, a normal distribution is adopted when the uncertainty associated with a given input is given as a standard deviation, relative standard deviation, and or coefficient of variation with the distribution unspecified. In cases where the uncertainty is given as a confidence interval x ± a without specification of the distribution, a normal distribution can be assumed. The standard uncertainties for the two most common distributions are therefore calculated as:

$$\boldsymbol{u_x = \frac{a}{1.96}\ (95\%\ confidence\ interval)} \tag{5.10}$$

$$\boldsymbol{u_x = \frac{a}{2.57}\ (99\%\ confidence\ interval)} \tag{5.11}$$

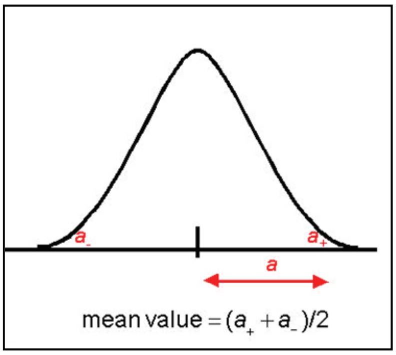


Figure 5.6: Normal distribution (Vetter, 2001)

Generally for most analytical tests for geochemical sampling and analysis, uncertainty components that are evaluated using Category B typically contribute less than components that can be evaluated by Category A. As such, quality control data are often employed to provide an estimate of the contribution of analysis to overall uncertainty. Procedures for estimating standard uncertainty are summarised in Figure 5.7.

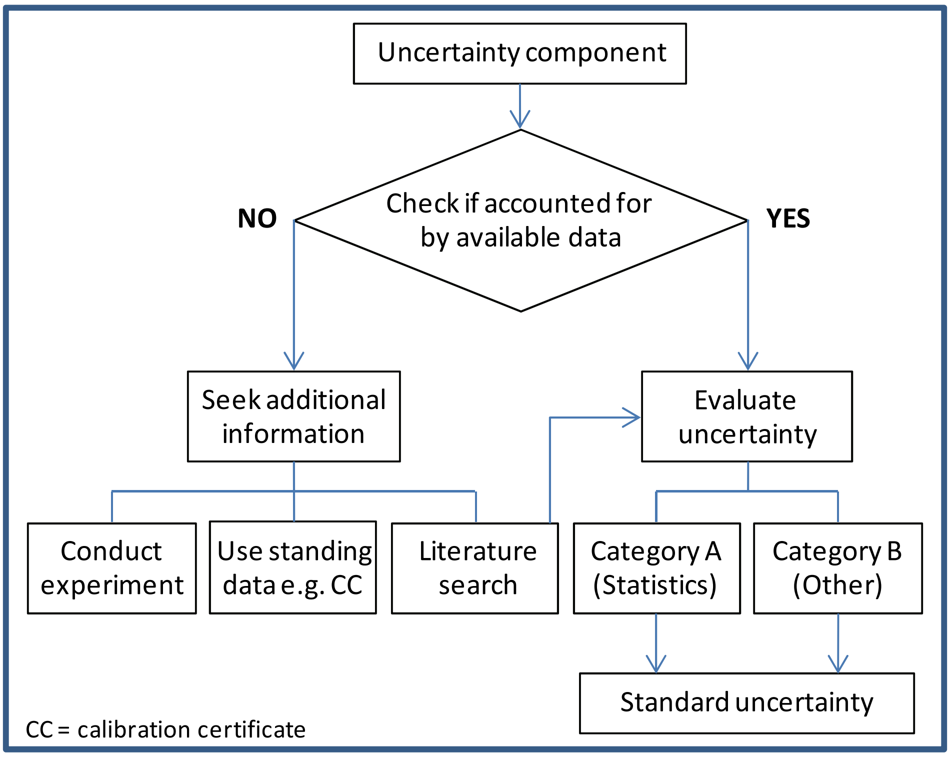


Figure 5.7: Flowchart for quantifying uncertainty sources

5.3.7 Step 7: Calculation of combined uncertainty

The combined standard uncertainty is the uncertainty of a result when it is obtained from the values of several other statistically independent quantities (Bronaugh and Heirman, 2004). Although uncertainty components are not errors, the individual components are combined using the laws of error propagation model. The combined standard uncertainty which is usually denoted by u_c is the uncertainty of a result when obtained from the values of several other statistically independent quantities.

Laws for combining uncertainty

There are two main rules for combining standard uncertainties (EURACHEM/CITAC, 2002):

Rule 1

In cases involving addition or subtraction of quantities such as:

x=f (w + s + t ± p….) where w, s, t, and p are uncorrelated, the combined uncertainty is calculated as:

$$u_x = \sqrt{u_w^2 + u_s^2 + u_t^2 + u_p^2} \ldots. \qquad \mathbf{5.12}$$

Rule 2

For cases involving multiplication or division for example x=w*f*h, combined uncertainty is given by

$$u_x = x\sqrt{\left[\frac{u(w)}{w}\right]^2 + \left[\frac{u(f)}{f}\right]^2} \qquad \mathbf{5.13}$$

In the case of geochemical investigations for ERA the combined uncertainty from the common possible factors can be written as:

$$U(s) = \sqrt{u_h^2 + u_v^2 + u_{rm}^2 + u_{mm}^2} \qquad 5.14$$

Where u_x^2 is the standard uncertainties from:

u_h^2 effect of heterogeneity

u_v^2volume measurement

u_{rm}^2Reference material

u_{mm}^2Mass measurement

Example VIII

Given that the pH measurement results for a certain target area with the tailings dams a, b and c have the following standard uncertainties derived from standard deviation of repeated measurement values for each dam, dam a = *u* (*a*) = 0.13, dam b= *u* (*b*) =0.15 and dam c = *u* (*c*) = 0.22.The combined uncertainty for these is calculated by applying rule 1

$$u_x = \sqrt{u_w^2 + u_s^2 + u_t^2} \ldots\ldots\ldots\ldots\ldots\ldots$$

$$u_{(pH)} = \sqrt{0.13^2 + 0.15^2 + 0.22^2}$$

$$= 0.296$$

Therefore the combined uncertainty for the pH measurements is $u_{(pH)} = 0.296$

5.3.8 Step 8: Calculating the expanded uncertainty

Expanded uncertainty is calculated to indicate how confident one is that the true measurand value lies within a given range of values obtained during the measurement process. It is obtained by multiplying the combined uncertainty by a coverage factor k and can be expressed by the Equation 5.15 below.

$$U = k \times u_c\,(y) \qquad \mathbf{5.15}$$

Where U is the expanded uncertainty, $u_c(y)$ is combined uncertainty, k is the coverage factor.

Usually a coverage factor (k)[9]of 2 is recommended when calculating expanded uncertainty (UKAS, 1997). This value provides a 95% confidence level, assuming the distribution is normal. If there is a larger contribution to uncertainty from one source in comparison to other sources, having the value k=1.96 will give a confidence level greater than 95%. When choosing the value of k, the level of confidence required should be considered.

Table 5.1: Coverage factors

Probability (%)	50	68	75	80	85	90	95	99
Coverage factor (k)	0.68	1	1.15	1.28	1.44	1.65	1.96	2.57

Example IX

Using the results from Example V, the expanded uncertainty associated with the combined uncertainty above is expressed as:

$$\mathbf{U = 1.96*0.296}$$
$$\mathbf{= 0.580\ (95\%\ confidence\ level)}$$

5.3.9 Step 9: Reporting the uncertainty

Instead of reporting a single estimate, it is necessary to include an interval in which the true measurand value is expected to lie. The uncertainty should be reported in the same units as the results. Usually the expanded uncertainty value obtained in the previous step is used when reporting uncertainty. This is illustrated below:

$$\boldsymbol{Result}: (\boldsymbol{y} \pm \boldsymbol{U})\boldsymbol{units} \qquad \mathbf{5.16}$$

Where y is the measurand value and U is the expanded uncertainty obtained from the previous step.

Example X

Assuming that the pH result obtained for the previous Example is 8.12, the uncertainty associated with this result is given as:

$$\mathbf{pH = 8.12 \pm 0.59}$$

The results should be reported whether positive or negative.

5.3.10 Advantages of the method

Some of the advantages associated with this method are:

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[9] Value may be insufficient when their degrees of freedom <6.

- The method is based on existing techniques.
- The guidelines enable the data users to identify the components of uncertainty, estimate the uncertainty associated with each component, and evaluate the contribution to uncertainty of each component.
- It also allows the analyst to determine which component is contributing more to uncertainty hence the analyst can see where an adjustment in the sampling or analyses process is required so as to minimize uncertainty.

5.3.11 Limitations of the technique

Some of the limitations in using the technique are:

- The definition of the element that is being measured is usually problematic. This is the case with geochemical sampling and analyses where a number of measurements and procedures are carried out.
- Some components of uncertainty are not readily quantifiable**.**

5.4 SUMMARY

The discussion from previous sections presented a simple and practical approach to estimating and combining the components of measurement uncertainty in geochemical investigations. The steps involved in estimating uncertainty using the method can be summarised as follows:

Definition of the objective of the study: Discuss in detail why the study or investigation is being carried out.

Definition of the target: Describe what is being sampled? What is its spatial extent?

Specification of the measurand: Give a detailed statement of the quantity being measured.

Description of the sampling and analytical protocol: Specify sampling and analyses procedure followed during the measurement process.

Identification of the uncertainty sources: List all potential uncertainty sources including the parameters on which the measurand depends.

Quantification of the uncertainty components: Provide an estimate of the size of the uncertainty component. This should be expressed as standard uncertainty.

Calculation of the combined uncertainty: Once the standard uncertainty of contributing components has been found, the various components are combined using one of the laws of error propagation, Equations 5.12 and 5.13.

Calculation of the expanded uncertainty: Provide the confidence interval required by multiplying the combined uncertainty value with a coverage factor (k).

Reporting measurement value: The result and uncertainty are reported as shown in Equation 5.16 – Result (x) ± expanded uncertainty value.

CHAPTER 6
APPLICATION OF METHODOLOGY OF QUANTIFYING UNCERTAINTY

6.1 INTRODUCTION

In the previous chapter, a methodology for quantifying uncertainty in geochemical sampling and analysis was discussed. This chapter demonstrates how the methodology can be applied. Acid Base Accounting (ABA) data results from the case study discussed in Chapter 3 with the parameters acid potential (AP), neutralizing potential (NP) and paste pH are used to illustrate the application of the methodology. The input values for the measurements are listed in Appendix E.

Since the measurement results for the various parameters shown in Appendix E are mean concentration values within each tailings dam, derived from averaging individual sample results from varying locations of the target, the standard uncertainties associated with these measurements are evaluated under Category A as discussed in Chapter 5. Equation 6.1 is used to determine the associated standard uncertainty:

$$\boldsymbol{u_{\bar{x}} = \frac{s}{\sqrt{n}}} \qquad \mathbf{6.1}$$

Where
$\boldsymbol{u_x}$ is standard uncertainty,
s is the standard deviation and
n is the sample size.

The standard uncertainties for uncertainty components falling under category B are evaluated using the appropriate probability distribution as discussed above in Chapter 5. The standard uncertainties are combined using the laws of error propagation stated in Equations 5.12 and 5.13.

Expanded uncertainty is calculated by multiplying the combined standard uncertainty by the coverage factor (k) of 1.96 which gives an approximately 95% confidence level. This value is used since the degrees of freedom are above six for most variables.

The majority of the calculations were carried out in Microsoft Excel 2003.The formulas for calculation of the various statistics in EXCEL including mean, count, standard deviation and standard are listed below:

Mean is calculated as:

=AVERAGE (C1: C5)

Where, C1 to C5 are the cell numbers containing the input values

Standard deviation as:

=STDEV (number1 [number2]….)

Where STDEV is standard deviation

Standard error of the mean with the formula in Equation 6.1 is calculated as

=STDEV (G5:G11)/SQRT (COUNT (G5:G11)

Where
STDEV is the standard deviation
G5:G11 refers to the location of the values used in the spreadsheet – that is values that are located in column G in rows 5 to 11
SQRT is the square root
COUNT is the sample size

Probability distributions are calculated as below:

=G8/SQRT (NUMBER).

The dividing number depends on the probability distribution chosen as discussed previously.

Combined Uncertainty as

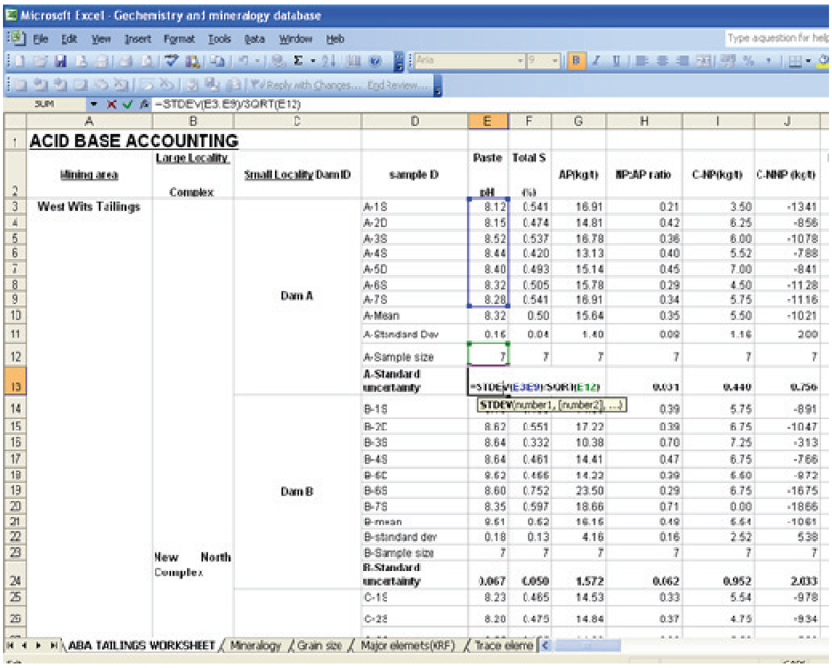
E.g. addition rule

=SQRT (SUMSQ (number1 [number2]……..)) for rule 1
=SQRT (SUMSQ (D8/D5, D20/D17……)) for rule 2.

Where SUMSQ is the sum of squares. These calculations are shown in Figure 6.1.

The following sections present examples showing how the methodology discussed in Chapter 5 can be applied. ABA data from West Wits tailings dams are used.

- Example 1 calculates uncertainty associated with Acid Potential (AP) measurement result for West Wits tailings dams,
- Example 2 evaluates uncertainty associated with Neutralizing Potential measurement result for all tailings dams.
- Example 3 quantifies uncertainty associated with pH results obtained from paste pH for West Wits tailings dams.



=STDEV(E3:E9)/SQRT(E12)

	A	B	C	D	E	F	G	H	I	J
1	ACID BASE ACCOUNTING									
2	Mining area	Large Locality Complex	Small Locality Dam ID	sample D	Paste pH	Total S (%)	AP(kg/t)	NP:AP ratio	C-NP(kg/t)	C-NNP (kg/t)
3	West Wits Tailings			A-1S	8.12	0.541	16.91	0.21	3.50	-1341
4				A-2D	8.15	0.474	14.81	0.42	6.25	-856
5				A-3S	8.52	0.537	16.78	0.36	6.00	-1078
6				A-4S	8.44	0.420	13.13	0.40	5.52	-788
7				A-5D	8.40	0.493	15.14	0.45	7.00	-841
8				A-6S	8.32	0.505	15.78	0.29	4.50	-1128
9			Dam A	A-7S	8.28	0.541	16.91	0.34	5.75	-1116
10				A-Mean	8.32	0.50	15.64	0.35	5.50	-1021
11				A-Standard Dev	0.16	0.04	1.40	0.09	1.16	200
12				A-Sample size	7	7	7	7	7	7
13				A-Standard uncertainty	=STDEV(E3:E9)/SQRT(E12)			0.031	0.440	0.756
14				B-1S	STDEV(number1, [number2], ...)			0.39	5.75	-891
15				B-2C	8.62	0.551	17.22	0.39	6.75	-1047
16				B-3S	8.64	0.332	10.38	0.70	7.25	-313
17				B-4S	8.64	0.461	14.41	0.47	6.75	-766
18				B-6C	8.62	0.466	14.22	0.39	6.60	-872
19			Dam B	B-6S	8.60	0.752	23.50	0.29	6.75	-1675
20				B-7S	8.35	0.597	18.66	0.71	0.00	-1866
21				B-mean	8.61	0.62	16.16	0.49	6.64	-1061
22				B-standard dev	0.18	0.13	4.16	0.16	2.52	538
23		New North Complex		B-Sample size	7	7	7	7	7	7
24				B-Standard uncertainty	0.067	0.050	1.572	0.062	0.952	2.033
25				C-1S	8.23	0.465	14.53	0.33	5.54	-978
26				C-2S	8.20	0.475	14.84	0.37	4.75	-934

Figure 6.1: Spreadsheet format for uncertainty determination

6.2 EXAMPLE 1: ACID POTENTIAL (AP)

Step 1: Definition of the purpose of AP determination

Acid Potential is one of the main measurements undertaken in Acid Base Accounting. It was determined in AMD prediction with the aim of assessing the amount of acid producing elements present in waste rock and tailings. Chemical elements contributing to acid production include sulphide minerals such as pyrite, and pyrrhotite. These elements, under favourable conditions, react with oxygen and water leading to the production of acidic discharges which have a negative effect on the environment. For example the oxidation of pyrite (FeS_2) produces acidic discharge as highlighted by the reaction below:

$$2FeS_2(s) + 7O_2\,(g) + 2H_2O\ (l) \rightarrow 2Fe^{2+}\,(aq) + 4SO_4^{2-}(aq) + 4H^{+}\,(aq)$$

Step 2: Definition of the sampling target

The targets are tailings dams occurring in the West Wits mining area. The area includes three tailings dams namely: The Old North tailings complex, the New North tailings complex and the South tailings complex. The Old North tailings complex covers an area of 108 ha containing an estimated 24.12×10^{6} m^3 of tailings. The complex consists of six dams but for this study only information for dam F was provided. The New North complex has 4 dams, A, B, C, and D occupying an area of 237 ha. The South tailings complex consists of 2 dams, M and N. Both dams occupy an area of 125 ha.

Step 3: Specification of the measurand

The aim of this step is to write down a clear statement of what is being measured. The measurand in this case is the assessment of the possibility of acid production potential (AP) of mine tailings in various dams .The measurand depends on two parameters which are total sulphur and weighed calcium carbonates. Total sulphur is determined using the method suggested by Sobek *et al.* (1978), and described in Step 4 below.

Acid Potential (AP) can be expressed as below:

AP = Sulphur content (%) x 1000 kg/100 x molecular weight of $CaCO_3$/atomic weight of sulphur

$$\boldsymbol{AP = Total\,Sulphur \times 31.25\; kg\; CaCO_3} \qquad \mathbf{6.2}$$

Step 4: Description of the sampling and analytical protocol

The goal of this step is to outline the protocol followed during sampling and analyses.

Sampling protocol (Sampling procedure followed)

- Sample positions were planned at 1 sample point per 10 hectares.
- Positions were marked on a plan and a GPS was used to locate each point.
- Samples were collected using a Dutch auger at an interval of 50 cm depth at each hole.
- At shallow sample sites, samples were taken to a depth of 2.5 m and deep holes were planned to go to 10 m. Due to the presence of a saturated zone, very little sample could be recovered at depth and the deep holes were therefore abandoned.
- Collected samples were labelled with each sample being labelled three times.
- For some proposed sampling points, the positions were changed due to inaccessibility.

Analytical protocol

The first step in determining AP was to calculate the total sulphur percentage. The total sulphur content was measured using a Leco sulphur analyser. In a Leco sulphur analyser, a sample is combusted in a high temperature tube furnace containing pure oxygen. The products of combustion are passed through a moisture trap to the sulphur IR cell where sulphur is measured as sulphur dioxide. Using a calibration curve based on known sulphur compounds, the measured sulphur dioxide is converted to sulphur content per unit weight of sample.

The obtained total sulphur value is multiplied by the molecular weight of calcium carbonate divided by its atomic weight according to a method proposed by Sobek – see Equation 3.1. According to Sobek *et al.* (1978), 3.125 g of $CaCO_3$ is capable of neutralizing the acid produced from 1 g of sulphur (S), in the form of FeS_2 – hence the amount of potential acidity in 1000 tons of overburden could be calculated by multiplying the percent S by 31.25. This argument is based on the equation below (Kania, 1998):

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \longrightarrow Fe(OH)_3 + 2SO_4^{-2} + 2Ca^{+2} + CO_2$$

Step 5: Identifying the potential sources of uncertainty

This section discusses the various factors which could have contributed to the uncertainty associated with the measurand.

Sampling

Sources of uncertainty associated with sampling include the following:

a) **Inconsistency of the sampling strategy**: The sampling strategy used when collecting samples introduced a certain amount of bias. Initially, numerous sampling points were planned but these were changed due to inaccessibility of some of the tailings dams and the sampling technicians ended up only collecting samples from areas which were accessible. Sampling of accessible areas violates the main principle of correct sampling which recommends equal selection opportunity for material or units occurring within the target.

b) **Heterogeneity (constitutional and distribution):** This is the major source of measurement uncertainty. The effect of this source can be displayed by variations in terms of the observable analyte concentration among samples collected from different points of a sampling target. Heterogeneity results from the fact that the distribution of elements in a sampling target is not uniform but varies. It is well known that the construction and deposition phenomena in a tailings dam result in significant heterogeneity in factors such as particle size distribution, water content, etc.

c) **Limited number of samples collected**: In some dams, very few samples were collected which resulted in high uncertainty values for such dams.

d) **Sample compositing:** As stated in Chapter 3, samples were composited and each composite sample was made up of several increments. Test samples were then extracted from these for laboratory analysis. Although a good practice, sample compositing may result in sample dilution, in which an individual increment with a high analyte concentration is combined with an increment with a low analyte concentration resulting in false test results.

e) **Sample collection tool:** The Dutch auger used for collection introduced a certain amount of error. According to the rule of thumb for sampling, “all the constituents of a lot to be sampled must be given an equal probability of being selected and preserved as part of the sample” (Pitard, 2005, pp. 56). This rule was violated by the tools used for sampling since the instrument failed to penetrate a depth greater than 2 meters which meant that the material occurring below this depth could not be sampled.

Analysis including sample preparation

In addition to the effects of mass, temperature, and calibration of the Leco analyser, the AP measurement result has an uncertainty contribution possibly resulting from:

- Incomplete combustion of the sample in the Leco Analyser which gives an underestimate of the total sulphur content.
- Formation of sulphur dioxide and trioxide: The formation of sulphur dioxide and sulphur trioxide during combustion results in inaccurate and imprecise results in measuring the total sulphur concentration.
- The molar mass of calcium carbonate $CaCO_3$ and atomic weight of sulphur. The uncertainty associated with atomic weight of the elements involved in the calculation of AP is listed in Table 6.1.
- Mass measurements for $CaCO_3$ depend on the calibration of the balance used and the effects of resolution.

Table 6.1: Atomic weights and their associated uncertainties (IUPAC, 2006)

Element	Atomic weight	Quoted uncertainty[10]
Ca	40.078	±0.004
C	12.0107	±0.0008
O	15.9994	±0.0003
S	32.065	±0.0005

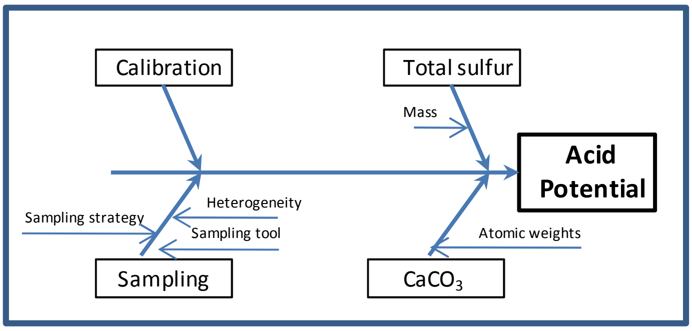


Figure 6.2: Cause and effect diagram for Acid Potential

Step 6: Quantifying Uncertainty

The aim of this step is to quantify uncertainty sources. It should be noted that due to limited information, the size of some sources of uncertainty mentioned in the previous section will not be estimated.

a. Variations between locations (effect of heterogeneity)

Samples taken from different parts of the sampling target exhibit variations in terms of the mean concentration values of acid producing elements, shown in Appendix E. As stated previously, the sampling target for the case study consists of 7 dams. Within each dam, several increments from different points of the dam were combined resulting in numerous composite samples. These

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[10] The tabulated value should be applicable to any normal material. Note that for some geological specimen, the uncertainty may exceed the stated uncertainty value.(IUPAC, 2006)

composite samples were treated and analysed separately. For example, the composite sample with the ID A-1S is made up of 5 increments, see Appendices D and E.

The mean of the single results constitutes the measurement result in agreement with the specification of the measurand. For dam A the final AP measurement value is derived from the average of the results for composite samples A-1S, A-2D, A-3S, A-4S, A-5S, A-6S and A-7S. The calculation procedure is true for all of the seven dams within the area.[11]

Since the measurement results for each dam are based on averaging all obtained sample values obtained as illustrated in the accompanying geochemical database, standard uncertainty associated with each dam's measurement results can therefore be calculated using Equation 3.1. The results are listed in Table 6.2.

Table 6.2: Descriptive statistics and standard uncertainties for AP measurement

Dam ID	Mean	Standard Deviation	Sample Size	Standard uncertainty $u_{(dam)}$(kg/t)
A	15.64	1.4	7	0.53
B	16.15	4.16	7	1.57
C	14.03	1.24	5	0.55
D	17.26	1.14	5	0.51
F	12.42	1.37	4	0.97
M	21.98	4.21	3	2.43
N	22.23	1.76	6	0.65
Combined standard uncertainty				3.25

Thus the uncertainty contribution from the effect of heterogeneity in AP measurements is 3.25 kg/t.

b. Molar mass of $CaCO_3$

Another source of uncertainty that could be identified is contribution from the molar weights of the various elements Ca, C, O and S. The standard uncertainties were calculated by dividing the quoted uncertainty by √3 (rectangular distribution).The results are listed in Table 6.3.

Table 6.3: Standard uncertainties for Ca, C and O

Elements	Atomic weight	Quoted uncertainty	Standard uncertainty
Ca	40.078	±0.004	0.00231
C	12.0107	±0.0008	0.00046
O	15.9994	±0.0003	0.00017
Combined standard uncertainty u_c ($CaCO_3$)			0.00236kg/t

Step 7: Combined uncertainties for AP

The combined uncertainty can be achieved by variance addition of the standard uncertainties from the various factors as shown below:

---

[11] Calculations were carried out in an Excel workbook

$$u_{c\,(AP)} = \sqrt{0.53^2 + 1.57^2 + 0.55^2 + 0.51^2 + 0.97^2 + 2.43^2 + 0.65^2} = 3.25 kg/t$$

The contribution from the atomic weights is minor when compared with that of variations between locations and it is therefore discarded. Results are illustrated in Table 6.4.

Table 6.4: Combined uncertainty from AP measurements for West Wits tailing Dams

Dam ID	Mean (kg/t)	Standard Dev	Sample Size	Standard uncertainty (kg/t)
A	15.64	1.40	7	0.53
B	16.15	4.16	7	1.57
C	14.94	1.24	5	0.55
D	17.256	1.14	5	0.51
F	12.42	1.68	3	0.97
M	21.98	4.21	3	2.43
N	21.75	1.45	5	0.65
	17.16		**U_c (btwn Loc)**	3.25

Step 8: Calculation of the expanded uncertainty

Expanded uncertainty is Uc ($_{AP}$) is obtained by multiplying the combined standard uncertainty with the coverage factor of k = 1.96 (approximately 95% confidence level).

The expanded uncertainty is:

$$U_{AP} = 1.96 \times 3.25\ kg/t = 6.37\ kg/t$$

Step 9: Reporting the result

The AP measurements for The West Wits tailings is

17.16 ± 6.37 kg/t at 95% confidence level

The value 17.16 represents the mean for all seven dams. The results above, show that the true concentration of AP elements lies somewhere between 10.66 and 23.66 kg/t. The contribution of various dams is summarised by Figure 6.3 below.

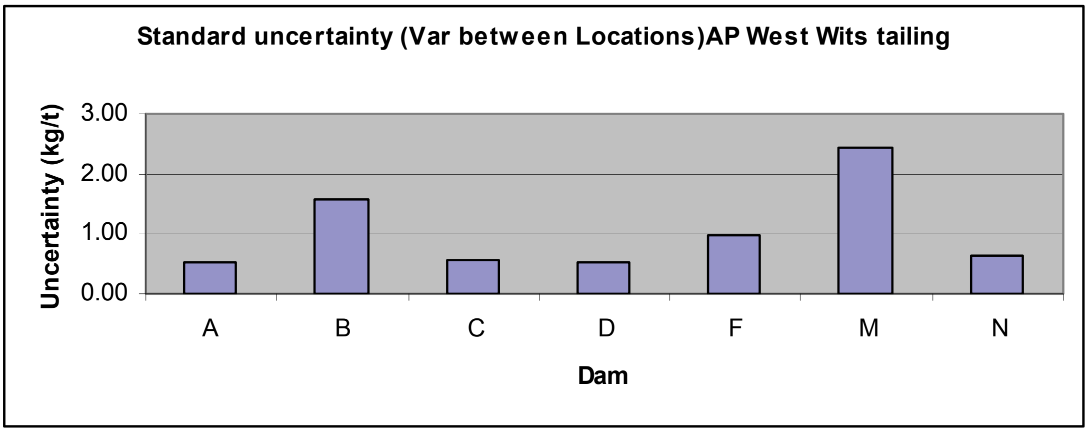

Figure 6.3: Standard uncertainty contribution for AP measurements

6.3 EXAMPLE 2: NEUTRALISATION POTENTIAL (NP)

Step 1: Definition of the purpose of NP determination

Neutralization Potential is another important measurement carried out in ABA. The main aim of undertaking NP measurements was to assess the amount of acid neutralizing elements present within the tailings. Acid neutralizing elements include carbonate minerals such as calcite and dolomite. When their concentration is larger than that of the AP elements then the risk of AMD is reduced.

Step 2: Definition of the sampling target

The targets are tailing dams occurring in the West Wits mining area. The area consists of three tailings dams namely: The Old North tailings complex, the New North tailings complex and the South tailings complex. The Old North tailings complex covers an area of 108 ha containing an estimated 24.12×10^6 m^3 of tailings. The complex consists of six dams but for this study only information for dam F was provided. The New North complex has 4 dams, A, B, C, and D occupying an area of 237 ha. The South tailings complex consists of 2 dams, M and N. Both dams occupy an area of 125 ha.

Step 3: Specification of the measurand

The measurand is the neutralization potential of tailings within the West Wits area. NP can be expressed by the following equation:

$$\boldsymbol{NP = \frac{50a\left[x\left(\frac{b}{a}\right)y\right]}{c}} \qquad \mathbf{6.3}$$

Where:-

a is the normality of HCl added in digestion,

b is the normality of NaOH used in the titration,

c is the mass of sample in grams,

x is the volume of HCl added in ml and

y is the volume of NaOH added in titration.

Step 4: Description of the sampling and analysis protocols

This step requires the analyst to give a detailed outline of the sampling and analytical procedure followed during measurement.

Sampling protocol

The sampling protocol adopted was discussed in Step 5 of Example 1.

Analytical protocol

The analytical protocol used is based on the methodology for NP measurement by Sobek *et al.* (1978).The procedure is outlined below.

1. Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.
2. Add one or two drops of 1:3 HCl to the sample. Presence of $CaCO_3$ is indicated by the bubbling or audible fizz
3. Rate the fizz in step 2 as shown in Table 6.5. The objective of the fizz test is to provide sufficient acid to complete the reaction with the acid.
4. Weigh 2.0 g ± 0.1 g of sample into a 250 ml beaker.
5. Add HCl as indicated in Table 6.5.
6. Heat nearly to boiling point, mixing occasionally until reaction is complete. Reaction is complete when all the gas (CO_2) has evolved.
7. Bring the volume to 125 ml by adding distilled water.
8. Heat the contents of the beaker to boiling point for a minute. Let it cool.
9. Titrate using 0.1N NaOH and pH meter to pH 7.00.
10. Calculate NP.

Table 6.5: Fizz ratings (Sobek *et al.,* 1978)

HCl		
Fizz rating	**ml**	**Normality**
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

Step 5: Identification of the potential sources of uncertainty

The aim of this step is to list all the possible sources of uncertainty for each of the parameters that affect the value of the measurand. A cause and effect diagram is also included. Various sources of uncertainty are highlighted in the cause and effect diagram illustrated in Figure 6.4 below.

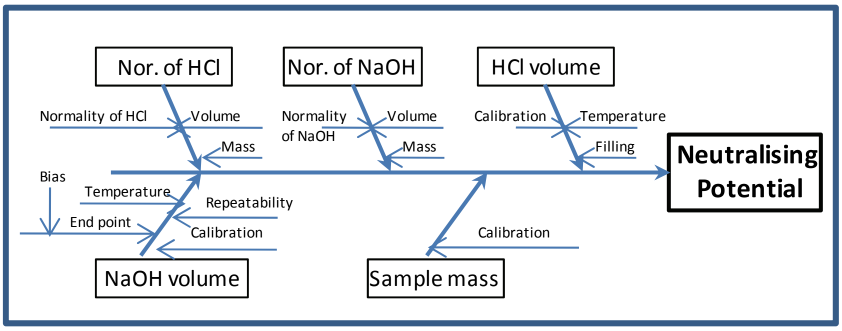

Figure 6.4: Cause and effect diagram for uncertainty components for NP

Sampling

Sources of uncertainty associated with sampling include the sampling strategy, heterogeneity of the target, sample compositing, and use of unsuitable sampling tools. These sources were discussed in detail in Example 1 under Step 5.

Analysis – including sample preparation:

a) Sample effect

During acid digestion, some minerals that co-exist with acid neutralizing elements may be digested at the same time as the carbonate minerals, thereby interfering with the whole analysis process. For example Kania (1998) found that the presence of siderite ($FeCO_3$) within the sample to be analysed may increase acidity and makes it difficult to hold the final end point of titration.

b) Mass Measurement

Assuming the measurements were carried out using a calibrated scale with an accuracy of ±0.1 g[12] common sources of uncertainty associated with using the measurement instrument include:

- Repeatability,
- Digital resolution (readability), and
- Sensitivity and linearity of the balance.

c) Volume measurements

The volume measurements are subject to three major uncertainty sources. These are:

- Variations in filling and reading the volume,
- Uncertainty in the certified internal volume of the beaker used, and
- Variation of the beaker and solution temperature from the temperature at which the volume of the beaker was calibrated.

In addition to the above stated factors affecting volume, the volume of NaOH for titration suffers from the uncertainty related to detection of end point for the titration process.

d) Molar Mass

NaOH and HCI have an uncertainty associated with their relative atomic masses. These are listed in Table 6.6.

Table 6.6: Atomic weights and their associated uncertainty

Elements	**Atomic weight**	**Quoted uncertainty** (IUPAC, 2006)	**Standard uncertainty**
Na	22.98976928	±0.00000002	1.1547E-08
O	15.9994	±0.0003	0.00017
H	1.00794	±0.00007	4.04145E-05
Cl	35.453	±0.002	0.001155
H	1.00794	±0.00007	4.04145E-05

e) Normality of NaOH

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[12] Most scales have an accuracy of +-0.1 g.

The volume of NaOH that is titrated has a normality of 0.1 ± 0.005.

Step 6: Quantifying uncertainty sources

a. Variation NP between locations (Effect of Heterogeneity)

Samples taken from different locations of the dams show variation in terms of NP values as shown in Appendix E. The standard uncertainty of the measurement results (mean value) are calculated from Equation 3.1. Results for the different locations are listed in Table 6.7.

Table 6.7: Standard uncertainties for NP measurement

Dam ID	**Mean**	**Standard Dev**	**Sample Size**	**Standard uncertainty**
A	5.50	1.16	7	0.44
B	5.54	2.52	7	0.95
C	5.96	1.73	5	0.78
D	6.15	1.94	5	0.87
F	6.30	0.92	3	0.53
M	9.42	1.23	3	0.71
N	8.30	1.34	5	0.60
	6.74			
			u_c (btwn Loc)	1.90

b. Molar Masses of NaOH and HCl

The standard uncertainties associated with molar masses of the NaOH and HCl are calculated using the rectangular distribution (Equation 5.7). No other information was given with reference to the atomic masses.

$$u(a) = s = \frac{a}{\sqrt{3}} \qquad 6.4$$

The standard uncertainties are listed in Table 6.8.

Table 6.8: Standard uncertainties associated with molar weights

Elements	**Standard uncertainty , $u_{(mm)}$**
Na	1.1547E-08
O	0.00017
H	4.04145E-05
Cl	0.001155
H	4.04145E-05
Combined uncertainty ($u_{c\ mm}$)	√.1547E-08^2+0.00017^2+4.04145E-05^2+0.001155^2 + 4.04145E-05^2 = 0.001168842

c. Uncertainty of the laboratory glassware used

A volumetric beaker of 125 ml was used during the analysis. Review of literature indicates that a 125 ml beaker usually has an accuracy of ±0.05% which is 0.04 ml.The standard uncertainty associated with the beaker is therefore:

$$u_{vol} = 0.04/\sqrt{3} \ = 0.02\ ml$$

d. Normality of NaOH

Because there is no additional information about the uncertainty value, a rectangular distribution is assumed. The uncertainty associated with NaOH normality is:

$$u_{normality} = 0.005\ /\ \sqrt{3} \quad = 0.002$$

e. Mass Measurement of the sample

The uncertainty associated with weighing 2.0 g of the sample is

$$u_{mass} = 0.1/\ \sqrt{3} \ = 0.06g$$

A rectangular distribution was assumed.

Step 7: Calculate the combined uncertainty

The combined uncertainty is calculated as below:

$$u_c\,(NP) = \sqrt{} u_{c\ (mm)}{}^2 + u_{c\ (vol)}{}^2 + u_{(mass)}{}^2 + u_{c\ (normality)}{}^2 + u_c\ \ (btwn\ Loc)^2$$

$$u_{c\,(NP)} = \sqrt{1.90^2} + 0.02^2 + 0.06^2 = 1.90\ kg/t$$

Therefore the combined uncertainty u_c (NP) for NP West Wits measurements is **1.90 kg/t.** The contribution to uncertainty from molar mass and normality are negligible and are therefore ignored.

Step 8: Calculating the expanded uncertainty

The expanded uncertainty Uc ($_{NP}$) is obtained by multiplying the combined standard uncertainty with the coverage factor of k= 1.96 (approximately 95% confidence level). The expanded uncertainty (Table 6.9) is

$$U_{AP} = 1.96\ \times 1.90\ kg/t\ = 3.72\ kg/t$$

Table 6.9: Expanded uncertainty for NP measurements for West Wits tailings

Dam ID	Mean	Standard Dev	Sample Size	Standard uncertainty
A	5.50	1.16	7	0.44
B	5.54	2.52	7	0.95
C	5.96	1.73	5	0.78
D	6.15	1.94	5	0.87
F	6.30	0.92	3	0.53
M	9.42	1.23	3	0.71

N	8.30	1.34	5	0.60
			u_c (btwn Loc)	1.90
			u_c (Vol)	0.03
			u_c (mass)	0.06
			u_c (NP)	1.90
			U	3.72

Reporting the result

Thus the amount of Neutralizing Potential within the West Wits tailing dams is

6.74±3.72 kg/t

Where the stated uncertainty is calculated using a coverage factor of 1.96 (95% confidence interval) and 6.74 is the mean of all the dams. Figure 6.5 is a plot of uncertainties of the various dams.

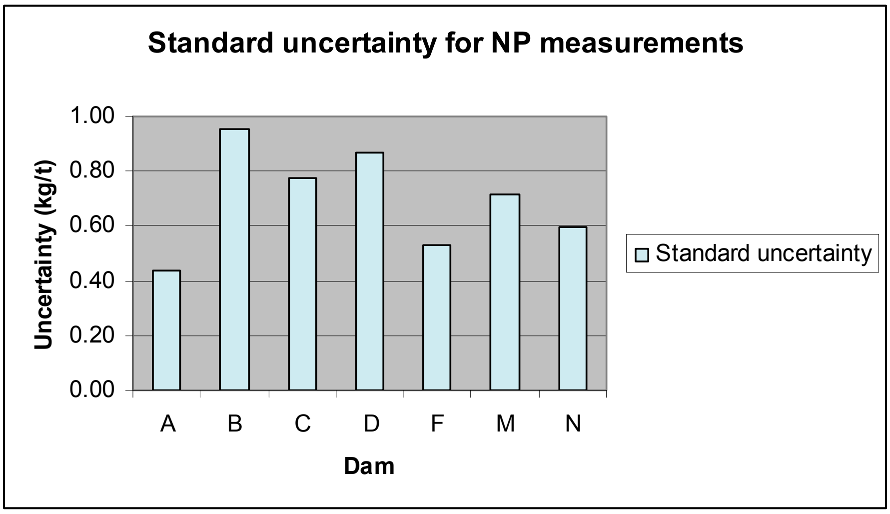

Figure 6.5: Standard uncertainty contribution for NP measurements

6.4 EXAMPLE 3: PASTE pH MEASUREMENTS

Overview

Ophardt (2003) defines pH as the negative logarithm of the hydrogen ion concentration. It is measured on a pH scale containing values ranging from 0 to 14. On the pH scale, a reading above 7 indicates alkalinity and below 7 is an indication of acidity (Table 6.10).

Table 6.10: pH scale

pH < 7	**Acidic**
pH = 7	**Neutral**
pH >7	**Basic**

For example, if the concentration of H^+ in a solution is 10^{-3} the pH is 3, acidic

Step 1: Defining the purpose of pH determination

The main aim of measuring the pH was to determine the concentration of hydrogen ions H^+, in the tailings within the target area. If the hydronium ion concentration exceeds that of the hydroxide ion concentration the material is said to be acidic. The reverse is true for basic materials which have a pH of above 7 at 25°C. The value obtained will be used in conjunction with AP and NP to assess and make a conclusion regarding the ARD generation potential of mine tailings.

Step 2: Definition of the sampling target

The targets are tailing dams occurring in the West Wits mining area. This area is made up of three tailings dams namely The Old North tailings complex, the New North tailings complex and the South tailings complex. The Old North tailings complex occupies an area of 108 ha containing an estimated 24.12×10^6 m^3 of tailings. The complex consists of six dams but for this study only information for dam F was provided. The New North complex has 4 dams, A, B, C, and D occupying an area of 237 ha. The South tailings complex consists of 2 dams, M and N. Both dams occupy an area of 125 ha.

Step 3: Specification of the measurand

The measurand is the concentration of the amount of hydrogen ions (H^+) in mine tailings. pH is equal to the negative log of H^+, Equation 6.5 (Prichard, 2003).

$$pH = -log_{10} a_{H+} \qquad 6.5$$

Step 4: Description of the sampling and analysis protocols followed

The aim of this step is to discuss the measurement procedure in paste pH.

Sampling protocol

The sampling protocol followed was discussed in Step 4 of Example 1.

Analytical protocol

The analytical procedure used is based on the method for measuring paste pH suggested by Sobek *et al.,* 1978.The steps can be summarised as below:

- The pH meter is calibrated for the test temperature using pH buffer solutions and standard procedures according to meter instructions.
- 10.0 g of sample is weighed into a beaker and approximately 5 ml of distilled water is added to the sample.
- The sample is stirred with a spatula to form a thin paste, adding more water or sample to keep the sample at saturation point. Paste should just slide off the spatula easily.
- A pH electrode is carefully placed into the paste and moved about to ensure contact between the paste and electrode. Care must be exercised to avoid impact and scratching of the electrode.
- Record the pH of the paste.

The procedures are summarised in Figure 6.6:

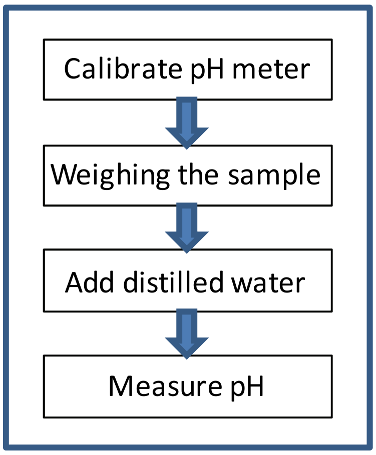

Figure 6.6: procedures involved in paste pH measurement

Step 5: Identifying potential sources of uncertainty

a. Sampling

Sources of uncertainty associated with sampling include the sampling strategy, heterogeneity, sample compositing and sampling tools used. The sources were discussed in detail under Step 5 of Example 1.

b. Analysis including sample preparation.

Most uncertainty sources for pH results are linked to the pH meter which is used in obtaining the measurement. Potential sources of uncertainty include:

a. Soluble salts: The presence of neutral salts affects pH readings by influencing ionic activities and in turn gives rise to activity errors.
b. Uncertainty of the certified pH values for standard buffer solutions.
c. Drifting: Drifting of the pH reading occurs if the glass electrode is insufficiently cleaned between samples. It also occurs due to absorption of CO_2 from the air or when alkali is leached from the glass.
d. Buffer solution: if the buffer solution does not have the exact pH value attributed to it, all the readings on the pH meter will be in error by the amount by which the pH of the buffer differs from its reputed value.
e. Temperature: The temperature at which the pH measurement is carried out may differ from the temperature at which the pH value for the standard buffer is valid. This usually results in a larger uncertainty contribution from temperature.
f. Reading the meter: figures may be rounded off
g. The pH meter only gives an accurate measurement for solutions between –5 and 60°C.

In addition, other contributing uncertainty sources include:

- The mass of the sample – factors contributing to uncertainty are listed in step 6 of example 1.
- The volume of the distilled water and sample contained in the beaker is subject to uncertainty sources as listed in step 5 of Example 2.

These sources are listed in Figure 6.7.

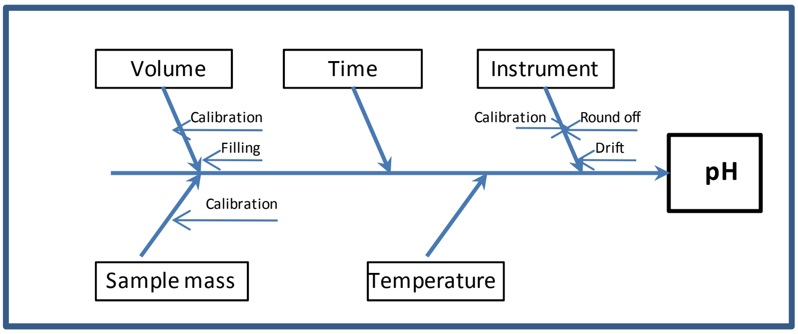

Figure 6.7: Cause and effect diagram for pH measurements

Step 6: Quantifying uncertainty components

Analysis

The uncertainty contribution from analysis was found to be 0.15. Therefore the standard uncertainty is:

$$u_c \text{ (analysis)} = 0.15$$

Variations of pH between locations due to the effect of heterogeneity

The effect of heterogeneity was discussed in detail under step 5 of example 1.Results showing the standard uncertainties resulting from variations between locations due to heterogeneity are listed in Table 6.11.

Table 6.11: Standard uncertainties for the dams

Dam ID	Mean	Standard Dev	Sample Size	Standard uncertainty
A	8.32	0.15	7	0.06
B	8.51	0.18	7	0.07
C	8.31	0.21	5	0.09
D	8.50	0.25	5	0.11
F	8.50	0.07	3	0.04
M	8.22	0.24	3	0.14
N	8.42	0.27	5	0.12
			u_c (btw Loc)	0.25

Step 7: Calculating the combined uncertainty

The combined uncertainty associated with pH measurements is:

$$\boldsymbol{u_c\ (pH) = \sqrt{0.25^2 + 0.15^2} = 0.29}$$

The spreadsheet calculations are listed in Table 6.12.

Table 6.12: Combined uncertainty for pH measurements.

Dam ID	Mean	Standard Dev	Sample Size	Standard uncertainty
A	8.32	0.15	**7**	0.06
B	8.51	0.18	7	0.07
C	8.31	0.21	5	0.09
D	8.50	0.25	5	0.11
F	8.50	0.07	3	0.04
M	8.22	0.24	3	0.14
N	8.42	0.27	5	0.12
	8.40		$\mathbf{u_c}$ (btw Loc)	0.25
			$\mathbf{u_c}$ (analysis)	0.15
			$\mathbf{u_c}$ (pH)	0.29

Step 8: Calculating the expanded uncertainty

Expanded uncertainty (Table, 6.13) is calculated by multiplying the combined uncertainty value by a coverage factor of k =1.96;

$$\boldsymbol{U_c(pH) = 1.96\ \times 0.29 = 0.57}$$

Table 6.13: Expanded uncertainty for pH measurements

Dam ID	Mean	Standard Dev	Sample Size	Standard uncertainty
A	8.32	0.15	**7**	0.06
B	8.51	0.18	7	0.07
C	8.31	0.21	5	0.09
D	8.50	0.25	5	0.11
F	8.50	0.07	3	0.04
M	8.22	0.24	3	0.14
N	8.42	0.27	5	0.12
	8.40		$\mathbf{u_c}$ (btw Loc)	0.25
			$\mathbf{u_c}$ (analysis)	0.15
			$\mathbf{u_c}$ (pH)	0.30
			U(pH)	0.57

Step 9: Reporting the result

Thus the pH (>7) for West Wits tailings is:

8.40 ± 0.57 (95% confidence interval)

Where the stated uncertainty is calculated using a coverage factor of 1.96. Uncertainties in pH measurements are displayed in Figure 6.8 below:

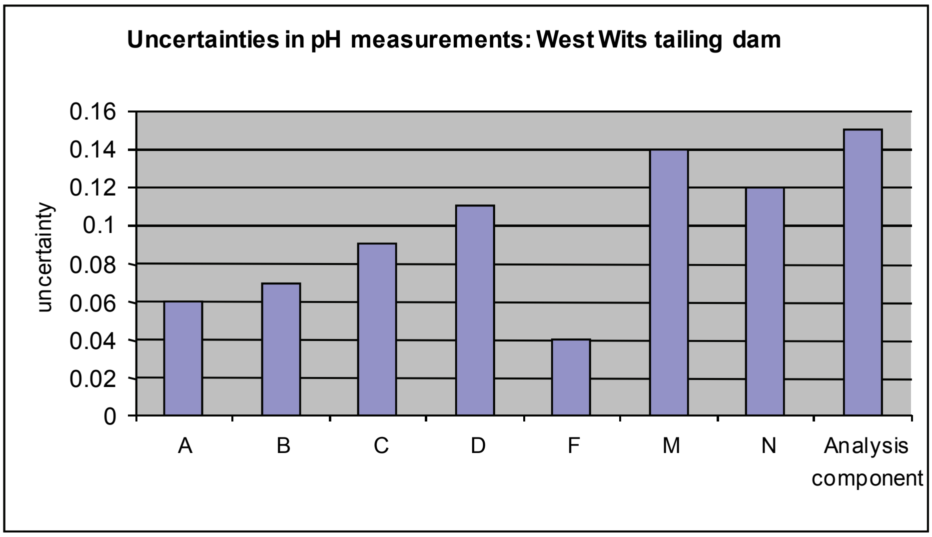

Figure 6.8: Uncertainties in pH measurements

6.4 SUMMARY

This chapter outlined the application of the methodology of quantifying uncertainties in geochemical sampling and analyses discussed in Chapter 5. The parameters of ABA, acid potential, neutralising potential and paste pH from the case study of AngloGold Ashanti Mine, presented in Chapter 3 were used as an example of how the method can be applied. Calculations were carried out in Excel spreadsheets. The uncertainty values were plotted and observable trends are discussed in subsequent chapters.

These uncertainties can then be considered when making decisions based on the measured data and can also be included into appropriate probabilistic geochemical models when these are being used.

CHAPTER 7
DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

7.1 INTRODUCTION

This chapter presents a discussion of the findings of the study, conclusions and recommendations for future studies. The chapter sets out to investigate if uncertainty in geochemical sampling and analyses can be quantified as a function of sample size and analyses.

7.2 DISCUSSION

7.2.1 Sample size determination

Chapter 4 outlined the statistical analysis technique for sample size determination. The principle behind this technique is that “the size of study sample is critical to producing meaningful results” (Germishuyse, Yibas, and Pulles, 2002). The approach is based on two main assumptions, which are:

(i) It is assumed that the selection of samples is random and unbiased.
(ii) The parameters used to calculate sample size are assumed to be normally distributed.

These conditions should be met before applying the method.

In order to determine a representative sample size using the presented approach, knowledge of the distribution of the variables is required. Additional factors on which sample size depend, include purpose of the study, confidence interval, spread of the population, homogeneity and the estimation error, among other important factors. Failure to recognize the impact of these factors on sample size may lead to poor results and hence poor decisions.

Adoption of the approach requires a good estimate of the variability and acceptable error. Unfortunately, there is no way of knowing for sure how variable the population is until after a study has been carried out (Townend, 2002). This information can be acquired from:

(i) Previous research of a similar nature: If, for example, paste pH has been used for geochemical research at a given mine residue deposit and the research was successful, the standard deviation value could be calculated from the data used in that specific research. This can be justified by the fact that while similar populations may differ in their means, they may differ slightly in terms of spread (standard deviation) (Chou, 1989).This same concept may be used to estimate acceptable error. However it should be borne in mind that the distributions of variables in mine residue deposits is governed by complex geochemical and other factors inherent to that specific geological and mining environment.

(ii) **Double sampling:** involves sampling in phases. Results obtained from the first phase, mean, variance or standard deviation are used to determine the sample size for the next phase.

(iii) **Use pilot study results:** If no information about the population to be studied is available, a preliminary or pilot study can be carried out. A pilot study aids in establishing procedures, understanding and protecting against things that can go wrong, and in obtaining the variable estimates needed in determining sample size.

7.2.1.1 Interpretation of results

The results of the exercise indicate a positive correlation between sample size and sample standard deviation. As the population variability, represented by sample standard deviations increases, the number of required samples n follows suit. This effect can be demonstrated by comparison of Neutralization Potential (NP) results for population A to NP results for population B. Close examination of the NP measurement results for population A and B shows that results for population A vary significantly from population B. Such variations in NP measurements results may be attributed to more non-uniform distribution of neutralizing elements in population A than in population B. Therefore, a large sample size was required for population A in order to capture all patterns existing in the target area. In the case of population B, which exhibited uniformity in terms of the distribution of neutralizing elements, fewer samples were required.

The results also highlight an exponential relationship between sample size (n) and acceptable error (d). The impact of estimation error on sample size can be demonstrated by taking AP results for population A. By selecting measurement results at random to create different sample sizes and calculating error associated with each as illustrated in Table 7.1, it can be seen that a low acceptable or estimation error is associated with large sample size. Figure 7.1 illustrates this relationship. The observable trend in this figure is that as the d value gets smaller, sample size increases significantly.

Table 7.1: Relationship between sample size and error

Sample size (n)	Mean (m) (kg/t)	Standard deviation (s)	Error (d) (kg/t)
12	6.8	2.8	2.2
10	7.4	2.7	2.3
9	6.7	2.9	2.8
6	6.3	3.0	3.6
3	7.1	2.9	**5.0**

The results from Chapter 4 also highlight the positive correlation between sample size and confidence level. Any increase in confidence level requires that more samples be collected. The problem with this is that an increase in sample size entails high expenditure. Therefore a trade-off among these competing factors must be reached, and it is necessary to agree on project degree of confidence and acceptable error with relevant stakeholders.

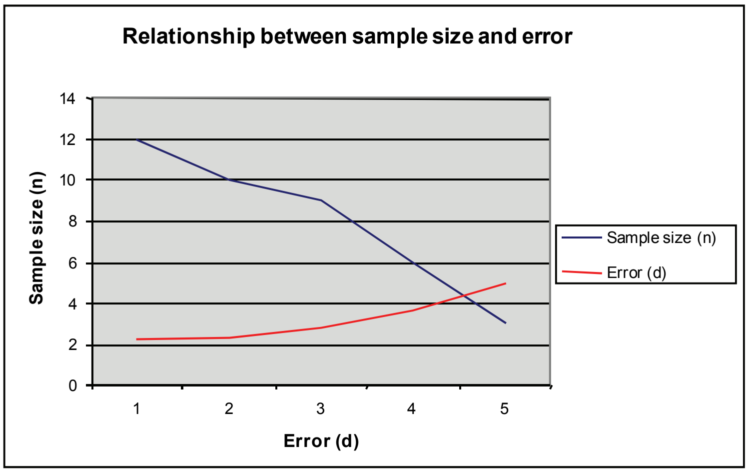

Figure 7.1: Relationship between sample size and error

Based on the results above, for population A, 30 samples are acceptable for AP and 24 samples are acceptable for NP; for population B, 12 samples are acceptable for AP and 25 samples are acceptable for NP. However, according to the proposed minimum sample constraint, at least 30 samples for each population should be collected.

7.2.1.2 Methods of reducing the required sample size

The relationship between sample size and the various parameters on which this depends can be used as a means of reducing the number of required samples and therefore cost. For example, one may increase the allowable or acceptable error in order to minimize the number of samples required. A major risk associated with increasing acceptable sampling error is the possibility of reducing the quality of results and representivity which may lead to poor decisions.

Decreasing material variability within population being sampled is another method that can be adopted in order to reduce the required number of samples. Methods that can be adopted include sample compositing. Mason (1992) recommends taking a large number of small increments and combining them to form a single composite sample which is submitted to the laboratory for analysis.

The use of parameters derived from a previous study of a similar nature is an effective means of minimizing the required sample size. It may be possible to use the standard deviation or acceptable error from a previous study. It must be borne in mind that the accuracy of sample size calculation relies heavily on the accuracy of estimates of the parameters used in the calculation.

7.2.2 Quantifying uncertainty

The methodology for quantifying uncertainty discussed in Chapter 6 follows existing methods for quantifying uncertainty. Such methods include those proposed by ISO, EURACHEM, UKAS and NIST, amongst others. The approach uses a predefined model which identifies each potential source of uncertainty, makes estimates of each component and sums them in order to make an overall estimate of uncertainty. Prior to combining uncertainty sources, sources are first converted to standard uncertainty (standard deviation) and then combined using the laws of uncertainty propagation. Unlike other techniques which use complicated procedures in estimating uncertainty, the methodology uses easy to follow steps for estimating measurement uncertainty. Furthermore, it employs simple statistical applications which are simple to comprehend.

The ability to identify individual uncertainty components and quantify their contribution, facilitates comparisons and enables identification of that uncertainty component with the largest contribution to the overall uncertainty. Based on this information, investigations can be carried out to determine the main cause and measures may be put in place to prevent recurrences. In addition, such assessments may lead to the development of new methods designed to minimize uncertainty.

Can uncertainty be quantified as a function of sample size and analyses?

This section interrogates if uncertainty can be quantified as function of sample size and analyses. As demonstrated in Equation 5.4, a relationship exists between uncertainty and sample size. This relationship is exponential: an increase in either sample size or uncertainty is followed by a decrease of the other parameter. This relationship can be illustrated by the following examples:

As an illustration, Acid Potential uncertainty results for West Wits tailing dams (Figure 7.2) show that dam M has the largest standard uncertainty value compared to the rest of the dams. The dam contributed 34% towards the overall uncertainty as illustrated below. Dam B trails behind, contributing only 22% toward overall uncertainty. Together, the two dams contributed more than 50% towards the overall uncertainty. On the other hand, dam A and D contributed 7% each.

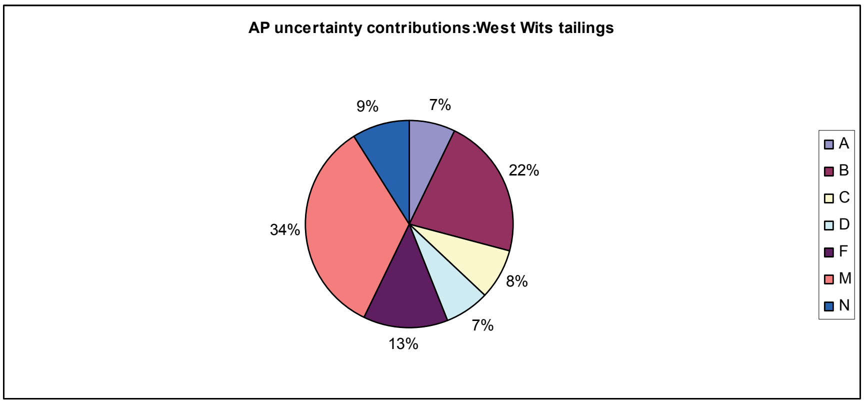

Figure 7.2: AP uncertainty; West Wits tailings

Such variation in uncertainty contribution from these dams is attributed to the differences in sample sizes. Dams A,C,D and N with sample sizes 7, 5, 5 and 6 .have uncertainty values of ± 0.61 which is generally lower than uncertainty values for Dams F and M with sample sizes of less than 5.

Based on this relationship, it is necessary to quadruple sample size in order to reduce uncertainty by a factor of two. This can be illustrated as follows:

Standard deviation for dam M = 4.21

If the initial 3 samples (sample size) are multiplied by 4 (quadrupling the sample size) a new sample size of 12 is obtained. Therefore standard uncertainty u_M is:

$$\boldsymbol{u_M = \frac{s}{\sqrt{n}} = \frac{4.21}{\sqrt{12}} = 1.215}$$

This trend is also visible in pH results for West Wits. Figure 7.3 highlights the sample size and standard uncertainty plot for pH values from West Wits tailings dams. A comparison of dam A, B, C and F results with dam M, supports the exponential relationship. A high uncertainty value is associated with small sample size.

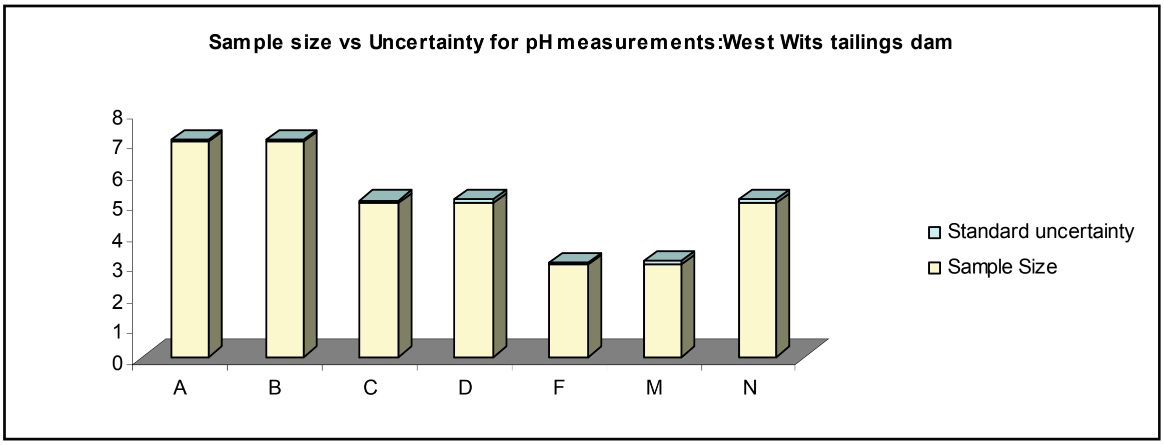

Figure 7.3: Sample size and uncertainty for pH measurements West Wits

In addition, if the original sample values listed in Appendix D are selected at random to form several sample sizes as shown in Table 7.2, the calculations show a remarkable decrease in uncertainty value with increase in sample size.

Table 7.2: Change in uncertainty at varying sample sizes

Sample size (n)	Standard dev (s)	Uncertainty (u_x)
35	0.21	0.04
28	0.23	0.04
18	0.22	0.05
13	0.22	0.06
9	0.26	0.09
6	0.30	0.12
3	0.28	0.16

Plotting the uncertainty against sample size produces a graph that gradually decreases as the number of samples increases – see Figure 7.4.

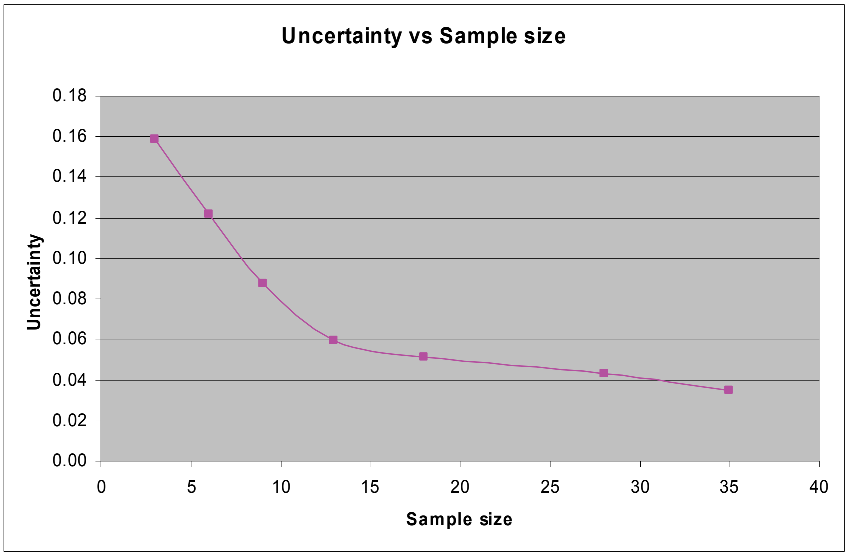

Figure 7.4: Uncertainty vs. sample size

It is therefore evident that a lower uncertainty value is associated with large sample sizes. The reason behind the association is that, as the sample size increases the value of the estimates moves closer to the actual value, based on the central limit theorem. Although it is difficult to tell with certainty whether the actual value lies within the stated range, the equation for determining uncertainty (Equation 5.4), provides at least 68% chance that the actual concentration value lies somewhere within the stipulated range. “Even if the true value lies outside this range, it will probably not be far outside” (Townend, 2002).

On the contrary, the Neutralizing Potential for West Wits dams disobeys this trend. A comparison of dam B and dam F shows that, although the sample size for dam B is larger than dam F, dam B has a larger uncertainty value (Figure 7-5). These uncertainty results indicated a different trend, independent of the known relationship between sample size and uncertainty. Such a trend can be explained in terms of selection bias as well as heterogeneity.

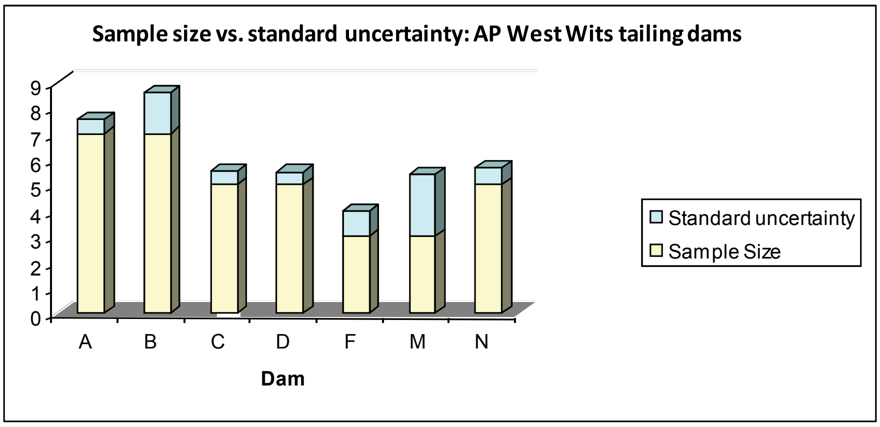

Figure 7.5: Sample size and standard uncertainty for NP measurements

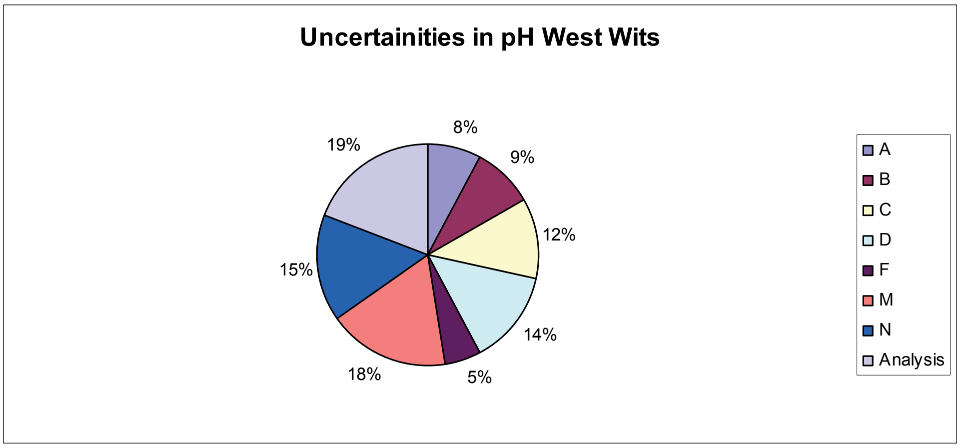

Figure 7.6: pH-uncertainty component contributions

Figure 7.6 shows various uncertainty contributions for pH results. The figure indicates a 19% contribution to uncertainty from analysis. This percentage is significantly smaller compared to the contributions from sources linked to sampling which have a total contribution of 81%. In the case of AP and NP for West Wits, the uncertainty contribution from analysis was extremely low hence they were deemed insignificant.

While both sample size and analysis are crucial aspects in the geochemical measurement process and contribute to uncertainty, from the results above, it is evident that it is not sufficient to quantify uncertainty solely based on the effect of sample size and analyses alone. This shows that uncertainty in geochemical investigations is an interplay of many factors and therefore cannot be quantified solely based on sample size. In addition to the effect of sample size, other factors associated with sampling, e.g. heterogeneity, poor sample preparation and flaws in the analytical procedure should also be considered and their effect acknowledged. Taylor (1996) stated:

> "The total uncertainty is the sum of the contributions from random uncertainty and systematic uncertainty. Taking more samples can reduce the random uncertainty but not the systematic component of uncertainty which is independent of the number of samples. The total uncertainty includes not only sampling uncertainty but also other types of uncertainty."

As highlighted in Chapter 2, the measurement process in geochemical investigations is a multifaceted process and all the processes involved must be considered as potential uncertainty sources.

7.3 CONCLUSIONS

Chapters 5, 6 and 7 provided practical methods for sample size determination and quantifying uncertainties in geochemical sampling and analyses and their applicability. This section outlines the conclusions reached and challenges faced.

7.3.1 Sample size determination

- Sample size determination is dependent on the purpose of the study, cost, acceptable error (risk that one is willing to accept), variability of the population (standard deviation) and confidence level required.
- An understanding of the geology as well as the distribution of contaminants of concern is crucial in geochemical investigations for ERA.
- The sample size chosen determines the accuracy and representivity of the results and hence decision making. In order to achieve high precision in the values, a large sample size is required.
- Various parameters or variables that are required in calculating sample size in Equation 3.1 may be derived from either historic datasets or conducting a pilot study.
- Use of information from a previous study of a similar nature is crucial especially when background information of the population to be studied is not available.
- A large sample size is required for a heterogeneous material, while fewer samples are need for homogeneous material.

7.3.2 Quantifying uncertainty

Conclusions reached are as follows:

- Both sampling and analyses contributed to the overall uncertainty associated with geochemical measurements for ERA. It is therefore crucial to consider all processes carried out during geochemical measurement as potential sources of uncertainty.
- The results also demonstrated the dominant contribution of sampling and related factors toward overall uncertainty when compared to analytical uncertainty.
- Uncertainties in geochemical measurement generally decrease with increases in sample size hence it can be concluded that uncertainty can be reduced by increasing the sample size.
- While there are many sources of uncertainty, heterogeneity of the material being sampled remained the most significant source of uncertainty as observed from variation in the geochemical measurements for the different parameters measured.
- In addition it can be seen from the examples that the effect of material heterogeneity cannot be reduced by increasing sample size as highlighted by tailings dams which had a large sample size but still have high uncertainty values.
- No matter how carefully geological materials are selected and homogenized, they always vary and there is always uncertainty.
- Not all sources of uncertainty are quantifiable. Although some of these sources are difficult to quantify and some insignificant, their effect is nevertheless essential to understand and control.

Uncertainties in geochemical measurements are unavoidable but can be minimised by the following:

- **Implementing quality assurance and quality control programs and adoption of good sampling practices**

  The quality and reliability of geochemical studies and results depend on the quality of field sampling and analytical procedures. A good QA/QC program should be put in place in order to minimize inconsistency and uncertainties in geochemical data. QC samples, such as external standards, duplicates and blanks, should be used in order to monitor the processes of sampling and geochemical analysis. Good sampling and analysis practices such as the use of clean gloves, decontamination of sampling devices and sampling containers are important in order to minimize contamination of the samples. Sampling techniques such as random sampling can be used to minimise sampling bias. Proper calibration of analytical instruments and sampling equipment is crucial.
- **Increasing sample size**

  In ideal circumstances, an increase in sample size would lead to a decrease in uncertainty. This is due to the fact that as the sample size increases, the estimate of a population parameter, for example sample mean, will move closer to the true population mean, thus increasing the precision and accuracy of the estimate.
- **Decreasing the particle size**

  Another method of minimising uncertainty is to decrease the particle size of the sample. Decreasing the particle size of the sample by grinding reduces the effect of heterogeneity which, in most cases, would otherwise result in large uncertainty.
- **Use of equipment made from inert material**

  The equipment used during the measurement process may introduce errors through cross contamination of the sample from the material the equipment is made from. Such contamination may occur during sample collection, preservation, preparation (grinding and milling) and analysis. In addition to decontamination of the equipment, the use of equipment made from inert material is recommended. Such materials include glass, ceramics and stainless steel.
- **Sample compositing**

  One commonly used method for homogenization is sample compositing. Sample compositing refers to the physical mixing of samples to form composites. It is an effective way to reduce inter-sample variance caused by heterogeneity. Mixing samples from different locations is also an effective means of reducing cost since it is only the composite sample that is analysed. Although a good practice, compositing samples may result in loss of information and sensitivity due to dilution of the samples. Therefore great caution should be taken when deciding on whether to composite samples or not.
- **Improving the sampling strategy**

  In order to improve the precision of the results, in addition to increasing the sample size, one may work towards improving the sample design. Stratified sampling ensures proper coverage unlike in simple random sampling where no specific order is followed. This minimizes the chances of some portions of the target being missed or left un-sampled. The various sampling methods can also be combined in order to ensure coverage and therefore sample representivity.

- **Establishing the site history**
  The history of the site should be known before carrying out the investigations. This involves having a list of all the previous activities undertaken at the site. Site history may be obtained from previous work performed in the area or local authorities such as municipalities. Knowledge of the site history assists in determining the suitable sampling design and strategy, which in turn helps in obtaining representative samples and therefore aids in the minimization of errors and uncertainty.
- **Improving quality of measurements**
  Since results obtained from geochemical sampling and analyses are used for long term prediction, it is important that measurements made in the past be compatible with those made in the future. This facilitates the monitoring of changes in quality and establishing whether the quality has improved or deteriorated over time. In addition it is also essential that a reliable method of archiving or storing data be put in place in order to monitor quality.

7.3.3 Challenges

One major drawback was lack of information and resources. This was mainly attributed to the fact that the author did not undertake any practical fieldwork but rather used and interrogated extensive datasets obtained from prior studies. This is further exacerbated by limited literature on the subject and lack of appreciation of the concept of “measurement uncertainty” in the field of geology and environmental sciences.

Although the author managed to identify possible uncertainty sources for the three examples given above, quantifying them was a challenge. Some potential sources of uncertainty were identified and listed but could not be further quantified due to limited information.

7.4 RECOMMENDATIONS

This section provides recommendations.

- It is recommended that in order to actually explore the practicality and applicability of the discussed method for uncertainty analysis and sample size determination, a detailed study coupled with extensive field data collection is required.
- Prior understanding of the concepts of geochemical sampling and analyses for ERA as well as sample size and uncertainty is necessary when embarking on studies of this nature.
- A study of this calibre require a proper sampling and analyses plan clearly specifying the objectives of the study and how sampling and analyses tasks will be executed. The draft plan should be accompanied by a QA/QC program.
- Since the concept of measurement uncertainty is not well known, especially among geoscience practitioners, as evidenced by limited literature on this subject, more research should be conducted in this field in order to develop a universally accepted and user friendly method for quantifying uncertainty in geochemical investigations and the geoscience field in general.

- As indicated above, it is therefore crucial that the sample planner seeks advice from experts such as statisticians, sampling technicians, decision makers as well as analytical chemists during the planning phase of the project.
- It is recommended that either the combined standard uncertainty or an expanded uncertainty be reported with every result obtained from a geochemical investigation in order to comply with requirements of ISO and other renounce bodies responsible for standardising laboratory practices.
- It is strongly recommended that in any geochemical assessment being undertaken, that discussion and agreement on acceptable confidence levels and acceptable error be facilitated with the key stakeholders and decision makers. This will ensure that there are realistic expectations from the study and that the sampling strategy can be developed at the outset to ensure that the required confidence can be placed in the study outcome.

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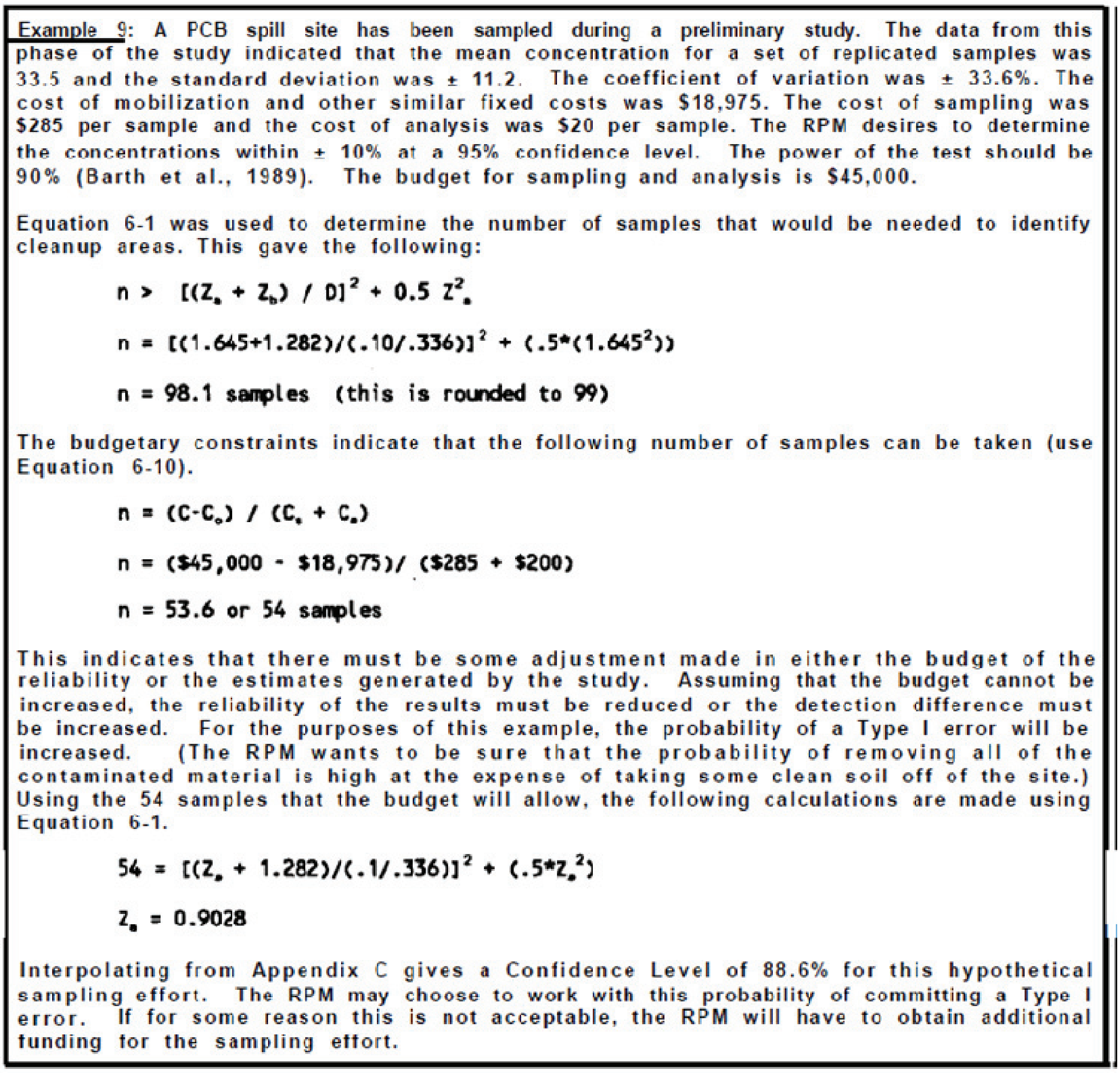
APPENDIX A
EPA SAMPLE SIZE DETERMINATION

NUMBER OF SAMPLES REQUIRED IN ONE SIDED ONE SAMPLE t-TEST TO ACHIEVE MINIMUM DETECTABLE RELATIVE DIFFERENCE AT A CONFIDENCE LEVEL (1-α) AND POWER OF (1-β) (Barth *et al.*, 1989)

Coefficient of Variation (%)	Power (%)	Confidence Level (%)	Minimum Detectable Relative Difference (%)				
			5	**10**	**20**	**30**	**40**
10	95	99	66	19	7	5	4
		95	45	13	5	3	3
		90	36	10	3	2	2
		80	26	7	2	2	1
	90	99	55	16	6	5	4
		95	36	10	4	3	2
		90	28	8	3	2	2
		80	19	5	2	1	1
	80	99	43	13	6	4	4
		95	27	8	3	3	2
		90	19	6	2	2	2
		80	12	4	2	1	1
15	95	99	145	39	12	7	5
		95	99	26	8	5	3
		90	78	21	6	3	3
		80	57	15	4	2	2
	90	99	120	32	11	6	5
		95	79	21	7	4	3
		90	60	16	5	3	2
		80	41	11	3	2	1
	80	99	94	26	9	6	5
		95	58	16	5	3	3
		90	42	11	4	2	2
		80	26	7	2	2	1
20	95	99	256	66	19	10	7
		95	175	45	13	9	5
		90	138	36	10	5	3
		80	100	26	7	4	2
	90	99	211	55	16	9	6
		95	139	36	10	6	4
		90	107	28	8	4	3
		80	73	19	5	3	2
	80	99	164	43	13	8	6
		95	101	27	8	5	3
		90	73	19	6	3	2
		80	46	12	4	2	2

Coefficient of Variation (%)	Power (%)	Confidence Level (%)	Minimum Detectable Relative Difference (%)				
			5	10	20	30	40
25	95	99	397	102	28	14	9
		95	272	69	19	9	6
		90	216	55	15	7	5
		80	155	40	11	5	3
	90	99	329	85	24	12	8
		95	272	70	19	9	6
		90	166	42	12	6	4
		80	114	29	8	4	3
	80	99	254	66	19	10	7
		95	156	41	12	6	4
		90	114	30	8	4	3
		80	72	19	5	3	2
30	95	99	571	145	39	19	12
		95	391	99	26	13	8
		90	310	78	21	10	6
		80	223	57	15	7	4
	90	99	472	120	32	16	11
		95	310	79	21	10	7
		90	238	61	16	8	5
		80	163	41	11	5	3
	80	99	364	84	26	13	9
		95	224	58	16	8	5
		90	164	42	11	6	4
		80	103	26	7	4	2
35	95	99	775	196	42	25	15
		95	532	134	35	17	10
		90	421	106	28	13	8
		80	304	77	20	9	6
	90	99	641	163	43	21	13
		95	421	107	28	14	8
		90	323	82	21	10	6
		80	222	56	15	7	4
	80	99	495	126	34	17	11
		95	305	78	21	10	7
		90	222	57	15	7	5
		80	140	36	10	5	3

APPENDIX B
SAMPLE SIZE DETERMINATION USING COMBINED COST AND STATISTICAL METHODS.
(Equations 1.7, 1.8 and 1.13)



Example 9: A PCB spill site has been sampled during a preliminary study. The data from this phase of the study indicated that the mean concentration for a set of replicated samples was 33.5 and the standard deviation was ± 11.2. The coefficient of variation was ± 33.6%. The cost of mobilization and other similar fixed costs was $18,975. The cost of sampling was $285 per sample and the cost of analysis was $20 per sample. The RPM desires to determine the concentrations within ± 10% at a 95% confidence level. The power of the test should be 90% (Barth et al., 1989). The budget for sampling and analysis is $45,000.

Equation 6-1 was used to determine the number of samples that would be needed to identify cleanup areas. This gave the following:

$$n > [(Z_a + Z_b) / D]^2 + 0.5 Z^2_a$$

$$n = [(1.645+1.282)/(.10/.336)]^2 + (.5*(1.645^2))$$

$$n = 98.1 \text{ samples (this is rounded to 99)}$$

The budgetary constraints indicate that the following number of samples can be taken (use Equation 6-10).

$$n = (C-C_o) / (C_s + C_a)$$

$$n = (\$45,000 - \$18,975)/ (\$285 + \$200)$$

$$n = 53.6 \text{ or } 54 \text{ samples}$$

This indicates that there must be some adjustment made in either the budget of the reliability or the estimates generated by the study. Assuming that the budget cannot be increased, the reliability of the results must be reduced or the detection difference must be increased. For the purposes of this example, the probability of a Type I error will be increased. (The RPM wants to be sure that the probability of removing all of the contaminated material is high at the expense of taking some clean soil off of the site.) Using the 54 samples that the budget will allow, the following calculations are made using Equation 6-1.

$$54 = [(Z_a + 1.282)/(.1/.336)]^2 + (.5*Z_a^2)$$

$$Z_a = 0.9028$$

Interpolating from Appendix C gives a Confidence Level of 88.6% for this hypothetical sampling effort. The RPM may choose to work with this probability of committing a Type I error. If for some reason this is not acceptable, the RPM will have to obtain additional funding for the sampling effort.

APPENDIX C
QUALITY CONTROL SAMPLES

Procedure	Description
Field Blank	A sample container filled with distilled deionized (DDI) Water, exposed during sampling and then analysed to detect accidental or incidental contamination.
Sample Bank Rinsate	A sample (last rinse of DDI water) of DDI water passed over the sample preparation apparatus, after cleaning, to check for residual contamination.
Field Rinsate	A sample (last rinse of DDI water) of DDI water passed over the sampling apparatus after cleaning to check for residual contamination.
Calibration Check Standard	A standard material to check instrument calibration.
Spiked Sample	A separate aliquot of the soil sample having an appropriate standard reference material added to check for soil and extract matrix effects on recovery.
Total Recoverable	A second aliquot of the sample which is analysed by a more rigorous method to check the efficacy of the protocol method.
Laboratory Control Standard	A sample of a soil standard carried through the analytical procedure to determine overall method bias.
Triplicate Samples (Splits)	The prepared sample is split into three portions to provide blind duplicates for the analytical laboratory and a third replicate for the referee laboratory to determine interlaboratory precision.
Duplicate Sample	An additional sample taken near the field sample to determine total within-batch measurement error.
Field Audit	A sample of well-characterized soil that is taken into the field with the sampling crew, sent through the sample bank to the laboratory with the field samples to detect bias in the entire measurement process and to determine batch to batch variability.
External Laboratory Audit	A sample of well-characterized soil sent directly to the laboratory for analysis. The analyte concentrations are unknown to the laboratory. This type of sample is used to estimate laboratory bias and batch-to-batch variability. It may also be used for external quality control of the laboratory.

Source: Van Ee, Blum, and Starks (1990)

APPENDIX D
SAMPLE RECORDS PRIOR TO ANALYSIS

Table D1. Sampling records of tailings dams, West Wits

Field Data					Laboratory Analyses												
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
Old North Complex	4	E-1SA	grey	0.5	Deep yellow	7.5	E-1S	E-F-G-COMP	1	1	1	1	1	1	1	1
		E-1SB	grey	1	Medium brown	7.9										
		E-1SC	light grey	1.5	Yellow	7.9										
		E-1SD	grey to yellowish	2	Deep yellow	8.2										
		E-1SE	grey to yellowish	2.5	Deep yellow	8.1										
		E-2S A	grey	0.5	Deep yellow	8.3	E-2S									
		E-2S B	light grey	1	Deep yellow	8.3										
		E-2S C	light grey	1.5	Deep yellow	8.3										
		E-2S D	light grey to yellowish	2	Yellow	8.4										
		E-2S E	light grey to yellowish	2.5	Deep yellow	8.4										
	3	F-1D A	light grey	0.5	Dark beige	8.4	F-1D-1									
		F-1D B	light grey	1	Yellow	8.2										
		F-1D C	light grey	1.5	Deep yellow	8.1										
		F-1D D		2	Greenish yellow	8.3										
		F-1D E	yellowish	2.5	Yellow	8.4										
		F-1D E	yellowish	2.7	ND	ND										
		F-1D F	light yellow with grey	3	Yellow	8.5										
		F-1D G	grey	3.5	Light yellow	8.5										
		F-1D H	grey	4	Deep yellow	8.4										
		F-1D I	grey	4.5	ND	ND										
		F-1D I	grey & yellowish	4.9	ND	ND										
		F-1D J	grey	5	Deep yellow	8.6										
		F-1D K	grey	5.5	ND	ND										
		F-1D K	dark grey colour	6	Dark greenish yellow	8.5	F-1D-2									
		F-1D L	grey	6.5	Dark greenish yellow	8.5										
		F-1D M	grey	7	Dark beige	8.7										
		F-1D N		7.5	Medium brown	8.5										
		F-4S A	silt grey	0.5	Deep yellow	8.3	F-4S									
		F-4S B	light grey to yellowish colour	1	Yellow	8.4										
		F-4S C	grey	1.5	Deep yellow	8.4										
		F-4S D	grey	2	Greenish yellow	8.5										
		F-4S E	grey	2.5	Dark greenish yellow	8.5										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
Old North Complex	3	F-2S A	light grey	0.5	Light brown	8.2	F-2S	E-F-G-COMP	1	1	1	1	1	1	1	1
		F-2S B	light yellowish colour	1	Light brown	8.3										
		F-2S C	light grey	1.5	Light brown	8.3										
		F-2S D	grey silt	2	Yellow	8.3										
		F-2S E	grey silt	2.5	Deep yellow	8.4										
		F-3S A	light grey	0.5	Yellow	8.2	F-3S									
		F-3S B	grey	1	Deep yellow	8.3										
		F-3S C	light grey	1.5	Greenish yellow	8.3										
		F-3S D	light grey	2	Greenish yellow	8.4										
		F-3S E	grey(least moist)	2.5	Deep yellow	8.4										
	6	G-2SA	grey	0.5	Greenish yellow	7.9	G-2S-1									
		G-2SB	grey	1	Dark greenish yellow	8.3										
		G-2SC	light grey	1.5	Dark greenish yellow	8.3										
		G-2SD	grey	2	Dark greenish yellow	8.4										
		G-2SE	grey	2.5	Dark greenish yellow	8.3										
		G-2SF		3	Light brown	8.8	G-2S-2									
		G-2SG		3.5	Medium brown	9.0										
		G-2SG		3.8	brown	9.0										
		G-1SA	light grey	0.5	Deep yellow	8.1	G-1S									
		G-1SB	light grey to yellowish	1	Deep yellow	8.3										
		G-1SC	light grey to yellowish	1.5	Deep yellow	8.2										
		G-1SD	light grey to yellowish	2	Greenish yellow	8.3										
		G-1SE	light grey to yellowish	2.5	Deep yellow	8.3										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
		H -1SA	yellow colour with orange inclusions	0.5	Yellow	4.3	H-1S	H-I-J_top-comp	1	0	1	0	1	1	1	
		H -1SB	yellow	1	Deep yellow	4.2										
		H -1SC	yellowish	1.5	Deep yellow	8.1										
		H -1SD	grey with yellowish inclusions	2	Deep yellow	3.1										
		H -1SE	light yellowish silt	2.5	Yellow	3.0										
		H -1SF		3	Deep yellow	4.3										
		H -1SG		3.5	Dark greenish yellow	3.7										
		H -1SI		4	Dark greenish yellow	8.3										
		I-1SA	yellow silt	0.5	Greenish yellow	4.2	I-1S-1									
		I-1SB	yellow silt	1	Greenish yellow	4.2										
		I-1SC	yellowish colour	1.5	Dark greenish yellow	3.7										
		I-1SD	yellowish colour with grey inclusions	2	Deep yellow	7.8	I-S-2									
		I-1SE	moist light yellowish	2.5	Medium brown	8.2										
		I-1SF		3	Light brown	8.2										
		I-1SG		3.5	Medium brown	8.2										
	1	J-1SA	yellowish and moist	0.5	Deep yellow	4.2	J-1S-1									
		J-1SB	yellowish with grey mixture	1	Deep yellow	4.6										
		J-1SC	yellow and dark grey mixture	1.5	Greenish yellow	5.9										
		J-1SD	dark grey	2	Greenish yellow	8.1	J-1S-2									
		J-1SE	yellow and dark grey mixture	2.5	Greenish yellow	8.3										
		J-1SF		3	Light brown	8.2										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
South Complex	Lower	N-7DA	grey with brownish staff		Light brown	7.5	N-7D	N-COMP	1	0	1	1	1	1	1	
		N-7DB	light grey to yellowish colour		Light brown	7.7										
		N-7DC	grey clay		Light brown	8.2										
		N-7DD	very moist grey clay		Medium brown	8.4										
		N-7DE	grey		Medium brown	8.2										
		N-7DF		3	Dark greenish yellow	8.0										
		N-7DG		3.5	Greenish yellow	7.6										
		N-7DH		4	Dark greenish yellow	8.1										
		N-6SA	grey	0.5	Dark greenish yellow	8.6	N-6S									
		N-6SB	grey	1	Dark greenish yellow	8.7										
		N-6SC	grey and very moist	1.5	Greenish yellow	8.4										
		N-6SD	grey	2	Greenish yellow	8.2										
		N-6SE	moist dark grey	2.5	Dark greenish yellow	8.5										
		N-5S A	grey with light yellowish inclusion	0.5	Medium brown	8.6	N-5S									
		N-5S B	silky grey	1	ND	ND										
		N-5S C	grey	1.5	Medium brown	8.3										
		N-5S D	grey	2	Medium brown	8.2										
		N-5S E	very moist grey	2.5	Medium brown	8.9										
		N-3DA	grey	0.5	Medium brown	8.7	N-3D									
		N-3DB	grey	1	C28-5	8.5										
		N-3DC	grey	1.5	Brown	8.8										
		N-3DD	grey	2	Medium brown	8.4										
		N-3DE	grey	2.5	Brown	8.1										
		N-2SA	stiff grey clay	0.5	Brown	8.7	N-2S									
		N-2SB	grey clay	1	Medium brown	8.9										
		N-2SC	grey and moist	1.5	Brown	8.3										
		N-2SD	grey	2	E17-7	8.6										
		N-2SE	grey	2.5	Brown	8.8										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
South Complex		N-1SA	grey	0.5	Dark grey	8.5	N-1S	N-COMP	1	0	1	1	1	1	1	
		N-1SB	stiff grey colour	1	Dark grey	8.7										
		N-1SC	grey	1.5	Dark greenish yellow	8.4										
		N-1SD	grey	2	Charcoal	8.2										
		N-1SE	grey with light yellowish inclusions	2.5	Brown	8.2										
	Upper	M-4DA	silky grey	0.5	Dark grey	7.7	M-4D	M-COMP	1	0	1	0	1	1	1	
		M-4DB	silky grey	1	Dark grey	7.8										
		M-4DC	grey	1.5	Dark grey	7.2										
		M-4DD	moist and grey in colour	2	Dark grey	8.6										
		M-4DE	very moist grey	2.5	Charcoal	8.6										
		M-5SA	grey with yellow inclusions	0.5	Dark grey	8.0	M-5S									
		M-5SB	grey	1	Dark grey	7.9										
		M-5SC	moist grey	1.5	Dark grey	8.5										
		M-5SD	dark grey and stiff	2	Dark grey	8.3										
		M-5SE	grey and moist	2.5	Charcoal	8.5										
		M-6SA	silky grey	0.5	Dark grey	8.0	M-6S									
		M-6SB	grey	1	Dark grey	8.6										
		M-6SC	silky grey	1.5	Dark grey	8.3										
		M-6SD	moist grey	2	Charcoal	8.2										
		M-6SE	moist grey	2.5	Dark grey	8.6										
		M-6SF		3	Dark greenish yellow	8.4										
		M-6SG		3.5	Dark greenish yellow	8.7										
		M-6SH		4	Greenish yellow	8.8										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
New North Complex	7B	A-1SA	grey with yellow inclusions	0.5	Charcoal	7.6	A-1S	A-COMP	1	0	1	0	1	1	1	
		A-1SB	grey	1	Dark grey	8.1										
		A-1SC	wet clay grey in colour	1.5	Grey	8.5										
		A-1SD	grey	2	Dark grey	8.2										
		A-1SE	dark grey	2.5	Dark grey	8.2										
		A-2DA	grey (yellow inc)	0.5	Dark grey	8.4	A-2D									
		A-2DB	stiff grey silt	1	Grey	8.0										
		A-2DC	grey	1.5	Dark grey	5.4										
		A-2DD	grey to light grey	2	Dark grey	8.5										
		A-2DE	grey	2.5	Dark grey	7.7										
		A-3SA	silt grey	0.5	Dark grey	8.5	A-3S									
		A-3SB	grey	1	Dark grey	8.8										
		A-3SC	grey	1.5	Charcoal	8.0										
		A-3SD	moist grey	2	Dark grey	8.6										
		A-3SE	moist grey	2.5	Dark grey	8.7										
		A-4SA	grey	0.5	Dark grey	8.6	A-4S									
		A-4SB	grey	1	Dark grey	8.7										
		A-4SC	grey	1.5	Charcoal	8.4										
		A-4SD	grey	2	Dark grey	8.2										
		A-4SE	grey	2.5	Grey	8.3										
		A-5SA	grey	0.5	Dark grey	8.4	A-5S									
		A-5SB	grey	1	Dark grey	8.5										
		A-5SC	grey	1.5	Dark greenish yellow	8.3										
		A-5SD	grey	2	Dark grey	8.5										
		A-5SE	grey	2.5	Dark grey	8.5										
		A-6S A	moist grey	0.5	Charcoal	8.6	A-6S									
		A-6S B	grey	1	Grey	8.5										
		A-6S C	grey	1.5	Dark grey	8.2										
		A-6S D	moist grey	2	Charcoal	8.1										
		A-6S E	moist grey	2.5	Dark grey	8.2										
		A-7SA	grey	0.5	Greenish yellow	8.2	A-7S									
		A-7SB	grey	1	Dark grey	8.3										
		A-7SC	grey	1.5	Dark grey	8.0										
		A-7SD	grey	2	Dark grey	8.3										
		A-7SE	grey	2.5	Deep yellow	8.6										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
New North Complex	7A	B-1SA	grey	0.5	Dark grey	8.2	B-1S	B-COMP	1	0	1	1	1	1	1	
		B-1SB	grey	1	Dark grey	8.1										
		B-1SC	moist grey	1.5	Greenish yellow	8.2										
		B-1SD	light grey to yellowish	2	Dark grey	8.3										
		B-1SE	silty grey	2.5	Dark grey	8.1										
		B-2SA	light grey	0.5	Dark greenish yellow	8.5	B-2S									
		B-2SB	grey	1	Dark grey	8.4										
		B-2SC	grey	1.5	Dark grey	8.6										
		B-2SD	moist grey	2	Dark grey	8.9										
		B-2SE	moist grey	2.5	Dark grey	8.7										
		B-3SA	grey	0.5	Dark grey	8.4	B-3S									
		B-3SB	grey	1	Charcoal	8.5										
		B-3SC	moist grey	1.5	Dark grey	8.7										
		B-3SD	moist grey	2	Dark grey	8.6										
		B-3SE	grey	2.5	Dark grey	9.0										
		B-4SA	grey	0.5	Charcoal	8.6	B-4S									
		B-4SB	grey	1	Dark grey	8.8										
		B-4SC	light grey	1.5	Dark grey	8.6										
		B-4SD	moist grey	2	Dark grey	8.6										
		B-4SE	moist grey	2.5	Dark grey	8.6										
		B-5DA	grey	0.5	Grey	8.1										
		B-5DB	moist clay	1	Dark grey	9.1										
		B-5DC	light grey to yellowish	1.5	Dark grey	8.5										
		B-5DD	grey	2	Greenish yellow	8.5										
		B-5DE	moist grey	2.5	Dark grey	8.4										
		B-6SA	grey	0.5	Dark grey	8.7	B-6S									
		B-6SB	silty grey	1	Dark grey	8.8										
		B-6SC	grey	1.5	Dark grey	8.4										
		B-6SD	grey	2	Deep yellow	8.4										
		B-6SE	grey	2.5	Dark grey	8.7										
		B-7SA	silty grey	0.5	Dark grey	8.5	B-7S									
		B-7SB	grey	1	Dark greenish yellow	8.4										
		B-7SC	grey	1.5	Grey	8.3										
		B-7SD	grey and moist	2	Dark grey	8.1										
		B-7SE	grey	2.5	Dark grey	8.1										
		B-7SF		3	Light brown	8.1	B-7S-2									
		B-7SG		3.5	Light brown	8.4										
		B-7SH		4	Dark greenish yellow	8.7										
		B-7SI		4.5	dark greenish yellow	8.6										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
New North Complex	5B	C-5DA	silty grey	0.5	Dark grey	8.2	C-5D	C-COMP	1	0	1	0	1	1	1	
		C-5DB	grey to light grey	1	ND	ND										
		C-5DC	grey	1.5	Dark grey	8.5										
		C-5DD	grey and moist	2	Medium brown	7.6										
		C-5DE	grey	2.5	Charcoal	7.5										
		C-5DF		3		8.4										
		C-5DG		3.5		8.2										
		C-5DH		4		8.1										
		C-3SA	grey	0.5	ND	ND	C-3S									
		C-3SB	silty grey	1	ND	ND										
		C-3SC	grey	1.5	Dark grey	8.6										
		C-3SD	grey	2	ND	ND										
		C-3SE	grey	2.5	Dark grey	8.5										
		C-4DA	grey	0.5	Light brown	4.5	C-4D									
		C-4DB	grey	1	Brown	4.4										
		C-4DC	light grey to yellowish	1.5	ND	ND										
		C-4DD	grey	2	ND	ND										
		C-4DE	moist grey	2.5	Charcoal	8.5										
		C-2SA	light grey	0.5	Dark grey	8.4	C-2S									
		C-2SB	grey	1	Dark grey	8.4										
		C-2SC	grey	1.5	ND	ND										
		C-2SD	moist grey	2	Dark grey	8.2										
		C-2SE	grey	2.5	C15-4	7.8										
		C-1SA	light grey	0.5	Dark grey	8.2	C-1S									
		C-1SB	moist and grey	1	Dark grey	8.3										
		C-1SC	grey	1.5	ND	ND										
		C-1SD	grey	2	ND	ND										
		C-1SE	grey	2.5	Dark grey	8.2										

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Table D1. Sampling records of tailings dams, West Wits – continued

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
New North Complex	5A	D-1SA	grey	0.5	Dark grey	8.2	D-1S	D-COMP	1	0	1	0	1	1	1	
		D-1SB	grey	1	Dark grey	8.0										
		D-1SC	grey	1.5	ND	ND										
		D-1SD	grey	2	ND	ND										
		D-1SE		2.5	Dark grey	8.6										
		D-3SA	grey	0.5	Dark grey	8.3	D-3S									
		D-3SB	light grey to yellowish	1	Dark grey	8.3										
		D-3SC	grey	1.5	Dark grey	8.3										
		D-3SD	grey	2	Deep yellow	8.4										
		D-3SE		2.5	Charcoal	8.5										
		D-2SA	grey	0.5	Dark grey	8.3	D-2S									
		D-2SB	grey	1	Dark grey	8.4										
		D-2SC	light grey to yellowish silt	1.5	ND	ND										
		D-2SD	grey	2	ND	ND										
		D-2SE		2.5	Dark grey	8.3										
		D-5DA	grey	0.5	Dark grey	8.8	D-5D									
		D-5DB	grey	1	Dark grey	8.9										
		D-5DC	grey	1.5	Dark grey	8.7										
		D-5DD	grey	2	ND	ND										
		D-5DE	grey	2.5	Dark grey	8.6										
		D-4DA	light grey	0.5	Dark grey	8.7	D-4D									
		D-4DB	dark grey	1	Dark grey	8.8										
		D-4DC	light grey	1.5	ND	ND										
		D-4DD	grey	2	ND	ND										
		D-4DE	grey	2.5	Dark grey	8.9										

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Field Data					Laboratory Analyses												
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West Complex		VR-A-1S A	grey in colour	0.5	Dark brown	4.3	VR-A-1S	VR-A-B_1-COMP	1	1	1	1	1	1	1	1
		VR-A-1S B	grey in colour	1	Brown	4.2										
		VR-A-1S C	saturated & grey in colour	1.5	Brown	4.3										
		VR-A-1S D	saturated & grey in colour	2	Brown	4.3										
		VR-A-1S E	mixture of yellow & grey colour	2.5	Medium brown	4.0										
		VR-A-1S F		3												
		VR-A-4D-A	saturated grey	0.5	Charcoal	7.4	VR-A-4D									
		VR-A-4D-B	saturated light grey	1	Brown	6.9										
		VR-A-4D-C	saturated grey	1.5	Dark brown	7.3										
		VR-A-4D-D	Extreme saturated	2	Brown	6.8										
		VR-A-4D-E	grey saturated	2.5	Brown	7.4										
		VR-B-1SA	grey in colour	0.5	Brown	4.4	VR-B-1S									
		VR-B-1SB	grey in colour	1	Light brown	4.2										
		VR-B-1SC	yellowish	1.5	Medium brown	4.2										
		VR-B-1SD	reddish in colour	2	Light brown	4.3										
		VR-B-1SE	reddish in colour	2.5	ND	ND										
		VR-B-2SA	light yellowish	0.5	Brown	4.3	VR-B-2S									
		VR-B-2SB	light yellowish	1	Medium brown	4.2										
		VR-B-2SC	greyish	1.5	Medium brown	4.3										
		VR-B-2SD	greyish	2	Light brown	4.6										
		VR-B-2SE	light yellowish	2.5	Medium brown	4.6										
		VR-B-3SA	light grey	0.5	Medium brown	4.2	VR-B-3S									
		VR-B-3SB	grey	1	Medium brown	4.4										
		VR-B-3SC	grey	1.5	Deep yellow	4.3										
		VR-B-3SD	grey in colour	2	Deep yellow	4.2										
		VR-B-3SE	yellowish in colour	2.5	Greenish yellow	4.3										

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Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West Complex		VR-B-4DA	grey	0.5	Greenish yellow	3.5	VR-B-4D	VR-A-B_1-COMP	1	1	1	1	1	1	1	1
		VR-B-4DB	grey	1	Medium brown	4.1										
		VR-B-4DC	light grey to yellowish	1.5	Medium brown	4.4										
		VR-B-4DD	grey	2	Brown	4.6										
		VR-B-4DE	light grey	2.5	Medium brown	4.4										
		VR-B-4DF	grey & yellow	3	Greenish yellow	3.7										
		VR-B-4DG	light grey to yellowish	3.5	Deep yellow	3.9										
		VR-B-4DH	grey, light grey to yellowish	4	Brown	4.2										
		VR-B-4DI	light grey	4.5	Brown	4.2										
		VR-B-4DJ	light grey to yellowish	5	Light brown	4.2										
		VR-B-4DK		5.5		4.7										
		VR-B-5DA	yellowish colour & whitish	0.5	ND	ND	VR-B-5D	VR-D-B_2COMP (include VRD-D-1S)	1	0	1	0	1	1	1	
		VR-B-5DB	grey & yellow mixture	1	Medium brown	4.2										
		VR-B-5DC		1.5	Light yellow	4.2										
		VR-B-5DD	light grey	2	Deep yellow	4.3										
		VR-B-5DE	yellow & white	2.5	Dark green yellowish	4.3										
		VR-B-5DF	light grey	3	Greenish yellow	4.4										
		VR-B-5DG	light yellowish	3.5	Medium brown	4.2										
		VR-B-5DH	light grey to yellowish	4	ND	ND										
		VR-B-5DI	light grey	4.5	Medium brown	4.0										
		VR-B-5DJ	light grey	5	Brown	4.0										
		VR-B-5Dk	light grey	5.5	Medium brown	3.8										
		VR-B-6SA	whitish silt with grey & reddish	0.5	Deep yellow	5.2	VR-B-6S									
		VR-B-6SB	yellowish and grey colour	1	Light yellow	4.8										
		VR-B-6SC	light grey	1.5	Deep yellow	4.3										
		VR-B-6SD	yellowish and whitish silt	2	Light yellow	4.4										
		VR-B-6SE	grey in colour	2.5	Light yellow	4.5										

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Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West complex		VR-B-7SA	light grey	0.5	Medium brown	5.8	VR-B-7S	VR-D-B_2COMP (include VRD-D-1S)	1	0	1	0	1	1	1	
		VR-B-7SB	yellowish and grey	1	Greenish yellow	4.8										
		VR-B-7SC	yellowish colour	1.5	Yellow	4.3										
		VR-B-7SD	Dark grey	2	Brown	4.3										
		VR-B-7SE	light yellowish	2.5	Light yellow	4.3										
		VR-B-8SA	grey	0.5	Medium brown	3.7	VR-B-8S									
		VR-B-8SB	D grey & yellowish	1	Deep yellow	4.0										
		VR-B-8SC	grey and yellowish	1.5	Deep yellow	4.5										
		VR-B-8SD	grey	2	Brown	4.5										
		VR-B-8SE	grey	2.5	ND	ND										
		VR-C-1D-A	Light grey	0.5	Medium brown	8.1	VR-C-1D	VR-C_1COMP	1	0	1	0	1	1	1	
		VR-C-1D-B	grey	1	Medium brown	8.0										
		VR-C-1D-C	Grey to yellowish	1.5	Medium brown	8.1										
		VR-C-1D-D	grey	2	Greenish yellow	8.2										
		VR-C-1D-E	yellowish silt	2.5	Light brown	8.1										
		VR-C-1D-F		3												
		VR-C-1D-G		3.5												
		VR-C-1D-H		4	Medium brown	3.7										
		VR-C-2S-A	light grey	0.5	Medium brown	8.6	VR-C-2S									
		VR-C-2S-B	grey	1	Medium brown	8.5										
		VR-C-2S-C	D grey clay	1.5	Medium brown	8.3										
		VR-C-2S-D	grey	2	Medium brown	8.4										
		VR-C-2S-E	grey	2.5	Medium brown	8.4										
		VR-C-3S A	grey	0.5	Medium brown	8.1	VR-C-3S									
		VR-C-3S B	grey	1	Medium brown	8.2										
		VR-C-3S C	grey	1.5	Medium brown	8.3										
		VR-C-3S D	grey	2	Medium brown	8.2										
		VR-C-3S E	grey	2.5	Medium brown	8.3										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West Complex		VR-C-4SA	grey	0.5	Medium brown	8.3	VR-C-4S	VR-C_1COMP	1	0	1	0	1	1	1	
		VR-C-4SB	grey	1	Medium brown	8.3										
		VR-C-4SC	grey clay	1.5	Medium brown	8.3										
		VR-C-4SD	grey	2	Medium brown	8.4										
		VR-C-4SE	grey	2.5	Medium brown	8.3										
		VR-C-5D A	light grey	0.5	Medium brown	8.0	VR-C-5D	VR-C_2COMP	1	0	1	0	1	1	1	
		VR-C-5D B	grey	1	Medium brown	8.4										
		VR-C-5D C	grey	1.5	Medium brown	8.3										
		VR-C-5D D	grey	2	Light brown	8.2										
		VR-C-5D E	grey	2.5	Medium brown	8.1										
		VR-C-6SA	grey	0.5	Brown	8.2	VR-C-6S									
		VR-C-6SB	grey	1	Medium brown	7.3										
		VR-C-6SC	grey	1.5	Medium brown	8.2										
		VR-C-6SD	grey to reddish	2	Brown	8.3										
		VR-C-6SE	grey	2.5	Brown	8.2										
		VR-C-7SA	grey	0.5	Brown	8.2	VR-C-7S									
		VR-C-7SB	grey to dark grey	1	Brown	8.3										
		VR-C-7SC	reddish with grey	1.5	Medium brown	8.3										
		VR-C-7SD	grey	2	Brown	8.2										
		VR-C-7SE	grey	2.5	Brown	8.1										
		VR-C-8S A	grey	0.5	Light brown	8.2	VR-C-8S									
		VR-C-8S B	grey & light grey	1	Medium brown	6.8										
		VR-C-8S C	light grey to yellowish	1.5	Brown	7.7										
		VR-C-8S D		2	Brown	8.0										
		VR-C-8S E	Yellowish brown	2.5	ND	ND										
		VR-D-1SA	yellowish & grey	0.5	Greenish yellow	2.8	VR-D-1S	Combined with VR-D-B_2COMP								
		VR-D-1SB	grey & whitish	1	Medium brown	4.2										
		VR-D-1SC	dark grey	1.5	Greenish yellow	4.4										
		VR-D-1SD	variable colours	2	Medium brown	4.1										
		VR-D-1SE	yellowish	2.5	Greenish yellow	3.9										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West Extension Complex		VR-F-1SA	grey silt	0.5	Light brown	8.1	VR-F-1S	VR-F_1COMP	1	0	1	1	1	1	1	
		VR-F-1SB	grey	1	Light brown	8.2										
		VR-F-1SC	grey	1.5	Light brown	8.1										
		VR-F-1SD	grey	2	Medium brown	8.5										
		VR-F-1SE	grey clay	2.5	Dark green yellowish	8.5										
		VR-F- 2SA	grey	0.5	Light brown	8.4	VR-F- 2S									
		VR-F- 2SB	grey	1	Light brown	8.5										
		VR-F- 2SC	grey	1.5	Light brown	8.4										
		VR-F- 2SD	grey	2	Light brown	8.5										
		VR-F- 2SE	grey	2.5	Medium brown	8.6										
		VR-F-4SA	grey	0.5	Medium brown	8.3	VR-F-4S									
		VR-F-4SB	grey	1	Medium brown	8.3										
		VR-F-4SC	grey	1.5	Medium brown	8.2										
		VR-F-4SD	grey	2	Medium brown	8.3										
		VR-F-4SE	grey	2.5	Medium brown	8.3										
		VR-F-5DA	grey & very light coloured silt	0.5	Light brown	8.0	VR-F-5D									
		VR-F-5DB	grey clay	1	Medium brown	8.3										
		VR-F-5DC	grey	1.5	Medium brown	8.4										
		VR-F-5DD	grey	2	Medium brown	8.5										
		VR-F-5DE	grey	2.5	Light brown	8.2										
		VR-F-6SA	grey	0.5	Medium brown	8.1	VR-F-6S									
		VR-F-6SB	grey	1	Medium brown	8.4										
		VR-F-6SC	grey	1.5	Medium brown	8.3										
		VR-F-6SD	grey	2	Medium brown	8.2										
		VR-F-6SE	grey clay	2.5	Medium brown	8.0										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

Field Data					Laboratory Analyses											
Complex	Dam	Sample No	Field colour description	Depth (m)	Colour	Paste pH	Composite for ABA	Composite for detailed analysis	XRD	XRF	M	SA	AI	WI	PSD	CL
West Extension Complex		VR-F-78SA	water logged area		ND	ND	VR-F-7S	VR-F_2COMP	1	0	1	0	1	1	1	
		VR-F-7SB			ND	ND										
		VR-F-7SC			ND	ND										
		VR-F-7SD			ND	ND										
		VR-F-7SE			ND	ND										
		VR-F-8SA	grey	0.5	Medium brown	9.1	VR-F-8S									
		VR-F-8SB	grey	1	Medium brown	8.5										
		VR-F-8SC	grey	1.5	Medium brown	8.8										
		VR-F-8SD	grey	2	Medium brown	8.6										
		VR-F-8SE	grey	2.5	Medium brown	8.7										
		VR-F-9DA	grey clay	0.5	Medium brown	8.0	VR-F-9D									
		VR-F-9DB	grey clay	1	Dark green yellowish	8.1										
		VR-F-9DC	grey	1.5	Dark green yellowish	8.2										
		VR-F-9DD	grey	2	Medium brown	8.1										
		VR-F-9DE	grey	2.5	Light brown	7.9										
		VR-F-9DF	dark grey to reddish	3	Light brown	8.2										
		VR-F-9DG	grey	3.5	Light brown	8.0										
		VR-F-9DH	grey	4	ND	ND										
		VR-F-9DI	grey clay	4.5	Dark green yellowish	8.2										
		VR-F-9DJ	light greyish silt	5	Medium brown	8.2										
		VR-F-9DK	grey silt	5.5	Medium brown	8.1										
		VR-F-9DM	grey silt	6	Medium brown	8.3										
		VR-F-10SA	grey	0.5	Medium brown	8.1	VR-F-10S									
		VR-F-10SB	grey	1	Medium brown	8.1										
		VR-F-10SC	grey	1.5	Medium brown	8.0										
		VR-F-10SD	grey	2	Medium brown	8.2										
		VR-F-10SE	grey	2.5	Medium brown	8.3										

M = Microscopy; SA = Surface area; AI = Aquaregia + ICP-MS; WI = Water extract + ICP-MS; PSD = Particle size distribution; CL = column leach

APPENDIX E
INPUT DATA (ABA) USED IN VARIOUS EXAMPLES

Location	Dam	ID	Paste pH	AP(kg/t)	C-NP(kg/t)	Latitude	Longitude
West Wits Tailings Dams	**A**	A-1S	8.12	16.91	3.50	-26.4327	27.3482
		A-2D	8.15	14.81	6.25	-26.4324	27.3511
		A-3S	8.52	16.78	6.00	-26.4344	27.3499
		A-4S	8.44	13.13	5.52	-26.4365	27.3485
		A-5D	8.40	15.14	7.00	-26.4371	27.3508
		A-6S	8.32	15.78	4.50	-26.4398	27.3491
		A-7S	8.28	16.91	5.75	-26.4391	27.3523
	B	B-1S	8.18	14.66	5.75	-26.4318	27.3544
		B-2D	8.62	17.22	6.75	-26.4316	27.3563
		B-3S	8.64	10.38	7.25	-26.4343	27.3550
		B-4S	8.64	14.41	6.75	-26.4343	27.3574
		B-5D	8.52	14.22	5.50	-26.4363	27.3564
		B-6S	8.60	23.50	6.75	-26.4386	27.3563
		B-7S	8.35	18.66	0.00	-26.4381	27.3591
	C	C-1S	8.23	14.53	5.54	-26.4298	27.3610
		C-2S	8.20	14.84	4.75	-26.4317	27.3609
		C-3S	8.55	14.22	5.50	-26.4329	27.3627
		C-4D	8.50	17.09	9.00	-26.4307	27.3267
		C-5D	8.07	14.03	5.00	-26.4303	27.3646
	D	D-1S	8.26	18.78	5.75	-26.4277	27.3654
		D-2S	8.33	15.72	7.50	-26.4274	27.3632
		D-3S	8.36	17.5	4.25	-26.4256	27.3649
		D-4D	8.80	17.59	8.75	-26.4261	27.3665
		D-5D	8.75	16.69	4.50	-26.4245	27.3682
	F	F-1S	8.43	10.66	6.91	-26.4228	27.3763
		F-2S	8.30	14.00	5.25	-26.4256	27.3773
		F-3D	8.32	12.59	6.75	-26.4235	27.3801
	M	M-4D	7.98	17.63	8.00	-26.4531	27.4053
		M-5S	8.24	22.28	10.25	-26.4508	27.4073
		M-6S	8.45	26.03	10.00	-26.4505	27.4053
	N	N-2S	8.66	20.5	7.50	-26.4557	27.4096
		N-3S	8.50	21.59	9.75	-26.4542	27.4120
		N-5S	8.50	23.88	7.50	-26.4516	27.4144
		N-6S	8.48	22.38	7.00	-26.4557	27.4170
		N-7D	7.96	20.38	9.75	-26.4497	27.4159
Vaal River Tailing Dams	**A**	VR-A-1S	3.98	11.22	0.00	-26.9353	26.6773
		VR-A-4D	6.10	31.53	2.50	-26.9440	26.6739
	B	VR-B-1S	3.99	31.09	1.25	-26.9384	26.6792
		VR-B-2S	4.01	39.69	1.25	-26.9384	26.6830
		VR-B-3S	4.07	16.39	2.50	-26.9415	26.6792
		VR-B-4D	3.79	16.22	0.00	-26.9415	26.6830
		VR-B-5D	3.72	16.94	0.00	-26.9415	26.6863
		VR-B-6S	4.04	14.13	5.75	-26.9446	26.6757
		VR-B-7S	4.26	17.84	3.50	-26.9446	26.6792
		VR-B-8S	3.87	10.47	6.00	-26.9446	26.6830
	C	VR-C-1D	6.83	20.19	5.00	-26.9322	26.6863
		VR-C-2S	6.28	27.38	5.50	-26.9322	26.6900
		VR-C-3S	6.55	26.16	6.50	-26.9352	26.6830
		VR-C-4S	6.72	32.75	5.50	-26.9352	26.6863
		VR-C-5D	6.85	36.25	7.75	-26.9362	26.6892
		VR-C-6S	7.18	27.97	5.00	-26.9384	26.6863
		VR-C-7S	7.17	25.03	7.00	-26.9384	26.6900
		VR-C-8S	7.20	36.84	5.25	-26.9415	26.6900
	F	VR-F-1S	7.4	41.25	6.75	-26.9290	26.7077
		VR-F-2S	7.45	26.75	7.25	-26.9330	26.7108
		VR-F-4S	7.63	24.72	4.00	-26.9322	26.7108
		VR-F-5D	7.65	25.78	4.50	-26.9331	26.7084
		VR-F-6S	7.78	25.03	4.50	-26.9352	26.7045
		VR-F-8S	8.05	31.41	6.25	-26.9352	26.7108
		VR-F-9D	7.87	23.97	3.75	-26.9372	26.7108
		VR-F-10S	7.76	21.47	4.75	-26.9384	26.7076

APPENDIX F
CAPACITY BUILDING

The project was undertaken in close cooperation with the University of Fort Hare.

Elizabeth Chihobvu was an MSc student in the Department of Geology, Faculty of Science, University of Fort Hare. She used this project as her MSc project and graduated on 8 May 2010.