NATIONAL ASSOCIATION OF TESTING AUTHORITIES (NATA) REQUIREMENTS FOR ACCREDITATION OF ICP-MS TECHNIQUES

The National Association of Testing Authorities' (NATA) requirements for accreditation have undergone significant changes with the introduction of a new standard AS ISO/IEC 17025:1999 "General requirements for the competence of testing and calibration laboratories". The new standard (AS ISO/IEC 17025:1999) replaces ISO/IEC Guide 25 1990 and contains the requirements that testing laboratories have to meet if they wish to demonstrate that they operate a quality system, are technically competent and are able to generate technically valid results. If testing laboratories comply with the requirement of this standard they will operate a quality system that also meets the requirements of either ISO 9001 or ISO 9002.

NATA's publication entitled "ISO/IEC 17025 Application Document – Supplementary Requirements for Accreditation in the Field of Chemical Testing"[1] provides an explanation of the application of ISO/IEC 17025 for Chemical Testing laboratories and also a description of the NATA accreditation procedures applied to this field. This document must be read in conjunction with the following references that together comprise the NATA Accreditation Requirements:

- About NATA and Accreditation[2]
- NATA Rules[3]
- Current Policy/Technical Circulars (see the NATA website http://www.nata.asn.au/)

This paper examines two aspects of NATA accreditation of analytical techniques:

- The issues that relate to accreditation of an analytical method with specific reference to ICP-MS accreditation
- Key issues contained in the new standard (AS ISO/IEC 17025:1999)

The issues listed and discussed below are the technical elements examined at laboratory assessments when ICP-MS techniques are part of the scope of the accreditation.

1. Dissolution procedures

No matter how sophisticated the detection technique is, an analytical result can only ever be as good as the sample presented. This is particularly relevant to laboratories undertaking analysis of environmental samples, and quoting compliance to a standard method, i.e. USEPA 200.8. Many laboratories put their own interpretation as to how "total recoverable element" dissolution should be undertaken, despite the fact that this USEPA standard method clearly outlines the dissolution process. NATA does consider "accreditation for variations of standard methods when technically justified and supported by a documented study of the effects of the changes", but laboratories cannot be accredited for methods "based on" standard methods.

2. Technical competence and expertise of staff

The number of ICP-MS instruments continues to increase annually; occasionally laboratories purchase, commission and use equipment without the benefits of adequately experienced personnel. Analytical instruments, and more specifically ICP-MS must not be treated as a "black box"; laboratory staff must have an understanding of the following:

(a) Instrumental Optimisation Procedures:

- Optimising instrument with
  - Torch xyz adjustments
  - RF power
  - Argon flow rates
  - Ion lens voltages
- Mass calibration
- Resolution checks
- Dual detector calibration (if applicable)
- Daily performance checks

- % RSD's
- Background counts
- Isotope intensity

(b) Interferences.

(i) Isobaric elemental interferences

These interferences must be recognised and then avoided by selection of an alternative analytical isotope, if unavoidable appropriate corrections must be made.

(ii) Isobaric molecular and doubly charged ion interferences.

These interferences must be recognised and corrections applied to data if these interferences cannot be avoided. Note instrumental plasma conditions and matrix components affect the production of these species, so effects should be minimised and measured before corrections are applied.

(iii) Abundance sensitivity

The potential presence of this source of interference must be recognised and spectrometer resolution adjusted to minimise effects.

(iv) Physical Effects

This can be due to transport process of sample to the plasma, sample conversion processes in the plasma and transmission of ions through the ICP-MS interface. The use of internal standard may compensate for physical interference effects.

3. Test and Calibration Methods and Method Validation

When laboratories use standard test methods like those published by Standards Australia, APHA or USEPA, the laboratory must verify the published test method to demonstrate it can achieve the expected results. Records of the verification must be retained. For published methods that do not include precision data, the laboratory must determine its own precision data based on test data. All methods must include criteria for rejecting suspect results.

Methods may be validated by comparison with other established methods using (certified) reference materials. In developing and validating test methods, the following issues (among others) need to be determined:

Characteristic evaluated	**Recommended procedure**
Precision (repeatability)	Replicate analysis of samples
Robustness	Analysis of natural and spiked samples and "in-house" reference materials
Reproducibility (ruggedness)	Analysis by different operators, different laboratories, using different equipment
Recovery	Analysis of spiked samples at appropriate concentrations i.e., near the detection limit, near the linearity range and the middle of the useable range
	Analysis of reference materials (CRMs)
Selectivity (interferences) Matrix effects	Analysis of spiked samples, standards and reference materials (CRMs)
Detection limit Quantitation limit	Analysis of blanks and low level spiked samples
Linearity range Accuracy	Analysis of spiked samples and standards, accuracy can also be determined by comparison with other established methods

The laboratory must document procedures for method validation. These procedures need to include details of the statistical analysis to be applied to when deriving precision data. Therefore, a statistically valid number of replicate analyses need to be done so that this can take place, e.g., at least 7-10 replicates. Records of the application of these procedures must be retained for review at each assessment. Because of the diversity of ICP-MS equipment available in the market place, instrument-operating conditions vary and accordingly there is no universal set of recommended operating conditions. The ICP-MS analyst has the responsibility of verifying

that the configuration and operating conditions satisfy the analytical requirements.

3.1. Uncertainty of Measurement

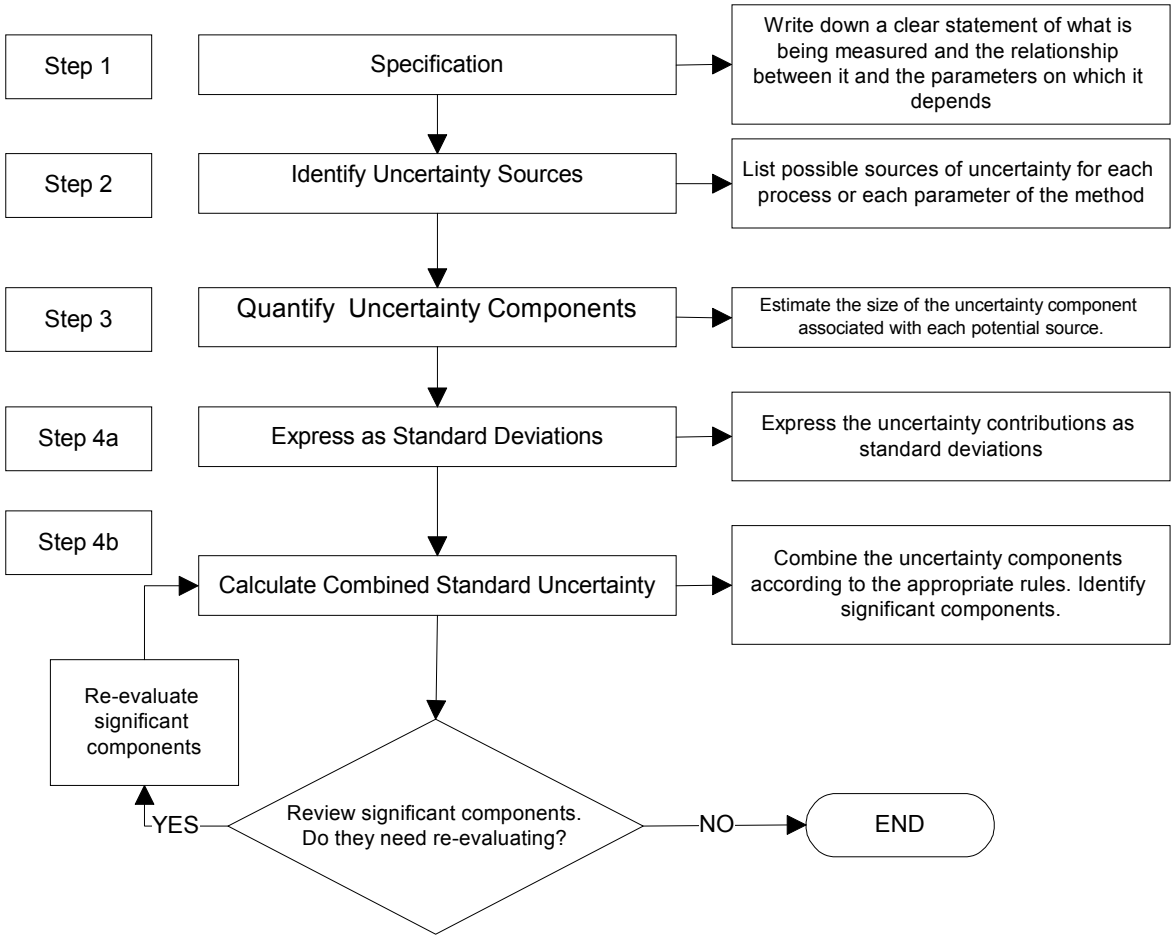
The new accreditation standard ISO/IEC 17025 requires laboratories to estimate the uncertainty of measurement.

"I used to be uncertain – now I'm not so sure"

Uncertainty does not inspire confidence, but from an analytical laboratory perspective, uncertainty defines the range of the values that could reasonably be attributed to an analytical result. Uncertainty arises as a result of random effects, such as short-term fluctuations in temperature, relative humidity and power source variations or a result of systematic effects, such as instrumental drift between calibrations. When laboratories report uncertainty it gives a quantitative indication of the quality of the analytical results, and it allows the user of the result to:

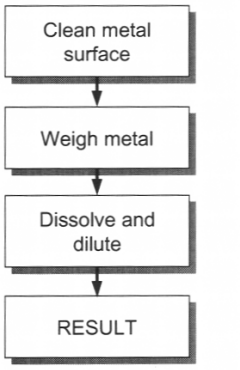
- Assess its reliability
- Assess the confidence that can be placed on a result, when comparing it with a limiting value defined in a specification or regulation
- Compare analytical results e.g., from different laboratories
- Assess the "fitness for purpose" of the result

3.1.1. The Process of Measurement Uncertainty Estimation



The following example of quantifying uncertainty is taken from EURACHEM/CITAC Guide[4], preparation of a 1000mgL^{-1} Cd calibration standard from high purity metal. The stages of the procedure are shown in the following flow chart, Figure 1.

Figure 1. Steps involved in preparing a 1000mgL^{-1} Cd calibration standard.



where

c_{Cd} :concentration of the calibration standard [mg l^{-1}]

1000 :conversion factor from [ml] to [l]

m :mass of the high purity metal [mg]

P :purity of the metal given as mass fraction

V :volume of the liquid of the calibration standard [ml]

$$c_{Cd} = \frac{1000 \cdot m \cdot P}{V} \text{ [mg l}^{-1}\text{]}$$

3.1.2. Identification of the uncertainty sources

For each stage of the analytical procedure list the sources of uncertainty. This can conveniently be done using a cause and effect diagram, showing how the sources of uncertainty relate to each other and indicating their influence on the uncertainty of the result. Cause and effect diagrams also help to avoid double counting of sources.

- Write the calculation equation, the parameters form the main branches of the diagram
- Consider each step in the analytical method and add contributing factors to the diagram
- Smaller branches (contributing factors) are added to the main branches, each representing an effect on the previous branch
- The diagram is "simplified" by:
  - Eliminating canceling effects – no net effect on result
  - 'Same effect – same time' are combined as a net effect
  - Restructure to group similar effects

The relevant uncertainty sources are shown in the cause and effect diagram below, Figure 2:

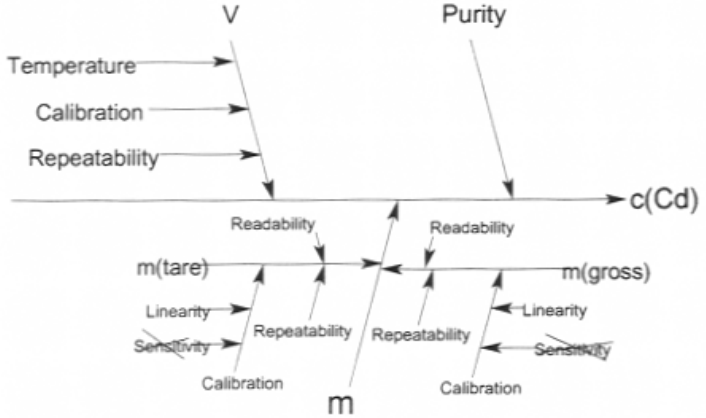


Figure 2. Sources of uncertainty in preparing a 1000mgL^{-1} Cd calibration standard shown in a cause and effect diagram

3.1.3. Quantitation of the uncertainty components

Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty defined. Much of the data for this step can be obtained from method validation data, calibration certificates, certified reference material certificates and proficiency testing data. It is important to consider whether available data account sufficiently for all sources of uncertainty, and plan additional experiments and studies to ensure all sources of uncertainty are adequately accounted for.

Uncertainty estimation relies on the use of statistical methods and therefore some knowledge of basic

statistical parameters. The following table shows chemists how to calculate a standard uncertainty from the parameters of the two most important distribution functions.

Distribution	Use when	Uncertainty
Rectangular	A certificate that specifies a range (±a) without confidence level	$u(x) = \frac{a}{\sqrt{3}}$
Triangular	A range value (±a) is more likely to be near the centre of the range	$u(x) = \frac{a}{\sqrt{6}}$

The values and their uncertainty are shown in the table below.

3.1.4. Combined Standard Uncertainty:

The combined standard uncertainty for the preparation of a 1002.7mgL^{-1} Cd calibration standard is 0.9mgL^{-1}.

Individual contributions to the uncertainty should be given in terms of a standard deviation. Uncertainties expressed as standard deviations are **standard uncertainties**. Standard deviation is a measure of the spread of data around the sample mean – a measure of precision. The standard deviation is considered an estimate of the population standard deviation from a sample of results. The relative standard deviation is a measure of the spread of the data in comparison to the mean. It is simply the standard deviation divided by the mean. Relative standard deviations are combined to calculate the total uncertainty. Variance also describes the spread of data, and is the square of the standard deviation.

There are two basic rules for combining standard uncertainties:

Rule 1

For models involving only a sum or difference of quantities e.g., combining the three contributions for the standard uncertainty *(uV)* of the volume use

$$u_c(y(p,q..)) = \sqrt{u(p)^2 + u(q)^2 + ...}$$

Rule 2

For models involving only a product or quotient e.g., combining standard uncertainties to calculate the uncertainty of the concentration of the cadmium calibration solution use

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

	Description	Value	Standard uncertainty	Relative standard uncertainty *u(x)/x*
P	Purity of the metal	0.9999	0.000058	0.000058
M	Mass of the metal	100.28mg	0.05mg	0.0005
V	Volume of the flask	100.0mL	0.07mL	0.0007
c_{Cd}	Concentration of the calibration standard	1002.7mgL^{-1}	0.9mgL^{-1}	0.0009

4. Traceability of results

"The record system shall allow retrieval for at least three years, of all original test data within the terms of accreditation. The record system shall provide a traceable pathway covering all activities from receipt to disposal."

For the ICP-MS analyst this means that the record system must include

- Unique sample identification
- Identification of analyst

- Test document identification
- Identity of test method
- Identity of test equipment, particularly where there are two or more items of the same item of equipment, such as balances, pipettes, etc.
- Original test observations and calculations
- An indication that calculations and manual data transfers have been checked.
- Any other information specified in the test method.

Calibration standard traceability often arises as an area of concern at assessments. Standard solutions require

(i) Documentation of standards preparation

(ii) Documentation on the standard bottle

- Analyte(s)
- Analyte concentration
- Solution matrix
- Initials of analyst preparing standard
- Date of preparation
- Expiry date (optional)

Standard concentrations need to be verified either by cross-checking "old" against "new" (assuming "old" has been characterised for traceability) or by comparison with a reference material. NIST traceability of calibrations standards has caused some confusion for laboratories and this is currently being addressed by NATA. Needless to say, beware of claims of "NIST traceability" without hard and exact supporting evidence. Indeed, the old adage of "buyer beware" holds for many materials purporting to be certified reference materials, unless a statement of their traceability is included with the information accompanying the material.

5. Quality Assurance Requirements

Quality assurance consists of two separate but related activities: quality control and quality assessment. Quality control (QC) techniques include all practices and procedures that lead to statistical control and to the achievement of the accuracy requirements of the measurement process[5]. This means that the ICP-MS analyst must include the following:

(i) Evaluation of reagent blanks

(ii) Monitoring intensities of internal standards

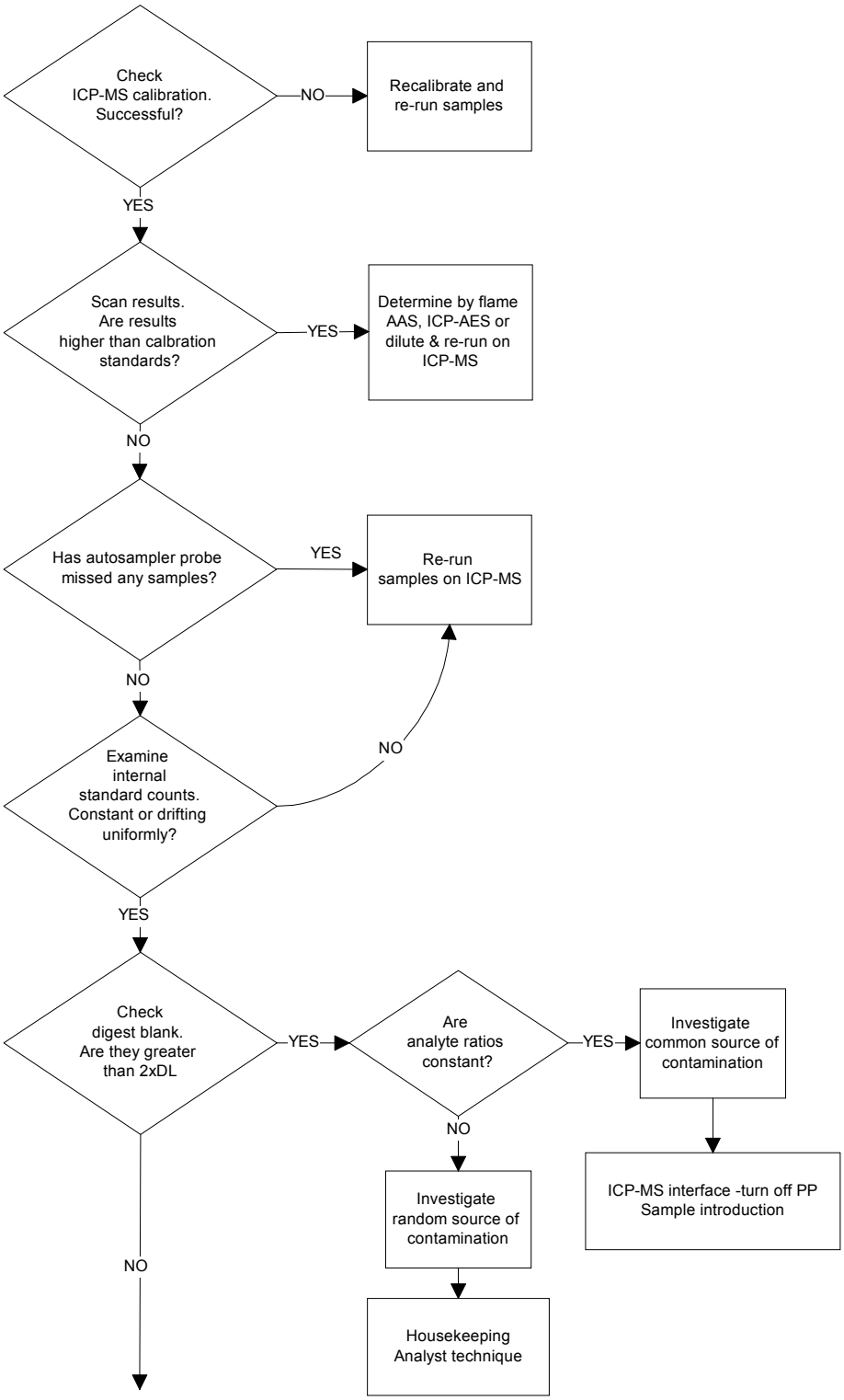
(iii) Monitoring of duplicate sample analysis

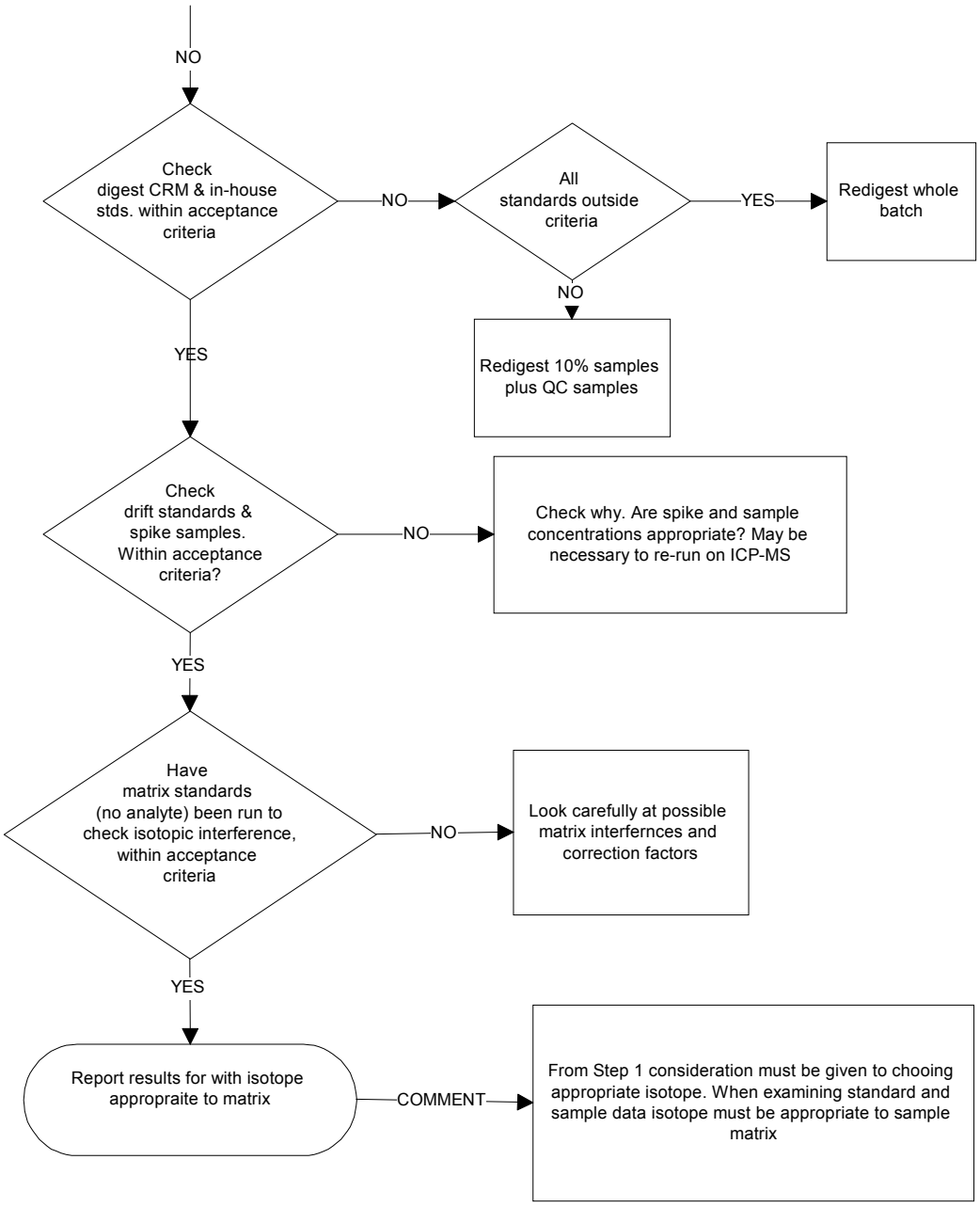
(iv) Monitoring solution concentrations are within the standard calibration range

(v) Monitoring recoveries of matrix spike additions - this is particularly relevant for environmental analysis - set acceptance criteria for QC results and review criteria periodically to ensure their effectiveness and applicability

(vi) Monitoring of control standards (CRMs or validated in-house standards) that have a high degree of similarity to actual samples analysed - set acceptance criteria for QC results and review criteria periodically to ensure their effectiveness and applicability

The flowchart shown below outlines the quality control steps typically reviewed during the quality assessment of an ICP-MS job run. If this flowchart is used effectively, the ICP-MS analyst can ensure that results from an analytical run are suitable to report.


Check ICP-MS calibration. Successful?
NO
Recalibrate and re-run samples
YES
Scan results. Are results higher than calbration standards?
YES
Determine by flame AAS, ICP-AES or dilute & re-run on ICP-MS
NO
Has autosampler probe missed any samples?
YES
Re-run samples on ICP-MS
NO
Examine internal standard counts. Constant or drifting uniformly?
NO
YES
Check digest blank. Are they greater than 2xDL
YES
Are analyte ratios constant?
YES
Investigate common source of contamination
NO
Investigate random source of contamination
ICP-MS interface -turn off PP Sample introduction
NO
Housekeeping Analyst technique



Probably the simplest method to monitor sample performance is through Control Charting. Control charts were first developed in 1934 by Dr Walter Shewhart[6] to monitor the outputs of manufacturing processes. In analytical chemistry, control charts are the simplest and most convenient method to monitor accuracy and precision of analytical methods. A control chart can be maintained for any individual repetitive quality control check such as analysis of reference materials, analysis of a constant concentration matrix spike or a matrix spike duplicate, these measurement results are plotted sequentially (time-ordered). X control charts assume that the distribution of values around the mean is binomial and the following distribution should be obtained:

Mean ± 1σ = 68% of observations
Mean ± 2σ = 95% of observations (Warning Limit)
Mean ± 3σ = 99.7% of observations (Control Limit)

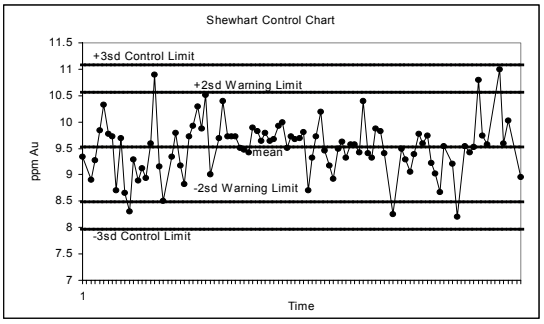


Figure 3. Shewhart control chart showing warning and control limits

With the establishment of control and warning limits based on 95% and 99.7% respectively, a system in statistical control should rarely exceed the limits. If out of control data is observed too often then either the limits are not realistic or the system has problems that need correction. Figure 4, below shows a Shewhart control chart derived from analysis of an SRM over an eighteen-month period. Although the laboratory recorded results in a QC database, they were never used to monitor analytical performance.

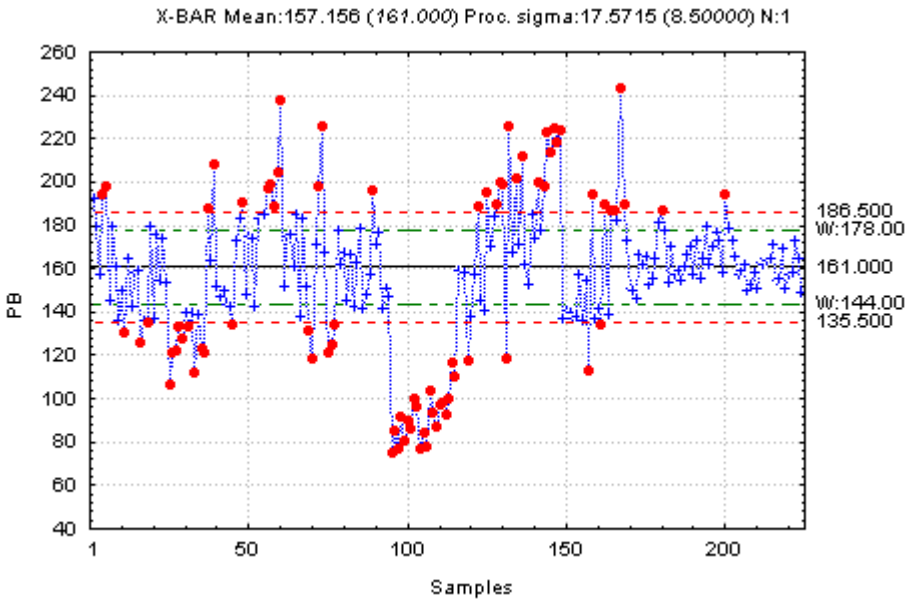


Figure 4. Shewhart control chart for lead analysis of a CRM.

Trend analysis of charts can show early warning of trouble and indicate the need for preventative action, i.e. series of points proceeding in the same direction (up or down) or points residing on the same side of the centre line. Remember that the probability of occurrence of seven consecutive results, as described above, is about 1 in 100.

On consideration of the foregoing discussion it should now be obvious that NATA accreditation for ICP-MS methods has no special requirements but rather laboratories are simply required to embrace the basic elements of Quality Assurance.

References

1. ISO/IEC 17025 Application Document – Supplementary Requirements for Accreditation in the Field of Chemical Testing, Version 1, 2000
2. About NATA and Accreditation, Version 1, 2000
3. NATA Rules – Memorandum of Association, Articles of Association, By-Laws, October 1999
4. EURACHEM/CITAC Guide, Quantifying Uncertainty in Analytical Measurement, Second Edition, 2000

5. Taylor, J.K., “Quality Assurance of Chemical Measurements”, Lewis Publishers Inc., Michigan USA, 1987.
6. Shewhart, W.A., Statistical Method from the Viewpoint of Quality Control, The Graduate School, U.S. Department of Agriculture, Washington DC, 1939