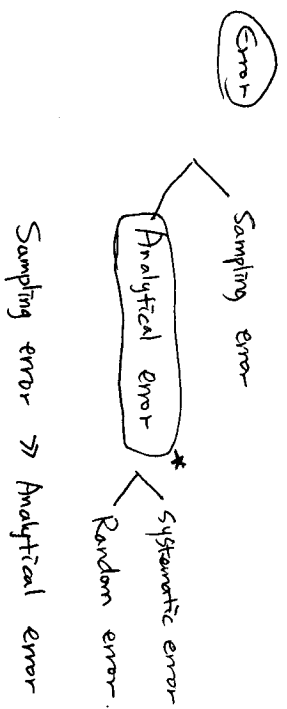


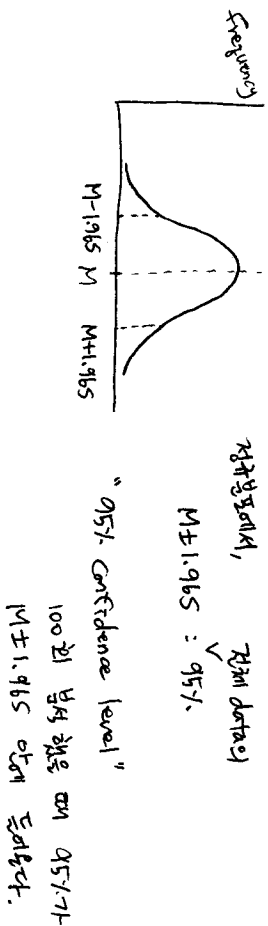
Solids → Geochemical analysis → Quantitative data
↳ reliable



"Quality Control"

Standard (known composition) : $\text{FeO}, \text{Fe}_2\text{O}_3$. NBS (National Bureau of Standard) in USA

ex) Mg in Standard → normal distribution



(Reference Mg) → $\text{FeO}, \text{Fe}_2\text{O}_3$ (-200 mesh) → Mg by AAS

$$\Rightarrow \text{Me} = M \pm 1.96S$$

low reference : background → Mg
high reference

ex) Sn analysis : Background < 3 ppm.

Granite $\frac{\text{Mg}}{\text{Mg}}$ → ref → Sn $\frac{\text{Mg}}{\text{Mg}}$ → 1-2 ppm.
 Ti → granite $\frac{\text{Mg}}{\text{Mg}}$ → ref → Sn $\frac{\text{Mg}}{\text{Mg}}$ → 15-20 ppm.
 $\Rightarrow M \pm 1.96S = \text{Mg}$ $\frac{\text{Mg}}{\text{Mg}}$ $\frac{\text{Mg}}{\text{Mg}}$ $\frac{\text{Mg}}{\text{Mg}}$

Chapter 2

CONTROL PROCEDURES IN GEOCHEMICAL ANALYSIS

M. THOMPSON

INTRODUCTION

Geochemical analysis and data quality

Analytical quality control is essential in geochemistry. It is a characteristic feature of geochemical analysis that large batches of samples, usually of soil or sediment, are required to be analysed with the shortest possible turn-around. Normally the samples are analysed in analytical batches that contain typically between 50 and 200 samples. The analytical methods used are mostly special adaptations of atomic absorption spectrophotometry, spectrography, or colorimetry and the overriding criterion against which these methods are judged is cost-effectiveness. As a result the methods are stripped of all refinements, and many short cuts and approximations are introduced. Generally the labour content is reduced to a minimum and the work is carried out by trained but chemically unqualified staff (Webb and Thompson, 1977). Thus the quality of the analytical data so produced tends to the lowest that can be tolerated without jeopardizing the interpretation. At this level any further deterioration causes loss of information, so a strict control of data quality is required, with a provision for rejection of batches of data if necessary. In spite of this requirement, it is surprising to find that the control procedures in use are often wholly misleading.

Whereas the relatively small number of control procedures that can be employed are in principle well-defined, the effectiveness of any one in practice varies enormously, depending on the amount of attention given to the details of application. Thus it is common to find in use for control purposes methodologies which give over-optimistic results, and are definitely misleading not only to the geochemist who uses the data but also to the analysts themselves. This stems from the uncritical application of sound statistical methods to inappropriately collected data. The use of statistical methods must rest on a detailed knowledge of the basic assumptions involved and the extent to which the data conforms to these assumptions. Statistical methods must be used as an aid to common sense, rather than a substitute

A comprehensive account of the theory of error in geochemical data has been given by Miesch (1967), who discusses both sampling error and analytical error in terms of *overall bias*, *variable bias*, *variable precision*, and *error frequency distribution*; however, he gives no detailed description of practical methods for estimating the various forms of analytical error. In addition Miesch's concepts of variable bias and variable precision in analysis are based on the *location* as the basic grouping of samples, whereas for the purposes of laboratory control, the basic grouping has to be the *analytical batch*.

Formal schemes have been described which are broadly based on Miesch's work, and which employ the analysis of variance to separate the components of sampling error and analytical error in completed data sets (Plant et al., 1975; Miesch, 1976; Garrett, 1969). However, it is important both to the analyst and the geochemical client that the quality of each batch of analysis can be assessed immediately after it is produced, i.e., before it is incorporated into a data set. For this purpose standard reference materials and replicates must be analysed among the samples. This has been done in some major geochemical surveys (e.g. Plant et al., 1975; Miesch, 1976; Webb et al., 1978), but the precautions that are required to ensure realistic results are not described.

Analysis of variance has a further limitation that is usually ignored during its application in geochemistry. This limitation results from the implicit assumption that both sampling error and analytical error are constant over the whole concentration range of the analyte under study. The practical outcome is that an average value of analytical error is extracted, which is usually optimistically biased with respect to the lower concentration ranges.

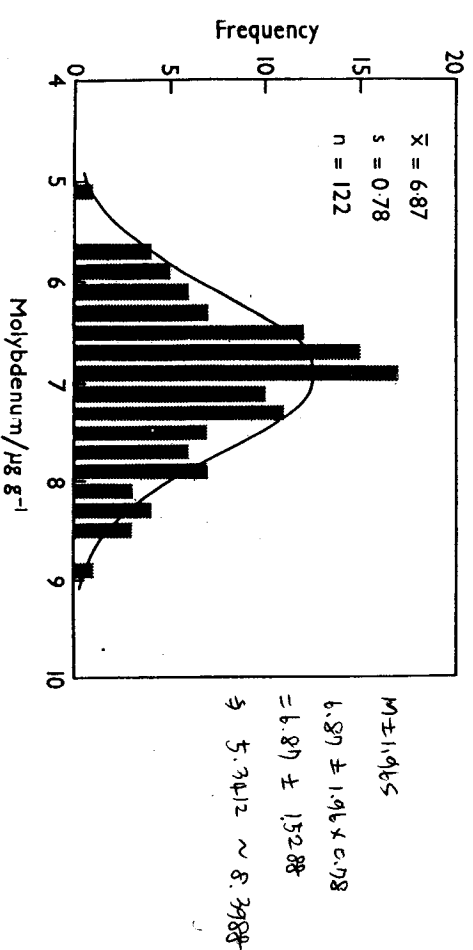


Fig. 2-1. Molybdenum results obtained on a standard sample analysed repeatedly in 122 successive batches. The Normal curve of error with the same parameters (mean, standard deviation and area) is shown superimposed. Analytical error is usually Normally distributed.

Log-transformation of the data is sometimes advocated as a remedy to this problem, on the mistaken grounds that analytical error is proportional to the analyte concentration. This notion has been shown to be incorrect, and quite inconsistent with a meaningful definition of detection limit (Thompson and Howarth, 1976).

Excellent guides to analytical quality control in clinical chemistry (Whitt et al., 1967) and the water industry (Cheseman and Wilson, 1978) describe in detail both the statistical basis of control procedures and the precautions that must be observed. Although some of the comments in these works are specific to their respective fields, most of the subject matter is quite general in application, and hence also suitable for geochemical analysis. The first volume in this Handbook Series (Fletcher, 1981) is, of course, concerned specifically with geochemical analysis.

THE STATISTICAL BASIS OF ANALYTICAL QUALITY CONTROL

Definitions

If a finely divided sample of geological material is analysed repeatedly by a fixed procedure, and if a sufficient number of significant figures is used to record each result, then variable results for the concentration of the analyte are obtained. The variations originate in the combination of all the small errors that are introduced at every stage of the procedure, e.g. weighing, handling, dissolving, measuring volume, etc. When a frequency distribution of the results is plotted, showing the number of results falling into adjacent equal concentration ranges, a histogram of characteristic shape is produced as in Fig. 2-1. This shape is usually indistinguishable from a random sample of values taken from a Gaussian (or Normal) error distribution, which is shown superimposed. Thus we can describe the variability in our analysis in terms of the two parameters of the probability distribution, i.e., the mean and standard deviation.

The spread of the results is quantified by the estimated standard deviation given by the formula:

$$s = \sqrt{\frac{\sum (\bar{x} - x_i)^2}{n-1}} = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2/n}{n-1}}$$

where x_i are the successive values of the n observations. This is often called the *repeatability* of the analysis. The term *reproducibility* is also used, sometimes in a special sense to indicate the variation between different laboratories when analysing the same sample by a fixed procedure.

The central tendency of the results is estimated by the arithmetic mean

given by the formula:

$$\bar{x} = \sum x_i/n$$

The term *accuracy* is used to denote the extent to which \bar{x} approaches the true concentration of the analyte, and the term *bias* for the difference between \bar{x} and the true value. Strictly, the true value cannot be ascertained. The best we can do is to produce a consensus of the estimates made by a variety of analytical methods based on different physical principles, each one given a weighting appropriate to the limitations of the method. This is the procedure employed by the agencies which set up International Standards, i.e., various national geological surveys. The result so produced is called the "preferred value", the "usable value", or the "accepted" value rather than the true value.

The Normal probability distribution has the useful property that the proportion of observations falling within given ranges (i.e., units of standard deviation above and below the mean) can be obtained from a standard table. This is illustrated in Fig. 2-2. Commonly used ranges are given in Table 2-1. For a finite number of observations there will be chance variations in the proportions falling within these ranges. This property of the normal distribution allows us to set up confidence boundaries for an analytical result. In Fig. 2-3 some of the repetitive results used in Fig. 2-1 are plotted sequentially instead of in a histogram. Confidence boundaries are inserted at $(\bar{x} + 1.96s)$ and $(\bar{x} - 1.96s)$ (95% confidence limits) to produce a control chart. An average of 5% of the results should fall "out of bounds" but in this case a higher proportion do so. It is generally agreed to be a sensible precaution to reject results falling out of these bounds, as possibly resulting from a mistake

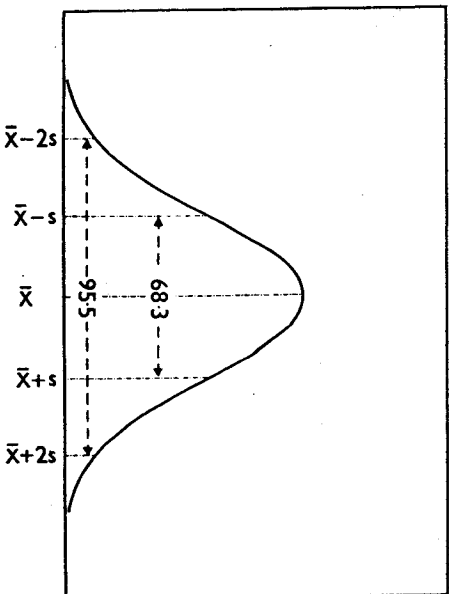


Fig. 2-2. The Normal curve of error showing that 68.3% of the area (or observations) falls within the range $\bar{x} \pm 1s$ 195.5% falls within the range $\bar{x} \pm 2s$.

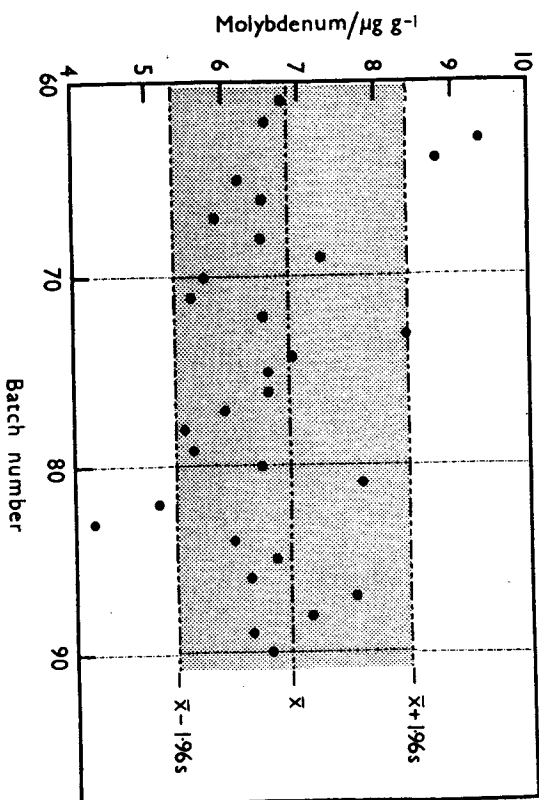


Fig. 2-3. Molybdenum results plotted as part of a control chart with 95% confidence limits. There are four results falling outside the limits which represent batches which should be considered for rejection. The general tendency in this part of the chart is for the results to be slightly low.

in the execution of the analytical procedure, rather than a random variation arising within the procedure. Naturally a small number of valid results will also be rejected, and some spurious data accepted. Confidence boundaries can be set at any convenient level, but the 95% confidence limit is generally regarded as being a suitable compromise between wrongful acceptance of false data and unnecessary rejection of valid data.

When comparing analytical methods, it is often more convenient to consider relative repeatability rather than the absolute value, because the concentrations of an analyte (and hence also the standard deviation of its determination) can vary over many orders of magnitude. There are several related measures of relative variability in current use, namely *coefficient of*

TABLE 2-1

Proportion of observations falling in ranges of the Normal distribution	
Range	Proportion
$\bar{x} \pm s$	0.6826
$\bar{x} \pm 1.96s$	0.9500
$\bar{x} \pm 2s$	0.9546
$\bar{x} \pm 3s$	0.9974

s = standard deviation

variation ($v = (s/\bar{x}) \times 100\%$), *relative standard deviation* ($\text{rsd} = s/\bar{x}$), and *precision*. Precision is usually defined in geochemistry as:

$$P = (2s/\bar{x}) \times 100\%$$

i.e., indicating relative to the concentration of the analyte the range in which approximately 95% of the observations fall. It should be noted that this definition of precision differs from the more usual concept in which high precision is the same as low variance. In addition it must not be confused with the term precision as used in mathematical statistics.

Deviations from the normal distribution

Whereas the definitions of \bar{x} and s are valid regardless of the frequency distribution of x , conclusions as to the numbers of observations falling within ranges defined by s and \bar{x} are valid only for the Normal frequency distribution. Under the conditions given above, a Normal distribution would usually be expected, but there are certain factors that can give rise to other distributions. Some of these produce inherently skewed forms. The most important occurs when the analyte is concentrated exclusively within particles of a single phase which itself forms a small proportion of the sample. Depending on the average particle size relative to the subsample size, there may be significant subsampling variation in the material taken for analysis. An extreme example is shown in Fig. 2-4 which shows results obtained when 15-mg subsamples of a stream sediment of average particle size about 100 μm were analysed spectrographically for tin, present as the

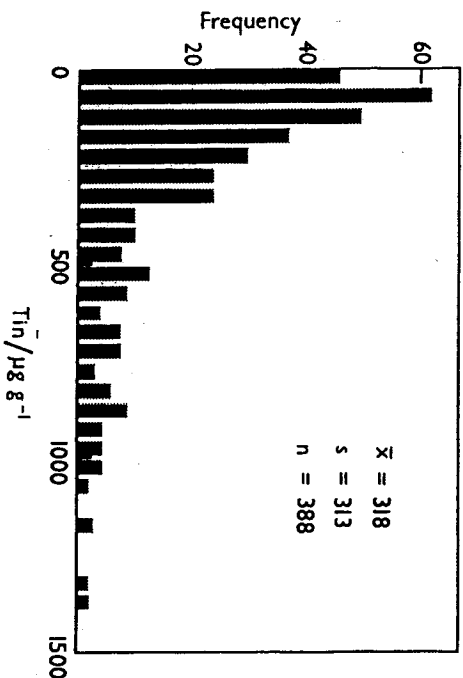


Fig. 2-4. Tin results obtained by the spectrographic analysis of a standard sample in 388 successive batches. Extreme deviation from the Normal curve of error is shown because of the small sample size, \bar{x} = particle size, and segregation of the tin in cassiterite.

resistant mineral cassiterite. This situation should be avoided wherever possible in geochemical analysis by fine grinding of the sample and by increasing the subsample size.

Another important kind of non-Normal behaviour stems from data recording practices. When data are recorded on a discontinuous scale, e.g. as in a popular method for arsenic (Stanton, 1976) which allows only the values 0 ppm, 0.4 ppm, 0.8 ppm, 1.2 ppm, etc., to be recorded, misleading conclusions can be drawn if Normal (parametric) statistics are employed. For instance, if analysis repeatedly produced a result of 4 ppm, then the false conclusion might be drawn that the precision was zero. Excessive rounding of parametric data will have the same effect. It is good practice, if at all possible, to *retain* rather than delete the first significant figure containing uncertainty.

Another practice that can lead to distorted distributions is the indiscriminate censoring of observations falling below an arbitrary limit, usually the detection limit or zero. Analysts are invariably reluctant to record a negative observation because of the impossibility of the existence of negative concentration. However, a clear distinction must be made between the obviously absurd idea of *negative concentration*, and a *negative observation* which is an estimate of a true (positive) concentration, to which confidence limits may be assigned. This idea is illustrated in Fig. 2-5. Fig. 2-5A shows the distribution of results with an unbiased mean of 8 ppm and a standard deviation of 2 ppm. Very few results fall below ($\bar{x} - 3s$) = 2 ppm. If a sample is substituted which has a concentration of 2 ppm but the same standard deviation then ($\bar{x} - s$) = 0 and a substantial proportion of the results fall below zero, as shown in Fig. 2-5B. Each result, whichever side of zero it falls, is an *estimate* of + 2 ppm, albeit produced by an unsuitable analytical method.

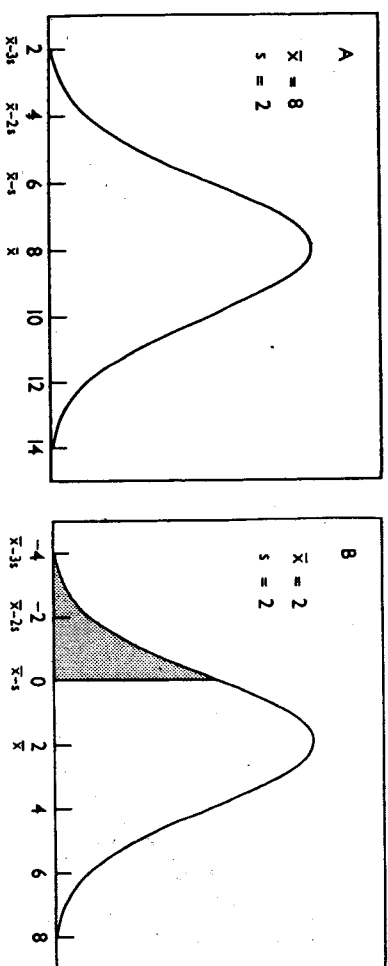


Fig. 2-5. A. The theoretical distribution of data resulting from an unbiased method with standard deviation of 2 ppm being applied to a sample containing 8 ppm of analyte; very few results fall below 2 ppm. B. Results from the same method applied to a sample containing 2 ppm; a substantial proportion (15.8%) of results fall below zero.

It may frequently be politic for the analyst to censor negative results in data produced for a client. However, in control samples, and in any attempts to measure precision near the zero point, *negative observations must be retained*. The same principle applies to the recording of data below the detection limit.

A different type of non-Normal distribution results from an occasional unnoticed deviation from the correct analytical procedure, for instance if two aliquots of a reagent are added to a particular sample instead of the correct amount of one aliquot. This can result in a wildly incorrect outlying result, commonly called a "flier" which is really an observation belonging to a different population. There are methods for detecting fliers, for example that of Harvey (1974). An excellent method for avoiding the distorting effect of fliers when estimating central tendency is to use the *median* (the central result) rather than the arithmetic mean. The median is quite unaffected by a small proportion of fliers, which is often present in "real" data sets as opposed to theoretical distributions. For the quantification of variability, corresponding statistics which eliminate the effect of outliers are the *interdecile range* ($\bar{x} \pm 1.28s$) or the *interquartile range* ($\bar{x} \pm 0.67s$). The total range, however, is very sensitive to outliers.

Variations of accuracy and precision

In geochemical analysis we encounter ranges of analyte concentration that can span several orders of magnitude. Our definitions of accuracy and precision so far refer only to the repetitive analysis of a particular sample, i.e., at a fixed true concentration. It would be more useful if we could define the accuracy and precision obtained on a suite of samples with a wide range of concentrations of the analyte. Often in the analytical literature the precision of a method is quoted without any reference to the concentration range of the analyte on the grounds that precision (as opposed to standard deviation) is invariant with changes of concentration. This can be quite misleading because precision as defined in this work may vary substantially in a set of samples if the concentration range is large (Thompson and Howarth, 1976). In such cases the relationship between the standard deviation of the measurement (s_c) and the concentration measured (c) can usually be expressed by a linear equation of the form:

$$s_c = s_0 + kc$$

where s_0 is the standard deviation at zero concentration and k is a constant. By substituting our definition of precision ($p = 200s_c/c$) into this equation we obtain:

$$p = 200s_0/c + k'$$

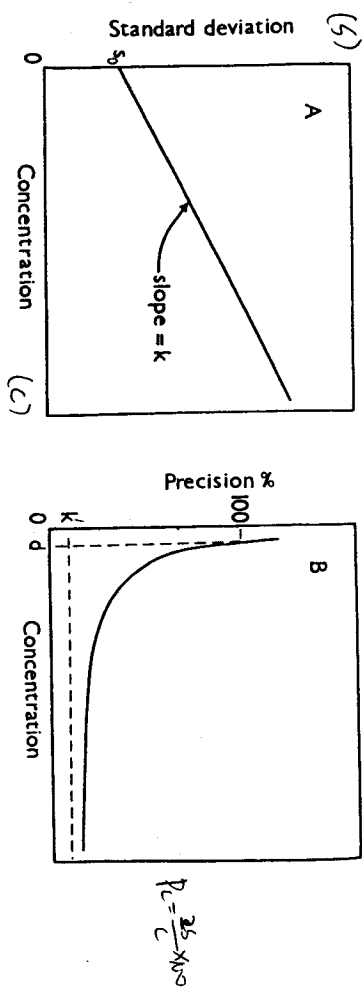


Fig. 2-6. A. The linear relationship between standard deviation and concentration which can often be observed in a suite of similar samples. Note the finite intercept s_0 . B. The same relationship expressed as precision. Precision falls from 100% at the detection limit asymptotically towards the value k' ($= 200k$) at higher concentrations.

where $k' = 200k$. Precision is thus a hyperbolic function of concentration. The two functions p and s_c are illustrated in Fig. 2-6. Precision falls asymptotically from high values at low concentrations towards a constant value (k') at high concentrations. At the point where the concentration is equal to 100%, twice the standard deviation is equal to the concentration which is measured. This point is usually regarded as the lowest concentration which can be meaningfully estimated by a single determination, and is called the *detection limit*. It is instructive to note that when the analyte concentration equals the detection limit, an average of 1 in 40 observations will fall below zero.

Because precision varies with concentration, the range must be specified if a single value is quoted. Unqualified values of precision are usually misleading. In addition it must be noted that the precision depends to some extent on the nature of the samples, and not just on the analytical procedure.

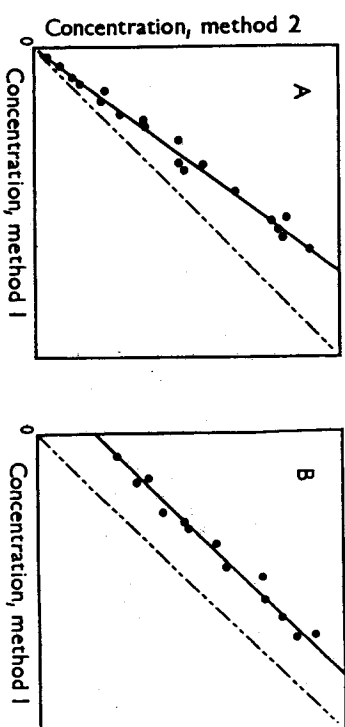


Fig. 2-7. A. A batch of samples analysed by two methods showing a constant factor (a rotational bias) between them. B. A batch of samples analysed by two methods showing a constant difference (translational bias) between them.

Thus statements of precision refer strictly to an analytical "system" consisting of a defined analytical procedure and a definite type of sample.

Accuracy also may vary with concentration. Generally the relative accuracy of two analytical methods (or two batches analysed by the same method) can vary in two distinct ways, or a combination of the two. The first type, shown in Fig. 2-7A stems from a constant factor relating results found by the two methods (a *rotational bias*). The second kind is illustrated in Fig. 2-7B and consists of a constant difference (a *translational bias*) between the methods (or batches) over the concentration range. Again, accuracy depends on the sample type. For instance an atomic absorption spectrophotometry (AAS) method which is accurate for the determination of cadmium in sandstone may be wildly inaccurate for its determination in limestone, because of the interference due to the presence of calcium.

LABORATORY CONTROL PROCEDURES

Factors that need to be controlled

In a batch analytical procedure there are essentially three factors that need to be controlled.

Within-batch variations. These stem from the small uncontrolled variations that arise at every stage of the analytical procedure. If these occur purely at random throughout the batch they can be quantified simply as within-batch precision. If there are *systematic* changes within the batch, they may become apparent as a change in accuracy, in the form of a drift, a periodic variation, or a discontinuity. These features are demonstrated in Fig. 2-8A—D which may be regarded as results from within an analytical batch consisting entirely of subsamples of a single standard material. Where present, these effects will increase the apparent within-batch variation.

Between-batch variations. These are variations from the mean result that are present systematically in every sample in the batch, in addition to the within-batch features. They result from changes that affect every member of the batch in the same manner (e.g. changes due to the use of a new standard calibrating solution, errors in sensitivity control setting of an instrument, or use of a different instrument, or analyst, in successive batches. These variations may be regarded as changes in accuracy between the batches, or alternatively as an additional source of variance, the between-batch precision. The between-batch precision is an important source of analytical variation, and it is sometimes significantly greater than the within-batch precision. Between-batch variation can contain both random and systematic compo-

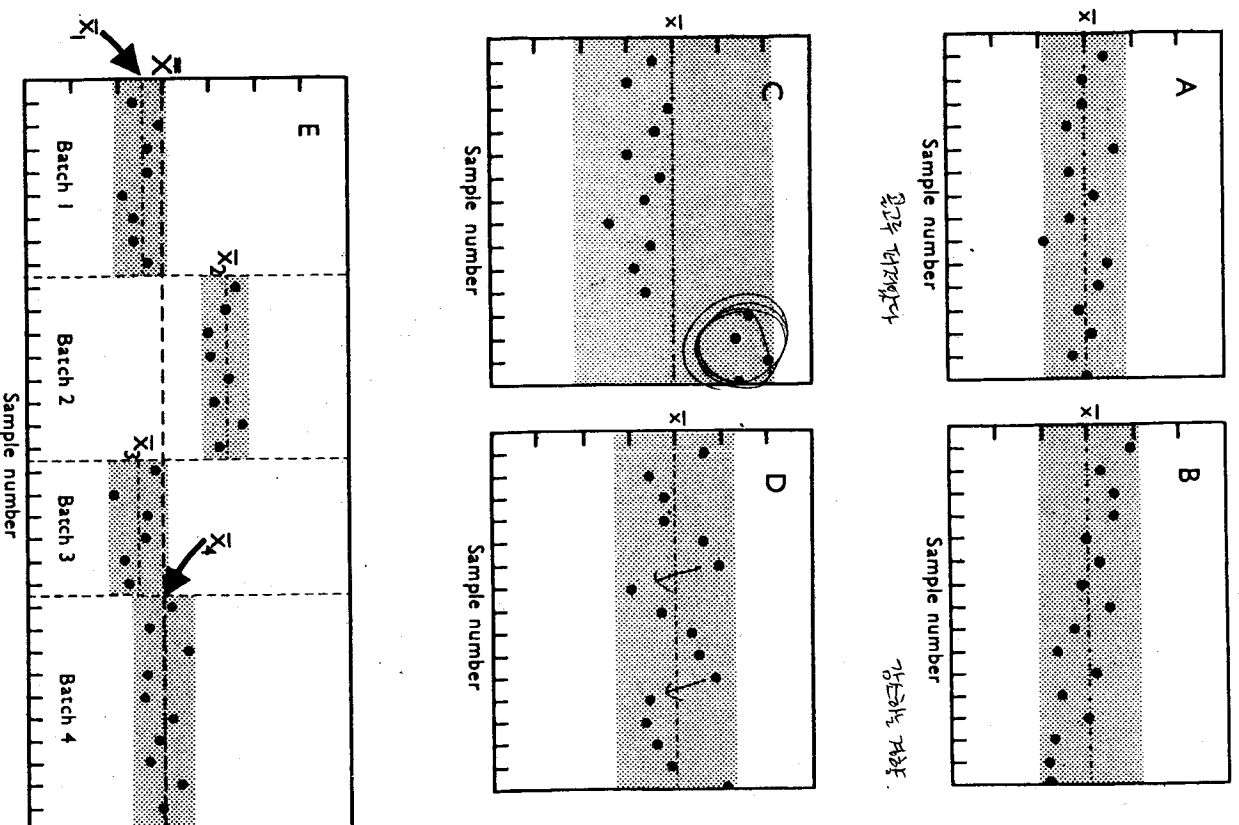


Fig. 2-8. Control charts showing various features. A. Within-batch variation of a random nature only. B. Within-batch variation containing both random fluctuations and a trend or "drift". C, D. Within-batch variation showing in addition to the random fluctuations a discontinuity and periodic fluctuations respectively. E. Within-batch and between-batch variations, showing the batch means ($\bar{x}_1 - \bar{x}_4$) and the grand mean (\bar{x}).

nents, of the same type as found in within-batch variation. Between-batch variation is illustrated in Fig. 2-8E.

Overall accuracy. This is the extent to which the multi-batch job as a whole is giving the correct results. It is demonstrated in Fig. 2-8E as the bias between the grand mean value (\bar{X}) and the true value for the material analysed. It is often stated that absolute accuracy is of no concern in exploration geochemistry. Whereas it is true that within a given area it is the relative or differential concentrations which form a distinct pattern, it is still necessary to have a check on accuracy when comparing the results obtained for two adjacent areas, or perhaps data produced by differing methods of analysis or sample digestion.

Control methods that utilize standards

An obvious and popular method of quality control consists of the insertion into each batch of samples of several portions of a reference material or "standard" which is then analysed just as if it were a normal sample. In principle, if the number of standards is sufficient, all of the effects illustrated in Fig. 2-8 may be detected and estimated. In practice, selecting a near-optimal strategy for carrying this out is difficult. There are many pitfalls in a simplistic approach to this problem, and if they are ignored, misleading results are likely to be obtained. The main problem is that of ensuring that the behaviour of the standard truly represents the behaviour of the samples. Some factors to be considered in the selection and use of standards are considered below.

Randomization. The standards should ideally be inserted at random positions within the analytical batch. If they are all together at the beginning or end of the batch, then estimates of precision will tend to be optimistically biased, and any systematic effects will be missed. If the standards are evenly spaced throughout the batch, then variance may be underestimated if the frequency of the standards corresponds with a periodic variation.

Compositional requirements. The standards used should be of a type similar to the samples, in terms both of bulk composition and mineralogical make-up, as both accuracy and precision for the determination of a trace analyte can be markedly affected by the major constituents present. This may be difficult to put into effect in the laboratory control scheme when the lithology of the incoming samples may be quite unknown.

State of comminution. The state of physical reduction in particle size should ideally be the same for the samples and the standards. For instance if the samples consisted of natural material passing through a 200- μ m sieve, the

standards should be prepared in the same manner. Fine grinding of the standard, although desirable on other grounds (see below), would tend to increase the effectiveness of chemical attack and improve the precision at various stages of the analysis, and so give an optimistically-biased result.

Concentration of the analyte. The whole concentration range of the analyte in the samples, or at least critical levels, should be represented by the standards. Preferably there should be at least standards corresponding to background, threshold, and anomalous levels in the samples.

Standard availability and stability. The standard must be available in large amounts of homogeneous material, with no tendency towards segregation of particular minerals. Homogeneity can be ensured by fine grinding, but this practice may be inconsistent with the third factor stated above. Where there is conflict between these two factors, homogeneity is the more important, as realistic estimates of precision can be made by other methods, i.e., duplication. The standards must also be indefinitely stable with respect to the concentration of the analyte.

Anonymity. At the time of analysis the standards should not be identifiable to the analyst, to obviate the otherwise unavoidable human tendency to give special attention to the analysis of the standards, or to repeat the analysis if the expected result is not obtained at the first attempt.

Proportion of standards in the batch. The cost of analysis per sample as well as the effectiveness of the control system increases with the proportion of standards among the samples. This must be weighed against (1) the probability and cost of unnecessarily rejecting a batch of good data, and (2) the outcome of wrongly accepting spurious data. These factors are difficult to assess quantitatively, but in practice a proportion of between 5 and 10% standards among the samples is generally used. This sets an upper limit on the number of compositional types and concentration ranges that can be represented.

Number of repetitions of each standard. A reasonable number of repetitions of each standard in a batch is required so that the detection of the various features illustrated in Fig. 2-8 can be attempted by statistical tests. Again a compromise is required between the number of repetitions of each standard and the number of different standards, if a fixed proportion is used.

International standards. Reference standards produced by bodies such as the U.S. Geological Survey, which have compositions validated by large-scale international collaborative analysis, are documented by Abhey (1975). These standards do not have wide application in quality control for exploration

analysis because (1) they are too precious for the large-scale usage required, and (2) they tend to be selected because they represent extreme types of rock rather than the sample types usually required (soil and sediment). However, the U.S. Geological Survey, in combination with the Association of Exploration Geochemists, has produced a set of six standards that are exploration oriented (Allcott and Lakin, 1975, 1978) to provide a useful cross-check on accuracy.

The "statistical series" method

This method of quality control by the addition of standard materials to the batch of samples was devised by Craven (1954) but has several defects which were pointed out by Stern (1959). However, it has enjoyed wide popularity in exploration analysis, and the original method of calculating precision has been simplified (James, 1970). Working instructions for the method are given by Stanton (1976).

In brief, the method is based on two standards, one having the analyte element at low background concentration and the other with the analyte at a level of two or three times the threshold. Eight mixtures of the two materials are prepared in the weight ratios 9:1, 8:2, 7:3, 6:4, 4:6, 3:7, 2:8, 1:9, giving ten standards in all. These standards are inserted in random positions in the analytical batch and are preferably analysed "blind". The results obtained in the mixtures are related by regression to the proportion of the high standard in them, as in Fig. 2-9. The solution of the normal equations is somewhat

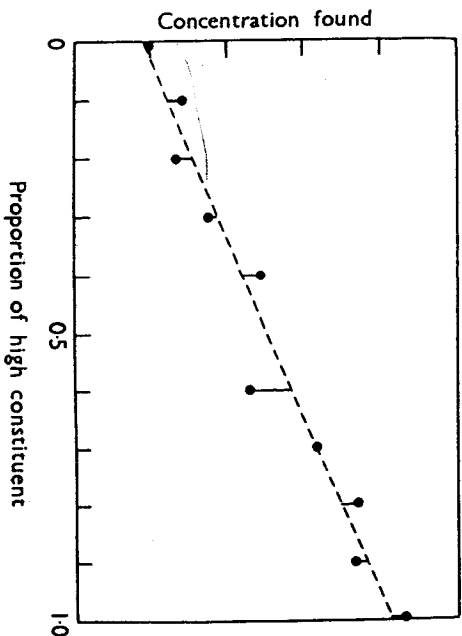


Fig. 2-9. The "statistical series" method. The concentrations determined in the ten members of the series are regressed against the proportion of the high constituent of each mixture. The standard deviation of the differences between the values determined (dots) and the regression line is calculated and used as a measure of variation within the concentration range spanned by the low and high constituents.

simplified because of the values chosen for the proportions in the mixtures. The statistic calculated is the "standard error of the difference", which is in effect the standard deviation of the distances of the determined values from the calculated regression line. This is converted into a precision figure in the usual way by dividing by the mean concentration of the high and low constituents, and multiplying by 200.

The main drawback of this method is in the obtaining of a mean precision for the concentration range. This has the unfortunate effect of underestimating the precision at the background level (as can be seen from Fig. 2-6) where the great majority of the sample results will fall. This is particularly serious if, as is often the case in exploration trace analysis, the low background level is close to the detection limit for the analyte. Practical problems associated with the method are the inordinate time required to prepare and to mix adequately the two constituents in their various ratios, and the somewhat time-consuming calculations required to obtain a result. In addition, the extensive grinding required for good mixing ensures that the standards are much more finely divided than the samples, which tends to optimistically bias the result. All of these problems are avoided by the use of a simple strategy described in the next section.

A scheme for the use of standards

The scheme described below is a simple compromise between the conflicting requirements discussed above:

- Select two standards of appropriate material with the concentration of the analyte at background and threshold levels respectively.
- Insert the standards into each batch of samples at random positions at an average rate of one standard per 10 samples, or at least five times each. This can be conveniently done at the time of weighing.
- For each standard calculate the mean and standard deviation of the results obtained in the batch and plot these on control charts. (When setting up a control chart for a statistic such as the batch mean, it is not possible to calculate the confidence limits from within-batch data. It should be clear from Fig. 2-8E that the standard deviation of the batch means is not equal either to the standard deviation of the individual results within a batch or to the standard error of the batch mean. The limits must be separately derived from the mean and standard deviation of the batch means. Provisional values of these can be calculated from the results from the first few batches, and subsequently refined as data for more batches become available.)
- Consider for rejection all batches where the statistic falls outside its 95% control limit. Additional confidence for rejection is appropriate if both standards fall simultaneously out of bounds. At this stage it is worth-

while to examine the individual results on the standards in case of outliers or systematic effects, and to back up the decision with confirmatory evidence if possible.

It is important to remember that a batch difference as indicated by standards may be *significant* but not *important* in terms of the overall geochemical requirement. For example, a batch bias which changes the concentration values obtained by 10% or less (relative) may well be significant (i.e., outside the 95% confidence limits), but would hardly be likely to affect interpretation in a stream sediment survey, and should not be rejected in this case. No general guideline can be given for this, however. In many cases it is more suitable to set rejection limits *ab initio* on the basis of user requirements. This certainly has to be done when a standard is first used and no information on its normal range is available.

A simpler approach to interpretation of the standard data, which involves no calculations, is to plot all the values individually as in Fig. 2-8E. Visual inspection of the range gives a rapid indication of the within-batch precision, systematic effects and the presence of fliers, while the median value for the batch can be subjected to a rejection test for between-batch precision.

Methods that do not require special standards

Most of the problems associated with ensuring that the standards are truly representative of the samples can be avoided by the use of control methods in which the results on the samples themselves form the control system. Only the requirements for randomization and anonymity remain. However, these methods are less informative and more time-consuming to apply.

Duplication. The analysis of a sample twice and comparison of the two results has long been a method by which analysts have gauged the repeatability of their analysis. Quantitative information on precision can be obtained from duplicated analyses in properly designed experiments (Thompson and Howarth, 1973, 1976). If a sufficient number (> 50) of duplicated observations are available, the variation of standard deviation over the concentration range of the analyte can be found. The valid range for this estimate is approximately the interdecile range of concentration. If a smaller number of duplicates are obtained (less than about 50) the precision can be rapidly tested against an empirical standard of precision defined by user requirements, by means of a special control chart, an example of which is shown in Fig. 2-10. A complete account of these methods is described by Thompson and Howarth (1978). Brief working instructions for the case when $n > 50$ are given here:

— From the corresponding pairs of analytical results (x_i, y_i) calculate the mean result $(x_i + y_i)/2$ and the absolute difference $|x_i - y_i|$.

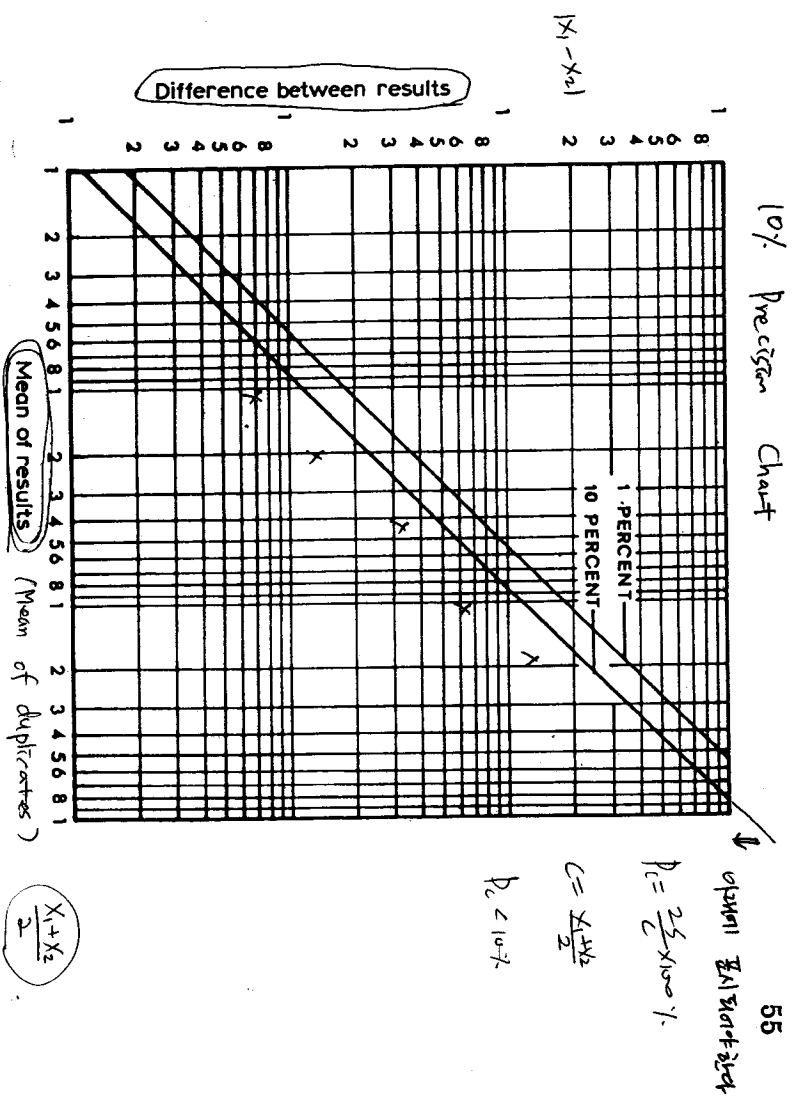


Fig. 2-10. A control chart, using duplicates, for 10% precision. In an analytical system exhibiting 10% precision, the results will be distributed on the chart such that on average 90% fall below the lower line, and 99% below the upper line.

— Arrange the results in increasing order of the mean results, keeping the correspondence between the means and the differences.

— From the first 11 results obtain the mean of the means and the median of the absolute differences.

— Repeat this procedure for each group of 11 results, ignoring any remainder less than 11.

— Perform a linear regression of the medians on the means, and multiply the intercept, coefficient, and their standard errors by 1.048. The intercept and coefficient are estimates of s_0 and k respectively, as defined above.

This procedure is illustrated in Fig. 2-11. A computer program that carries out these operations has been published (Thompson, 1978). The factor 1.048 is derived from the relationship between standard deviation and median absolute difference between duplicates. The group size of 11 results can be varied, but has been empirically found to be near optimal.

For a realistic estimate of precision the position of the two duplicate subsamples in the sample sequence must be completely randomized. The common practice of analysing duplicate pairs consecutively will be optimistically-

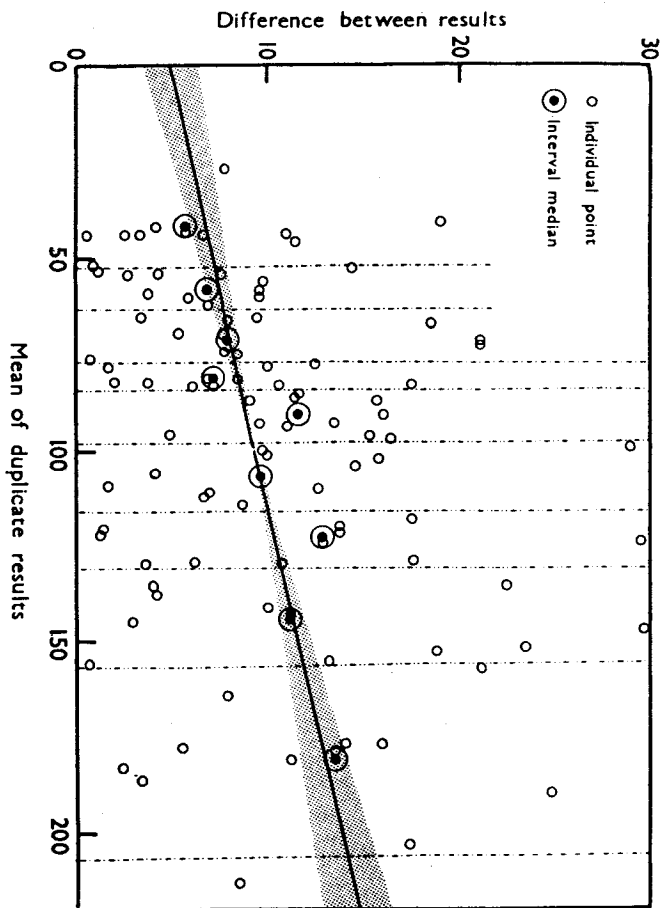


Fig. 2-11. The estimation of s_0 and k from duplicated analysis. The individual results are open circles. The group medians are full circles. The regression line is shown with its 95% confidence limits.

biased estimates. Also the two subsamples have to be taken independently through the whole analytical procedure. If only a fraction of the samples is duplicated, these must be selected at random. Because geochemical samples tend to become available in discrete batches, randomization can be carried out only within these batches, so duplication is primarily a method for testing within-batch precision. Where all the samples in a project are available before analysis begins a completely randomized scheme can be devised (Howarth, 1977). This enables overall precision to be estimated, but provides no immediate information for the analyst as to whether particular batches of data should be rejected.

Between-batch precision. In a completely randomized scheme, significant changes in accuracy between batches can be detected as variations in the mean value of all the samples in each batch. This is most clearly recognisable where the normal range of the analyte is small, as in the example cited by Plant et al. (1975), but the method gives surprisingly good results even when the concentration range is wide. This can be a useful check on the interpretation of standard results in dubious cases. However, randomization of the whole sample set is absolutely necessary, otherwise differences between batches may reflect regional differences in geochemistry rather than system-

atic changes of accuracy. This method cannot provide information on batch accuracy at different concentration ranges, but gives a kind of average value.

Overall accuracy. The overall accuracy of a method can be tested by the re-analysis of a small proportion of the samples, selected at random, by means of a separate method of recognised accuracy. This "referee" method will necessarily be more time-consuming and expensive than the working method. The results obtained by the two methods can be plotted as in Fig. 2-7. This type of comparison will have been carried out at the development stage of the working method, but it is good practice to test the accuracy periodically, because gradual changes in technique are evolved by the analysts during the long-term use of an analytical method, even where they are not deliberately introduced. An additional method of checking overall accuracy is the occasional insertion of international reference standards into the analytical batches.

Special problems in multi-element analysis

Analytical methods where many elements are determined simultaneously by a process such as optical emission spectrometry, present special difficulties in data quality control. Firstly, it is difficult to find materials to use as standards in which all of the analytes of interest are present at useful concentrations. Use of synthetic standards is not generally successful because they cannot usually be made in a chemical and physical form which adequately represents the samples. Secondly, it is a time-consuming exercise to update and interpret a large number of separate control charts.

The most important difficulty, however, stems from the combinative aspect of the variation. If there are n analytes and the error on each is independent, the probability that all the results will fall within their respective 95% confidence limits is $(0.95)^n$. If $n = 20$ this probability is equal to $(0.95)^{20}$ or 0.3585. In other words there will be one or more analytes out of bounds in 64.15% of all batches, which on a simplistic interpretation suggests that about two-thirds of all batches should be rejected even when nothing is actually wrong with the sample data. In practice there will normally be both correlated error, e.g. due to variations in excitation which affect all the analytes simultaneously, and independent error, which is due to variations in separate measurement channels.

This problem does not seem to have been dealt with satisfactorily to date. A provisionally acceptable method may be to widen the control limits for multi-element analysis to $\bar{x} \pm 3s$. This would have the effect of reducing the probability of false batch rejection for purely independent error to 1 - $(0.9974)^n$ which is 0.51 when $n = 20$. A simultaneous out-of-bounds condition for many elements, due most probably to a correlated variation, would of course add considerable weight to the hypothesis that the system was truly out of control.

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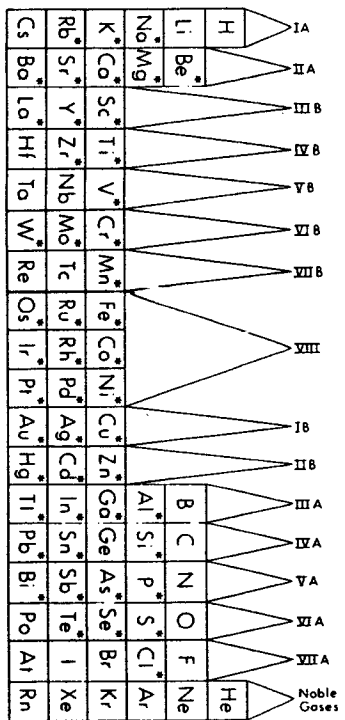


Figure 1.1. Periodic table of the elements. Elements covered by procedures in this book.

Table 1.8
Some Common Geochemical Associations of Elements*

Group	Association
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Generally associated elements	K-Rb Ca-Sr Al-Ga Si-Ge Zr-Hf Nb-Ta Rare earths - La - Y Pt-Ru-Rh-Pd-Os-Ir (PGE)
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Plutonic rocks
General association (lithophile elements)

Specific association	Si-K-Na Al-Na-Zr-Ti-Nb-Ta-F-P-rare earths Fe-Mg-Ti-V Mg-Fe-Cr-Ni-Co Li-Be-B-Rb-Cs-rare earths-Nb-Ta-U-Th Mo-W-Sn K-Ba-Pb K-Na-Rb-Cs-Tl Fe-Mg-Mn-Cu-Zn-Co-Ni
Sedimentary rocks	Fe-As-Co-Ni-Se Mn-As-Ba-Co-Mo-Ni-V-Zn P-Ag-Mo-Pb-F-U Al-Ag-As-Au-Bi-Cd-Mo-Ni-Pb-Sb-V-Zn

*Source: Rees, 12-14.
*For additional association in ore bodies see Table 1.9.

* Analytical method for geochemical exploration (Khanam)

Table 1.9
Associated Elements (Pathfinders) Useful in Ore Typing

Type of deposit	Major components	Associated elements
Magmatic deposits		
Chromite ores (Bushveld)	Cr	Ni, Fe, Mg
Layered magnetite (Bushveld)	Fe	V, Ti, P
Immiscible Cu-Ni-sulfide (Sudbury)	Cu, Ni, S	Pt, Co, As, Au
Pt-Ni-Cu in layered intrusion (Bushveld)	Pt, Ni, Cu	Cr, Co, S
Immiscible Fe-Ti-oxide (Allard Lake)	Fe, Ti	P
Nb-Ta carbonate (Oka)	Nb, Ta	Na, Zr, P
Rare-metal pegmatite	Be, Li, Cs, Rb	B, U, Th rare earths
Hydrothermal deposits		
Porphyry copper (Bingham)	Cu, S	Mo, Au, Ag, Re, As, Pb, Zn, K
Porphyry molybdenum (Climax)	Mo, S	W, Sn, F, Cu
Skarn-magnetite (Iron Springs)	Fe	Cu, Co, S
Skarn-Cu (Yerington)	Cu, Fe, S	Au, Ag
Skarn-Pb-Zn (Harover)	Pb, Zn, S	Cu, Co
Skarn-W-Mo-Sn (Bishop)	W, Mo, Sn	F, S, Cu, Be, Bi
Base-metal veins	Pb, Zn, Cu, S	Ag, Au, As, Sb, Mn
Sn-W greisens	Sn, W	Cu, Mo, Bi, Li, Rb, Si, Cs, Re, F, B
Sr-sulfide vein	Sn, S	Cu, Pb, Zn, Ag, Sb
Co-Ni-Ag vein (cobalt)	Co, Ni, Ag, S	As, Sb, Bi, U
"Epithermal" precious metal	Au, Ag	Sb, As, Hg, Te, Se, S, U
Mercury	Hg, S	Sb, As
Uranium vein	U	Mo, Pb, F
Copper in basalt (Lake Superior type)	Cu	Ag, As, S
Volcanogenic massive-sulfide Cu	Cu, S	Zn, Au
Volcanogenic massive-sulfide Zn-Cu-Pb	Zn, Pb, Cu, S	Ag, Ba, Au, As
Au-As-rich Fe formation	Au, As, S	Sb
Mississippi Valley Pb-Zn	Zn, Pb, S	Ba, F, Cd, Cu, Ni, Co, Hg
Mississippi Valley fluoride	F	Ba, Pb, Zn
Sandstone-type U	U	Se, Mo, V, Cu, Pb
Red-bed Cu	Cu, S	Ag, Pb
Calcrete U	U	V
Sedimentary types		
Copper shale (Kupferschiefer)	Cu, S	Ag, Zn, Pb, Co, Ni, Cd, Hg
Copper sandstone	Cu, S	Ag, Co, Ni

Source: Rees, 14 and 15.

화학분석 및 분석자료의 Quality Control

환경지구화학에서의 많은 분석기법들은 경제적인 광상을 찾기위한 지구화학탐사에서 응용하여 이용되고 있다. 이는 탐사목적의 구조적 광역지역 자료가 인간의 질병과 관련된 미량원소의 지구화학적 매질에서의 분산과, 가축이나 농작물에서의 미량원소 축적이나, 자연적·인위적 오염 범위를 규명하는 연구에도 직접적으로 적용할 수 있다는 사실에서 기인한 것이다. 또한 시료의 선택과 채취기법도 탐사 목적의 그것과 매우 비슷하게 실시되고 있어, 그 분석기법들도 큰 차이없이 적용할 수 있다. 따라서 지구화학탐사의 분석에서 요구되는 조건 즉, 극소량을 측정가능하기에 충분한 감도(detection limit) (sensitivity), 높은 이상(anomaly)을 놓치지 않는 신뢰성(confidence level) (reliability), 신속 간편하고, 저렴한 비용의 조건들이 그대로 환경지구화학의 분석기법에서도 요구된다. 그러나 지구화학적 이상지역만을 찾고자 하는 탐사목적에서보다 환경지구화학적 연구에서는 더 요구되는 사항이 있다. 즉, 환경지구화학에서는 배경치 주위의 수준도 그 자체로 큰 관심사가 되며, 정확하게 측정되어야 한다. 미량원소의 부족현상을 연구하기 위해서는 이상적으로 낮은 수준의 지역 연구도 필요하며, 게다가 환경에 관한 연구는 보다 공공의 관심사가 되고, 법적인 조치가 뒤따를 수도 있으므로 분석의 정확도가 서로 다른 실험실간이나 서로 다른 분석기법에서도 일치하여 우수하게 나와야 한다.

분석비용의 측면에서는 많은 시료의 분석의 경우, 큰 문제가 되지않을 수도 있다. 실제로 보다 강력한 분석능력을 지닌 기기로 발전해가는 경향으로 나타나고 있다. 비색법(1940년대 부터)으로부터 원자흡광분석(AAS)(1960년대에 소개), 유도분극플라즈마 분광분석(ICP)(1970년대말 소개)으로 선호되어지고 있다. 물론 이러한 분석기법들은 원소의 화학종별 해석이 불가능하므로 이를 위해 화학적 평형상수 개념이나 선택적 추출기법이 적용되고 있다.

이 장에서는 채취된 시료의 분석을 위한 사전처리와 분해, 정량분석, 또 분석결과의 신뢰도를 높이기 위한 Quality Control에 대해 알아 본다.

1 시료의 사전처리(Sample Preparation)

퇴적물이나 토양시료의 화학분석을 위한 사전처리는 일반적으로 건조(drying)와 체질(sieving)을 통해 이루어지며, 암석시료의 경우 파쇄(crushing)와 분쇄(grinding)

rock : crushing → grinding → pulverizing

등에 의해 분말로 만들게 된다. 이러한 분말시료는 표면적이 증가되어 화학적인 분해도 잘 되고 시료를 균질화시키는 데도 도움이 된다. 물시료는 시료채취 이후에 조성변화를 최소화시켜야 한다는 점에서 다른 어려운 문제가 된다. 최종분석을 위해 현장시료의 전체가 사용되는 경우는 드물며, 시료의 사전처리는 분석을 위해 전체 시료를 대표할 수 있도록 이루어져야 한다. 또한 이러한 사전처리 과정에서 오염의 영향을 최소화하여야 함은 물론이다. 실험실 기자재에 의해 발생가능한 오염원은 표 3-1과 같다.

1-1 암석 시료

암석시료는 ^{Saw-crusher}철판 죠-크랏샤로 보통 6~10mm 크기로 파쇄하고 다시 디스크밀, 스윙밀 또는 볼밀을 이용하여 분쇄하게 된다. 디스크밀의 경우, 수 킬로그램의 시료를 빠르게 100메쉬 이하의 크기로 분쇄할 수 있다. 그 이하의 분쇄에는 스윙밀이나 볼밀이 더 효과적이다. 일반적으로 암석 시료는 60~200메쉬(250~75 μ m)를 통과하도록 분쇄해야 한다.

다양한 재질로 만들어진 실험실 파쇄나 분쇄기구는 시료의 오염을 불가피하게 일으키게 된다(표 3-1). 따라서 이러한 오염을 최소화하기 위해 죠-크랏샤와 같이 철판이 붙은 파쇄기구로는 약간 큰 덩어리 정도로만 파쇄하고, 더 미분의 분쇄는 막자와 유발을 이용하기도 한다. 오염의 가능성뿐 아니라, 시료의 분쇄과정에서 휘발성물질의 손실이나 2가 철이 3가 철로의 산화가 일어나기도 하므로 주의해야 한다.

Material	Potential contaminants
<i>Grinding equipment</i>	
Steel and iron grinding plates	Fe, Co, Cr, Cu, Mo, Mn, Ni, V
Alumina ceramic plates ¹	Al, Cu, Fe, Ga, Li, Ti, B, Ba, Co, Mn, Zn, Zr
Tungsten carbide	Co, Ti, W
Lubricants	Mo
<i>Packaging materials ²</i>	
Polythene	Ti, Ba, Zn, Cd
Polypropylene	Ti
PVC	Ti, Zn, Na, Cd
Brown paper	Si
Rubber	Zn

¹ Thompson and Bankston (1970).

² Scott and Ure (1972).

표 3-1 실험실 기구를 통한 잠재적 오염원. [3]

SAMPLE PREPARATION

TABLE

Approximate equivalent mesh sizes in the British Standard(B.S.), American Society for Testing Material(ASTM) and Tyler sieve series

Approximate aperture (μ m)	B.S.	ASTM	Tyler
2000	8	10	9
1000	16	18	16
850	18	20	20
420	36	40	35
355	44	45	42
300	52	50	48
250	60	60	60
212	72	70	65
180	85	80	80
150	100	100	100
125	120	120	115
90	170	170	175
75	200	200	200
63	240	230	250
53	300	270	270
45	350	325	325
38	-	400	400

1-2 토양및 퇴적물 시료

토양이나 퇴적물 시료는 건조와 분쇄, 체질의 과정으로 분석에 적절한 크기로 처리 되게 된다. 건조는 보통 나무가지나 들, 생물잔해 등을 제거하면서, 햇볕과 바람을 이용하거나 전기건조기를 사용한다. 건조기를 이용할 경우, 점토성분이 굳지않게 65℃ 이하에서 실시하는 것이 좋고, 굳어진 덩어리는 나무망치나 막자와 유발을 이용해 분해하게 된다. 이 분쇄과정은 분쇄가 목적이 아니므로 주의하여 실시한다. 체질은 나일론이나 알루미늄 재질이 오염을 막을 수 있고 뿔뿔한 붓솔을 이용, 시료간에 오염을 최소화한다.

80메쉬의 체가 일반적으로 사용되고 시료의 -80메쉬 부분이 지구화학적 분석에 용이하며, 대부분의 토양이나 퇴적물에서 분석에 필요로 하는 수 그램을 얻는데 충분히 들어있다. 그러나 성인파악을 위해 2mm 이상의 조립질이 선택되기도 하며, 토양 pH 측정을 위해서는 2mm 이하 80메쉬 이상의 부분만을 처리하기도 한다. 즉, 분석목적에 따라 적합한 크기의 체를 사용하는 것이 바람직하다.

1-3 식물시료

식물시료는 채취과정에서 부터 주의를 기울여 부패하지 않게 유지하는 것이 중요하며 유기물을 파괴하기 위하여 일반적으로 회화(ashing)하게 되는데, 회화 후 시료양이 건조한 시료의 3~10% 밖에 되지 않으므로 적절한 시료양을 고려하여야 한다. 식물시료는 처리과정에서 증류수로 세척하여 흙이나 다른 오염물질을 제거하고 건조한 온실이나 강제통풍식 오븐에서 건조시킨다. 건조된 시료는 해머밀등을 이용, 분말시킨 후 450~600℃의 전기로 속에서 12시간 동안 서서히 회화시킨다. 이때 휘발성 성분의 손실이 발생하므로 휘발성원소(Hg, Sb, As, Se, Te, Pb 등)가 분석대상이라면 습식회화법이 필요하다.

(Dry ashing
Wet ashing : 산 이용)

1-4 물시료

물시료내의 대부분의 원소들은 직접 AAS나 ICP의 분석기기로 측정가능하다. 그러나 Cu, Pb, Zn, Cd 등을 포함하는 중금속들은 직접 측정하기에는 그 함량이 너무 낮아 추출이나 예비농축(preconcentration)의 과정이 필요하다. 예비농축은 킬레이팅 수지

(chelating resins)를 이용한 이온교환법이고, 용매추출은 유기리간드를 이용하여 이루어진다. 현재의 방법으로는 다량의 물시료가 필요하며(11정도) 농축비는 50배까지 밖에 올리지 못한다. 그러나 ICP의 활용으로 다원소분석이 가능하여 농축비도 높이고 시료양도 줄일 수 있다. 물론 농축비를 지나치게 높이는 것은 추출제나 용기에 의한 오염의 영향이 있으므로 주의해야 한다.

2 시료의 분해

현재 응용지구화학에서 일반적으로 사용되는 분석방법에서는, 고체시료를 분해하여 분석하고자 하는 원소가 용액내로 추출되게 하는 과정이 필요하다. 또 시료내 분석하고자 하는 원소의 함량이 매우 낮을 경우, 분석기법의 측정가능 범위내에 들게 하기 위하여 미리 농축시키는 과정이 필요하기도 하다. 특히 이 과정은 자연수내의 중금속 분석에 있어서는 일반적이다.

화학분석을 위한 시료분석에 있어서의 일반적인 경향은 분석스케일을 줄이고 과정을 단순화하며, 추출제의 양을 최소화하는데 있다. 이러한 경향의 장점은 비싼 추출제의 사용을 줄이고, 분석과정에서의 오염을 막고, 분석 공간을 효율적으로 활용할 수 있다는 점이다. 또한 ICP의 사용이 확대되면서 소량의 시료만이 필요하여 이러한 추세가 심화되고 있다.

환경지구화학에서의 시료분해와 분해정도는 탐사작업에서의 그것보다 약하게 요구되는데, 이는 분해가 어려운 광물이라면 그만큼 환경에의 오염 영향도 적을 것으로 판단하기 때문이다(그러나 반드시 성립하는 것은 아니다. 석석(cassiterite)을 포함하는 토양내의 특정식물은 Sn을 과다 함유하고 있지만, 석석은 일반 산혼합물로서는 분해가 어렵다.). 그럼에도 불구하고 강산추출이 주로 이루어지는데 이는 정밀도를 높일 수 있고, 해석이 편리하기 때문이다.

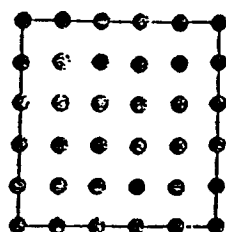
보다 약한 추출제를 사용하는 선택적 추출방법은 분석시료내의 특정 화학형태나 특정한 상(phase)만을 용해시켜 환경지구화학적 연구에 더욱 관련이 있는 결과를 유도할 수 있다. 그러나 이 분석법도 원소의 특정한 형태가 부정확하며, 추출제의 양이나 온도, 반응시간 등에 의해 임의적인 제한을 가지고 있다. 따라서 강산으로 처리하는 "total" 분해에 비해 시료에 따라 그 효율성이 변하는, 예측이 어려운 방법이다. 응용 분해(fusion)는 환경지구화학적 물질의 분석에는 잘 이용되지 않고 있다.

PbS (Galena, 방연석)

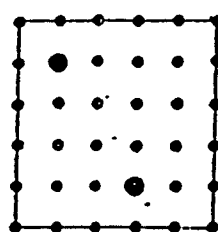
: 결정 격자 내에

$KAlSi_3O_8$ 의

K에 Pb가 포함되어 있다.

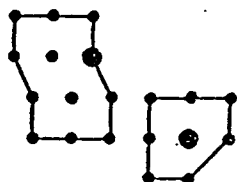


Trace mineral

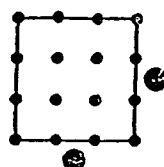


Trace element in well-crystallized mineral

7.2%
Chemical attack



Trace element in fine-grained poorly crystallized mineral



Trace element adsorbed on surface

0.5% Chemical attack

Fig. Schematic diagrams of four modes of occurrence of trace elements. (●) Atom of trace element; (•) atom of major element.

- (i) As a major element in a trace material, such as Pb in anglesite ($PbSO_4$), Cu in malachite ($Cu_2CO_3(OH)_2$), or Au as the native metal. The mobility of trace elements in these forms is dependent mainly on simple solubility and solution chemistry, or on physical processes transporting the grains.
- (ii) As a trace constituent in the crystal structure of a well-crystallized mineral, such as Zn in magnetite, Pb in K-feldspar, or Cu in biotite. Well-crystallized minerals are most commonly formed by igneous, metamorphic, and hydrothermal processes. The behavior of a trace element occurring in this form depends primarily on the properties of the host mineral. If and when this host is destroyed or decomposed, then the trace element will be governed by simple solution chemistry and solubility.
- (iii) As a trace element in a poorly crystallized material, or occluded as a trace mineral in such a phase, or adsorbed on such a material and trapped by further precipitation. Such materials are commonly formed in the surface environment. Examples are Co or Cu in Fe-Mn-oxides, Zn in the strongly bonded octahedral sites of a montmorillonite clay, and Hg in organic compounds. Basically, the controls on the behavior of such trace elements are the same as in (ii), but because of the poorly crystalline nature of the host, the trace elements tend to be more accessible to the surrounding solutions than those in coarser-grained, more nearly perfect lattices of minerals formed in igneous, metamorphic, or diagenetic environments. In spite of this, partial dissolution of the host or a strong acid attack is usually required to liberate trace elements in this form.
- (iv) As a trace element adsorbed on the surface of a colloidal particle of Fe-Mn-oxide, clay or organic material, or in the exchange layer of a clay mineral. Elements in these sites are controlled mainly by ion exchange equilibria. Even minor changes in composition of surrounding solutions may liberate the trace element to solution.

Classification of some decomposition techniques

Decomposition	Reagents
Strong decompositions	
(1) Digestions with hot, usually concentrated, mineral acids	HNO ₃ , HCl, HClO ₄ , HF
(2) Fusions: $M_2O + H_2O \leftarrow \text{sample} + \text{flux}$	
acid fusions	KHSO ₄ , K ₂ S ₂ O ₇
ammonium halide sublimations	NH ₄ I, NH ₄ Cl
alkaline fusions	Na ₂ CO ₃ , NaOH, LiBO ₂
oxidative-alkali fusions	Na ₂ CO ₃ or NaOH with KNO ₃ or Na ₂ O ₂
Partial decompositions	
(1) Non-selective decompositions:	
cold dilute mineral acids: e.g.	0.1–1.0 N HCl
buffers: e.g.	NH ₄ -citrate/NH ₂ OH · HCl, pH 2–8
chelating agents: e.g.	0.05–0.25 M EDTA, pH 4–7
(1) Selective decompositions:	
(a) removal of exchangeable metals	NH ₄ -acetate; MgCl ₂
(b) removal of organic matter	H ₂ O ₂ ; NaOCl
(c) secondary iron and manganese oxides	Na-dithionite; hydrazine; hydroxylamine hydrochloride; NH ₄ -oxalate
(d) sulphides	KClO ₃ /HCl; ascorbic acid/H ₂ O ₂ ; bromine

분해, HCl 등
 부식 물질에 따라
 선택해야 한다.

MATERIAL	SAMPLE PREPARATION	DISSOLUTION OF SAMPLE	ANALYTICAL METHOD
ROCKS		<div>Partial Extraction or Acid Attack</div> <div>Fusion</div>	Atomic absorption
	Dry		Plasma emission
	Crush and Grind		Colorimetry
			DC-arc emission
SOILS AND SEDIMENTS		<div>Partial Extraction or Acid Attack</div> <div>Fusion</div>	XRF
	Dry, Disaggregate, and Sieve		Atomic absorption
	Ignite at 450°C		Plasma emission
			Colorimetry
VEGETATION		Acid Attack	DC-arc emission
	Dry at 110°C		XRF
	Ignite at 450°C		Atomic absorption
			Plasma emission
WATER		<div>Evaporation</div> <div>Solvent Extraction or Ion Exchange</div> <div>Precipitation</div>	Colorimetry
			XRF
			Plasma emission
			Atomic absorption

$$ratio = \left(\frac{M_{e \text{ partial}}}{M_{e \text{ total}}} \right)$$

Fig. Some of the pathways for preparation, dissolution and analytical method.

2-1 강산을 이용한 분해

강산으로 질산과 염산 혹은 과염소산의 혼합산이 일반적으로 많이 사용되고 있다. 하지만 반응온도와 반응시간은 실험실마다 다양하게 변하고 있다. 이때는 유리질 테스트튜브의 사용이 가능하나, 불산을 사용할 경우 폴리테트라플로에틸렌(PTFE) 비이커가 필요하다.

(a) 불산(Hydrofluoric acid)

불산이 첨가된 혼합산, 특히 질산, 과염소산과 혼합된 경우 대부분의 규산염광물을 효과적으로 분해할 수 있다. 이때 발생하는 금속여과액은 증발시키고 남은 잔류물은 염산을 이용, 용해시켜 분석에 이용하게 된다.

AAS의 경우, 인산이온이나 황산이온과 같은 음이온에 의한 간섭현상을 일으킬 수도 있지만, 염산, 질산 혹은 과염소산의 희석된 용액이 분석에 자주 이용되는 매질이다. 반면 ICP는 이러한 제한이 없다. Ca를 많이 함유하는 시료는 CaF의 분해를 위해 과염소산을 이용한 분해가 연장되기도 한다. 분해되지 않은 CaF는 시료내에 존재하는 Pb와 결합하여 용액내로의 추출을 방해할 수도 있기 때문이다.

(b) 과염소산과 질산(Perchloric and nitric acid)

과염소산과 질산의 1:4 혼합산은 암석이나 토양, 퇴적물 등의 시료 0.25g과 반응, 증발시킬 경우 대부분의 중금속을 효과적으로 분해할 수 있다. 증발 잔류물은 10ml의 염산으로 처리한다. 이때 점토광물내의 규소 잔류물과 분해가 안된 규산염광물이 남게 되나, 침전시키고 용액만으로 분석을 실시하는 것이 일반적이다. 이러한 추출법으로 Cu, Pb, Zn, Cd, Mn, Fe, Co, Ni, Mo, P 등의 분석에 만족할만한 결과를 얻을 수 있다. 또한 최종온도를 170℃ 이상 올리지 않는다면 Se의 분석에도 적절하다.

(c) 질산(Nitric acid)

농축된 질산은 자체로는(100℃에서 한시간) 혼합산 보다 효과가 약하여, 철산화물을 강하게 분해하지는 못한다. 하지만 Cu, Pb, Zn, Cd, Hg, Ag 등에 효율적인 방법이 되기도 한다.

(d) 염산(Hydrochloric acid)

강하게 농축된 염산은 철을 함유하는 광물이나 As, Sb의 좋은 용매제이다. 그러나 추출제 자체의 휘발성과 As, Sb의 염화물로의 휘발이 발생하므로 테스트튜브를 밀봉하여 사용한다.

2-2 선택적 추출법(Selective extractions)

선택적 추출법은 주로 토양과 같은 복합적 시료내의 중금속 분포를 결정하는데 이용되며, 적절한 추출제를 사용, 토양내 중금속의 여러 형태를 선택적으로 추출한다는 이론에 바탕을 둔 것이다. 많은 선택적 추출법이 특정한 상의 미량원소를 추출하기 위해 개발되어 왔다. 완전히 새로운 개념은 아니지만, 선택된 추출제가 목표로 한 토양 성분만을 분해하여 특정 금속부분만을 추출하는지는 의심스럽고, 결과적으로 얻어진 부분이 실제 특정 광물상이나 화학성분에 "associated with" 또는 "bound to"된 것인지의 의문이 간다. 그러나 정성적인 개념으로 해석가능하며 토양성분의 중금속 흡착에 관한 상대적 역할이나 중요성 평가에 유용하다. 추출제는 불활성 전해질, 강산, 약산, 산화제, 환원제, 착화제 등으로 분류할 수 있으며, 추출순서는 연구자에 따라 다르게 나타나고 있다. 주로 사용되는 추출제는 다음과 같다.

- ① 0.5M 아세트산(acetic acid) : 토양내의 식물이 흡수할 수 있는 부분.
- ② 암모늄아세테이트(ammonium acetate)(pH7) : 점토광물내의 이온교환성 부분.
- ③ EDTA의 디암모늄염(diammonium salt)(0.05M 용액, pH4) : 토양내의 흡수가 가능한 Cu.
- ④ 환원제와 중성 암모늄아세테이트(ammonium acetate) : 망간수산화물내의 금속이온.

3 정량 분석

환경지구화학에서 정량 분석은 지구화학 탐사에서 활용되는 분석기법을 응용하여 이루어진다. 현재는 많은 수의 시료와 많은 대상 원소를 분석함에 따라 보다 강력한 분석기법을 추구하는 경향이 있다. 여기서는 환경지구화학에서 주로 사용하는 AAS와 ICP법에 대해 소개한다.

Speciation
or
(chemical form)

TABLE 4-IX
Four sequential extraction procedures (intermediate extraction steps, to redissolve any precipitates formed, are not included)

Step	Extraction procedure			
	Hoffman and Fletcher (1979)	Gatehouse et al. (1977)	Rose and Suhr (1971)	Chao and Theobald (1976)
I	sodium hypochlorite ¹ , pH 9.5 [OM, S] ²	H ₂ O	sodium acetate/acetic acid, pH 5 [exch., carb.]	0.1 M hydroxylamine hy- drochloride in 0.01 M HNO ₃ [Mnox.]
II	hydroxylamine hydro- chloride, pH 2.5	ammonium acetate/acetic acid, pH 4.5	hydrogen peroxide	0.25 M hydroxylamine hydrochloride in 0.25 M HCL
III	[Mnox.] ammonium oxalate, pH 3.5	[exch.] hydroxylamine hydro- chloride, pH 4.5	[OM, S, Mnox.] ¹ sodium dithionite- citrate-bicarbonate [Feox.] ¹	[amor. Feox.] sodium dithionite
IV	[amor. Feox] sodium dithionite/citrate/ bicarbonate, pH 7.0	hydrogen peroxide	size fraction and spectro- graphic (DC-arc) analysis of residues	[xst. Feox.] ¹ potassium chlorate/ hydrochloric acid
V	[xst. Feox.] ¹ size fraction and HNO ₃ / HClO ₄ acid decomposition of residues	[OM, S] hydrazine chloride ¹ [Feox.]		[S] silicate residue with HF/HNO ₃
VI	size fractions separated: HClO ₄ acid digestion			

¹ Precipitates formed with these extractions must be redissolved (see original references).

² [Fractions decomposed]: OM = organic matter; S = sulphides; Mnox. = manganese oxides; amor. Feox. = amorphous iron oxides; xst. Feox. = crystalline iron oxides; Feox. = iron oxides; exch. = exchangeable; carb. = carbonates.

⇒ bioavailability of

(bioavailability)

TABLE 1-IV

Evaluation of performance of analytical methods commonly used in exploration geochemistry (see Figs. 1-9, 1-10 and 1-11 for analytical sensitivities)

Method	Cost (\$)	Precision	Freedom from interferences	Multi-element capability	Determinations per man day	Solid samples	Comments
1. Colorimetry	1 × 10 ³	poor-good	good	no	20-100	no	very simple: adaptable to field use; special reagents needed for each element
2. Atomic absorption	2 × 10 ⁴	good	very good	no	500	no	easy to set-up and operate: several elements can be determined on same solution; special methods for Hg, As, Te, Se; dilutions required for high concentrations
3. Emission spectroscopy							
visual comparison	4 × 10 ⁴	very poor	very poor	yes	500	yes	simple robust equipment: requires comparator and darkroom; results semi-quantitative
direct reader	1-2 × 10 ⁵	poor	poor	yes	>1000	yes	sophisticated equipment: requires experienced analyst to set-up and supervise operations; requires dedicated computer or access to computer
ICP-direct reader	1-2 × 10 ⁵	good	good	yes	>1000	no	
4. X-ray fluorescence (XRF)							
wavelength dispersive WDS	3 × 10 ⁵	good	good	yes	>1000	yes	sophisticated equipment: requires supervision by a skilled analyst; dedicated computer or access to computer; very simple sample preparation
energy dispersive EDS	1 × 10 ⁵	good (?)	good (?)	yes	>500	yes	

Use of Reference Materials (RHM)

* Preparation

- 1) composition and mineralogy
- 2) comminution (preparing large amounts, homogeneity) 간편 양을 지니.
- 3) concentration (two representative analyte)
 - background levels (low RHM) low standard
 - threshold (high RHM) High Standard
- 4) availability (1~2 kg)
- 5) stability (volatile?, mineralized rock?)

* Use

- 1) randomisation
- 2) anonymity
- 3) total proportion of RHM
- 4) number of repetitions in one batch
- 5) number of RHMs used - 2 RHMs per batch ideal

화학분석

시료의 화학분석 방법은 시료와 대상원소에 따라 적합한 분해방법을 사용하여야 한다. 물론, 각 연구자에 따라 분석방법이 다양하므로 연구 및 보고서에서는 시료처리의 전과정에 대한 세부적인 기술이 필요하다.

1. 토양

일반적으로 토양중에 함유된 유독성원소를 측정하는 방법은 원자흡광분광광도계 (Atomic Absorption Spectrometry, AAS)와 유도분극 플라즈마 원자발광광도계 (Inductively Coupled Plasma - Atomic Emission Spectrometry, ICP-AES)를 이용한다. 원소에 따라 분석기기의 정확도와 정밀도, 측정한계값 등이 다르므로 적절한 분석기기의 사용이 중요하다. AAS와 ICP-AES는 액상의 물질내에 존재하는 원소들의 함량을 측정하므로 고체로 된 시료를 용액으로 만드는 과정이 필요하다. 이러한 과정은 주로 산을 사용하여 시료를 분해하며 각 산의 농도와 혼합비율에 따라 추출되어 나오는 시료들의 중금속함량이 다를 수 있다. 일반적으로 사용되는 산분해 방법은 다음과 같다.

1. 질산에 의한 분해
2. 질산-염산 (왕수)에 의한 분해
3. 질산-황산에 의한 분해
4. 질산-과염소산에 의한 분해
5. 질산-과염소산-불산에 의한 분해

이러한 방법을 사용하여 분해된 용액을 AAS 또는 ICP-AES를 이용하여 화학분석을 실시하고 있다. 특히 국내에는 1996년 1월에 '토양환경보전법' 이 제정되고 여기에는 0.1N 염산을 이용하여 시료를 분해한다. 이 방법을 자세히 기술하면 다음과 같다.

< 0.1N 염산으로 분해하여 Cd, Cu, Pb 측정 >

1. 대상원소 : Cd, Cu, Pb
2. 대상시료 : 토양
3. 처리요약 : 0.1 N 염산을 이용한 산가용성침출법
4. 시료무게 : 10g
5. 최종부피 : 50ml
6. 회석배율 : 5ml/g
7. 배치구성 : 중복시료, 공시료, 표준시료를 포함 소요시간 : 총 1일
8. 분석의 정밀도와 정확도 검정

공시료 (reagent blanks, 5%), 중복시료 (duplicated samples, 10%)

표준시료 (reference materials - 낮은 함량과 높은 함량용 각각 5%)

9. 실험장비 : 증탕기, 천칭, 삼각플라스크, 원심분리기

시약 : 0.1 N 염산 (보통의 진한 염산은 약 11.6 N 임)

=> 진한 염산 8.6ml를 넣은 후 증류수로 1,000ml를 만듦

10. 처리방법

1) 자연건조하여 채질한 시료 10g을 정밀하게 취하여 100ml 삼각플라스크에 넣고 0.1 N 염산 50ml를 넣는다.

2) 항온수평진탕기 (100회/1분, 진폭 10cm)를 이용하여 30℃를 유지하면서 1시간 진탕한 다음 여과한다.

< 1N 염산으로 분해하여 As 측정 >

1 N 염산을 넣고 항온 수평진탕기 (100회/1분, 진폭 10cm)를 이용하여 30℃를 유지하면서 30분간 진탕한 다음 여과한다. 이 용액을 hydride generation method를 이용하여 분석한다.

2. 식물

채취된 식물시료는 세척, 건조와 미분쇄과정을 통하여 사전 처리를 한다. 식물분석방법은 크게 3종류로 나눌수 있다.

1. 세척한 무게를 기준 (fresh weight) : 시료를 증류수로 세척한 후, 습윤한 상태에서 산을 가함.

2. 건조한 시료의 무게를 기준 (dry weight) : 시료를 세척한 후, 건조하여 산을 가함.

3. 회화시킨 무게를 기준 (ash weight) : 시료를 450℃로 회화시킨 후 산 처리함.

이러한 방법중에서 일반적으로는 건조무게를 기준으로 처리한다. 일반적으로 식물을 분해하는 방법은 다음과 같은 방법을 이용한다.

1. 대상원소 : 다원소 (주성분, 부성분, 미량원소 등)

2. 처리요약 : 질산-과염소산으로 시료를 분해

3. 시료무게 : 2.0g

4. 최종부피 : 10.0ml

5. 회석배율 : 5ml/g

6. 배치구성 : 시료수 : 중복시료, 공시료, 표준시료를 포함

소요시간 : 총 3일

7. 정확도와 정밀도 측정

공시료 (reagent blanks, 5%), 중복시료 (duplicated samples, 10%)

표준시료 (reference materials - 낮은 함량과 높은 함량용 각각 5%)

8. 실험장비 : 길이가 긴 시험관 및 꽃이,

알루미늄으로 제작된 heating block

디스펜서, 시험관 믹서기, 천칭

9. 시약 : 2차 증류수
진한 질산 (70% w/w)
취발성 질산
과염소산 (60% w/w)
5M 염산 (진한 염산 430ml에 증류수로 채워 1000ml를 만듦)

10. 처리방법 :

- 1) 시료 2.0g을 천칭으로 잰 후 시험관에 넣는다.
- 2) 5ml의 질산으로 시료를 충분히 적신다.
- 3) 취발성 질산 5ml를 순서대로 넣고 믹서기로 섞는다 (3회 반복).
- 4) 3번 과정에서 반응이 일어나면 (자연 발화) 증류수로 끈다.
- 5) 반응이 일어나지 않도록 1시간 정도 방치한 후, 히팅블록으로 옮긴다.
- 6) 온도를 올린다 (50℃로 3시간, 100℃로 3시간, 150℃로 10시간, 160℃에서 완전건조).
- 7) 식힌 후, 3ml의 과염소산을 넣고 다시 가열한다 (50℃로 10분, 100℃로 18시간, 160℃에서 완전건조)
- 8) 식힌 후, 5M 염산 2ml를 넣고 70℃에서 30분간 가열한다.
- 9) 시험관을 식힌 후, 증류수 8ml를 넣고 믹서기로 섞어준다.
- 10) 화학분석을 실시한다.

3. 하상퇴적물

하상퇴적물의 분해와 화학분석은 토양시료와 동일하다.

4. 자연수

자연수의 화학분석은 AAS와 ICP-AES를 이용하여 양이온을 측정하고 IC (Ion Chromatography)를 이용하여 음이온을 측정한다. 양이온의 함량이 매우 낮은 경우에는 증발법 및 용매농축법을 이용하여 시료를 농축하여 화학분석을 실시하기도 한다.

※ HNO_3 - HClO_4 attack for rock, soil, or sediments

Reagent

- 1) HClO_4 (60%)
- 2) HNO_3 (70%)
- 3) HCl (5M)

Equipment

- 1) PTFE tubes
- 2) Graduated plastic test tube (10ml)
- 3) Metal block sited in a suitable fume cupboard

- 4) Polyethylene measuring cylinder and plastic tray
- 5) Liquid dispensers

Procedures

- 1) Weigh each sample (250mg, -180mesh) into a clean, dry, numbered PTFE tube.
- 2) Weigh standard (reference) and duplicate samples and leave empty tubes at random intervals for blank determinations.
- 3) Add HNO_3 (4ml) followed by HClO_4 (1ml) to each tube.
- 4) Heat the tubes on a metal block for 3hrs at 50°C .
- 5) Heat the tubes for 3 hrs more at 150°C .
- 6) Raise temperature to 180°C and evaporate to dryness.
- 7) Knock the top of tubes with plastic rod to fall down the bubbles into the tubes.
- 8) Remove each tube into a rack in the fume cupboard, and allow them all to cool.
- 9) Add HCl (2ml) to each tube and leach for 1hr at 70°C .
- 10) Transfer the solutions from the tubes to graduated test tubes and dilute to 10ml with water. (dilution factor = 40)

*** HNO_3 - HClO_4 - HF attack for rock, soil, or sediments**

Reagent

- 1) HF (40%)
- 2) HClO_4 (60%)
- 3) HNO_3 (70%)
- 4) HCl (6M)

Equipment

- 1) PTFE tubes
- 2) Graduated plastic test tube (10ml)
- 3) Metal block sited in a suitable fume cupboard
- 4) Polyethylene measuring cylinder and plastic tray for dispensing HF acid
- 5) Liquid dispensers

Procedures

- 1) Weigh each sample (100mg, -200mesh) into a clean, dry, numbered PTFE tube.
- 2) Weigh standard (reference) and duplicate samples and leave empty tubes at random intervals for blank determinations.
- 3) Add HNO_3 (2ml) followed by HClO_4 (1ml) to each tube.
- 4) Then add HF (5ml) to each tube.
- 5) Heat the tubes on a metal block for 3hrs at 90°C .
- 6) Heat overnight at 140°C .
- 7) Raise temperature to 160°C and evaporate to dryness.
- 8) Knock the top of tubes with plastic rod to fall down the bubbles into the tubes.
- 9) Remove each tube into a rack in the fume cupboard, and allow them all to cool.
- 10) Add HCl (2ml) to each tube and leach for 1hr at 70°C .
- 11) Transfer the solutions from the tubes to graduated test tubes and dilute to 10ml with water. (dilution factor = 100) \rightarrow Total concentration

※ 원소를 이용한 토양시료내 중금속의 총함량 분석

- 1) 분석용 시료(건조상태, -80mesh 입도)와 함께 quality control을 위한 중복시료, 공시료를 적절하게 설정하여 분석배치를 작성한다.
- 2) 분석배치에 따라 PTFE tube에 각 시료를 250mg씩 칭량한다.
- 3) 질산 1ml를 투여한다.
- 4) 염산 3ml를 투여한다.
- 5) heating block에서 70°C 로 1시간 가열한다.
- 6) heating block에서 PTFE tube를 옮겨 냉각시킨다.
- 7) 증류수를 첨가하여 최종용액 10ml로 정량한다.
- 8) 최종용액을 분석용 tube로 옮겨 원심분리를 실시하고 각 원소의 AAS 정량분석에 들어간다.

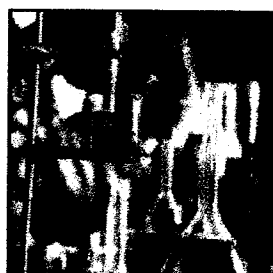
$$\text{Dilution factor} = 10 \text{ ml} / 0.25 \text{ g} = 40 \text{ ml} / \text{g}$$



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Trace Element Geochemistry

All elements are in ppm except where noted.

Code	Aqua Regia Extraction										Near Total Metals						
	Au+14 1EPI	Au+23 1EPI/MS	Au+34 1D	Au+34 1D enh.	1E	ICP/OES 1E1	ICP/OES 1E2	ICP/OES 1E3	ICP/MS Ultratrace 1	ICP/MS Ultratrace 2	ICP+ICP/MS 1F	Near Total 1F2	Au+48 1H	Au+53 1H2	Au+63 Ultratrace 3	ICP/MS Ultratrace 4	ICP/MS Ultratrace 5
Ag	0.2	0.2	5	5	0.2	0.2	0.2	0.2	0.002	0.002	0.3	0.3	0.3	0.3	0.05	0.05	0.05
Al						*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%
As	2	2	5	0.5		*10	*5	*5	*0.1	*0.1	5	5	0.5	0.5	0.5	0.1	0.5
Au	0.002	0.002	0.002	0.002					*0.5 ppb	*0.5 ppb			0.002	0.002	0.002		0.002
B																	
Ba	100	100	100	50		*1	*1	*10	*0.5	*0.5		*7	50	50	*1	*1	*1
Be						*1	*1	*0.5	*0.1	*0.1	1	1	1	1	0.1	0.1	0.1
Bi		0.1				10	2	2	0.02	0.02	2	2	2	0.1	0.02	0.02	0.02
Br			1	0.5									0.5	0.5	0.5		0.5
Ca		*0.01%	1%	1%		*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%
Cd																	
Ce																	
Co																	
Cr																	
Cs																	
Cu	1	1			1	1	1	1	0.01	0.01	1	1	1	1	0.2	0.2	0.2
Dy									*0.1	*0.1					*0.1	*0.1	*0.1
Er									*0.1	*0.1					*0.1	*0.1	*0.1
Eu			0.2	0.2					*0.1	*0.1			0.2	0.2	*0.05	*0.05	*0.05
Fe		0.02%	0.02%	0.01%		*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	0.01	0.01%	0.01%	0.01%	*0.01%	*0.01%
Ga																	
Gd																	
Ge																	
Hf																	
Hg	1	1	1	1					*0.1	*0.1							1
**Hg-CV	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)	(5 ppb)
Ho									*0.1	*0.1					*0.1	*0.1	*0.1
In									*0.02	*0.02					0.2	0.1	0.1
Ir			5 ppb	5 ppb									5 ppb	5 ppb	5 ppb		
K		*0.01%				*0.01%	*0.01%	*0.01%	*0.01%	*0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%
La																	
Lu																	
Mg																	
Mn	2	2															
Mo	2	2	5	1	*2	*2	*2	*1	*0.01	*0.01	1	1	1	1	1	0.1	0.2
Na			0.05%	0.01%		*0.01%	*0.001%	*0.001%	*0.001%	*0.001%	0.01%	0.01%	0.01%	0.01%	0.01%	0.001%	0.01%
Nb									*0.1	*0.1					*0.1	*0.1	*0.1
Nd			5	5					*0.02	*0.02			5	5	*0.1	*0.1	*0.1
Ni	*1	*1	50	20	*1	*1	*1	*1	*0.1	*0.1	1	1	1	1	0.5	0.5	0.5
P																	
Pb	2	2															
Pr																	
Rb																	
Re																	
S	+100	+100			+100	+100	+100	+0.01%	+10	+10	+100	+100	+100	+100	+100		
Sb	0.2	0.2	0.2	0.1		*10	*5	*2	*0.02	*0.02		5	0.1	0.1	0.1	0.1	0.1
Sc			0.1	0.1		*1	*0.1	*1	*0.1	*0.1		4	0.1	0.1	0.1		0.1
Se		0.1	5	3					*0.1	*0.1			3	3	0.1	0.1	0.1
Sm			0.1	0.1					*0.1	*0.1			0.1	0.1	*0.1	*0.1	*0.1
Sn						*10	*5		*0.05	*0.05			*0.01%	*1	*1	*1	*1
Sr						*1	*1		*0.5	*0.5				1	0.2	0.2	0.2
Ta									*0.05	*0.05			0.5	0.5	*0.1	*0.1	*0.1
Tb																	
Tc		0.1							*0.1	*0.1			0.1	0.1	*0.1	*0.1	*0.1
Th			0.5	0.2					*0.1	*0.1			0.2	0.2	*0.1	*0.1	*0.1
Ti		*0.1							*0.02	*0.02		5	0.1	0.05	0.05	0.05	
Tl						*0.01%	*0.01%	*0.01%			0.01%	0.01%	0.01%	0.01%	0.01%		
Tm									*0.1	*0.1					*0.1	*0.1	*0.1
U			0.5	0.5				10	*0.1	*0.1		*10	0.5	0.5	0.1	0.1	0.1
V						*1	*1	*1	*1	*1	2	2	2	2	1	1	1
W	4	4	4	1		*10	*1	*10	*0.1	*0.1			1	1	1	*0.1	*1
Y						*1	*1	*1	*0.01	*0.01	*1	*1	*1	*1	*0.1	*0.1	*0.1
Yb			0.2	0.2					*0.1	*0.1			0.2	0.2	*0.1	*0.1	*0.1
Zn	*1	*1	50	50		*1	*1	*2	*0.1	*0.1	1	1	1	1	0.5	0.2	0.5
Zr						*1	*1	*1	*0.1	*0.1					*1	*1	*1
Price	\$19.00	\$26.00	\$14.50	\$16.75	\$8.50	\$10.00	\$10.50	\$10.50	\$16.75	\$21.00	\$12.75	\$14.75	\$24.00	\$33.50	\$35.25	\$19.00	\$27.00

* Partial extraction only

** Hg add on by cold vapour FIMS (CODE 1G), add \$7.00

Elements in brackets are optional - see notes, page 10-11
+ only sulphide sulphur is extracted

Code 1EPI

The "Au+14" group of elements provides a high quality, low cost package for epithermal gold exploration [by INAA (Au, As, Sb, Ba, Hg and W), aqua regia ICP (base metals and sulphur) and optional cold vapour FIMS (Hg)]. A sample of ~30 g is used for Au analysis. An enhanced package (Code 1EPI enhanced) with better detection limits for Au (2 ppb) and As (0.5 ppm) also is available for an additional \$2.00 per sample. (35 g required). Sulphur (+) from barite will not be reported. If total S is required, see Code 4F-S. See Code 1E for notes on base metals.

이런 원소도 분석?
이런 분석 방법?
폐산료?

Trace Element Geochemistry



Which digestion do I use?

1. **AQUA REGIA DIGESTION** - This leach uses a combination of concentrated hydrochloric and nitric acids to leach sulphides, some oxides and some silicates. Mineral phases which are hardly (if at all) attacked include barite, zircon, monazite, sphene, chromite, gahnite, garnet, ilmenite, rutile and cassiterite. The balance of silicates and oxides are only slightly to moderately attacked, depending on the degree of alteration. Generally, but not always, most base metals and gold are usually dissolved if the sample is ground finely enough.
2. **"TOTAL" DIGESTION** - This acid attack is the most vigorous used in geochemistry. It will employ hydrochloric, nitric, perchloric and hydrofluoric acids. Even with this digestion, certain minerals (barite, gahnite, chromite and cassiterite) may not go into solution. Other minerals including zircon, sphene and magnetite may not be totally dissolved. Most other silicates will be dissolved, however some elements will be erratically volatilized, including Si, As, Sb, Cr and Au. Total digestions cannot be used for accurate determinations of REE, Ta, Nb, As, Sb, Sn, Hf, Cr, Au and Si.
3. **FUSION TECHNIQUE** - The most aggressive fusion technique employs a lithium metaborate/tetraborate fusion. The resulting molten bead is rapidly digested in a weak nitric acid solution. The fusion ensures that the entire sample is dissolved. It is only with this attack that major oxides including SiO_2 , REE and other high field strength elements are put into solution. High sulphide bearing rocks may require different treatment, but can still be adequately analyzed.

NOTE: Results from aqua regia or total digestions may be lab dependent or lab operator dependent. Actlabs has automated this aspect of digestion using a microprocessor designed hotbox to accurately reproduce digestion conditions every time.

Code 1EPI/MS - The "Au+23" group of elements is similar to Code 1EPI but includes a suite of elements by ICP/MS to provide virtually all elements used for epithermal gold exploration. The multielement acid attack will only dissolve the soluble forms of barium, while INAA will provide the total barium concentration. The total Ba to soluble Ba ratio will be a direct indicator of barite concentration. **Code 1EPI/MS Enhanced** is available which offers Au - 2 ppb, As - 0.5 ppm, Sb - 0.1 ppm for an additional \$2.00 per sample (35 g required). See Code 1E for notes on base metals.

Code 1D - The sample is encapsulated, irradiated and measured in a multielement mode by INAA for Au+34 elements. The elements in this package are determined non-destructively and the total metals help the geologist determine rock types, alteration and pathfinder elements. The 30 g aliquot provides a representative sample size for gold analysis (0.5 to 30 g required).

Code 1D enhanced - This INAA package is similar to Code 1D but has enhanced detection limits. This package has become very popular for rock, soil, lake sediment and stream sediment samples (0.5 to 30 g required).

Code 1E - This package determines a base metal suite and sulphide sulphur by an aqua regia extraction with an ICP/OES finish. If accuracy better than +/- 10-15% is required for higher level samples we recommend assays (Code 8) (+/- 3%) for Cu, Zn and Ni over 10,000 ppm and certainly over 50,000 ppm. Assays are also recommended for Pb >5000 ppm and Ag >100 ppm due to potential solubility problems. Values exceeding these limits are estimates and are provided for information only. (0.5 g of sample required).

Prices: first element \$5.00; each additional element \$2.00.

Code 1E1 - This analytical package uses the same digestion as Code 1E. The same comments apply as in Code 1E for base metals. In addition, a variety of other elements are obtained non-quantitatively since chromite, barite, silicates, magnetite, sphene and some other mineral phases are not soluble with this digestion. Zinc in gahnite or sphene will not be soluble in aqua regia and all Ni in silicate phases may not be totally leachable. (0.5 g of sample required).

Code 1E2, 1E3 - These are similar to Code 1E1, but offer an enhanced list of analytes. (0.5 g of sample is required).

Code 1F, 1F2 - These packages use a "near total" digestion employing HF, HClO_4 , HNO_3 and HCl to get as much of the sample into solution as possible without fusing the sample. The resulting metals are determined by ICP/OES. Sulphide sulphur is included. The sulphur associated with barite will not be dissolved. Other phases which may not be totally digested include zircon, monazite, sphene, gahnite, chromite, magnetite, barite, cassiterite, ilmenite and rutile. The same comments apply as in Code 1E for base metals. (0.25 g of sample required).

Code ULTRATRACE-1 - This partial extraction is analyzed by ICP/MS to provide lower detection limits. Upper limits are up to 20,000 times the detection limits. (0.5 g of sample is required).

Code ULTRATRACE-2 - This combines ULTRATRACE-1 with Code 1E2 to provide a few additional elements from the ICP/OES as well as extend the upper limits of the ULTRATRACE-2 elements. (0.5 g of sample is required).

✓ **Code 1H "Au+48"** - This package provides a trace element scan for virtually all types of economic mineralization. It also provides useful information on alteration, rock types, and pathfinder elements. The Code 1D enhanced (INAA) and Code 1F (4-acid digestion ICP technique) provide 49 elements. The elements determined by INAA are Au, As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Sn, Ta, Th, Tb, U, W, Yb and Lu. The remaining elements are determined by the 4 acid ICP (Code 1F above) technique. SiO_2 is not analyzed due to volatilization. (0.75 - 35 g required depending on sample size you wish to be analyzed for Au).

Code 1H2 "Au+63" - This package is similar to Code 1H but also uses ICP/MS on an acid digest solution to obtain additional elements. If Au is important, a larger sample size (up to 35 g) should be submitted.

Code ULTRATRACE-3 - This combines INAA, 4-acid digestion ICP and ICP/MS analysis to provide the most comprehensive near total metal package available using an acid digestion. Note that this package is not suitable for chondrite plots as not all REE are quantitatively extracted from zircon, monazite, etc. (1.0 to 35 g of sample required).

Code ULTRATRACE-4 - Near total digestion employing HF, HClO_4 , HNO_3 and HCl with ICP/MS finish (0.5 g of sample required) This digestion may not be completely total if resistate minerals are present. As, Sb and Cr may be partially volatilized.

Code ULTRATRACE-5 - Combines INAA with a 4-acid digestion (HF, HClO_4 , HNO_3 and HCl) to attempt to give as total metal as is possible with acids. Some of the resistate elements are provided by INAA.