TECHNICAL REPORT

ISO/TR 18336

First edition
2016-02-15

Guidelines for good XRF laboratory practice for the iron ore industry

Lignes directrices de bonnes pratiques de laboratoire de spectrométrie de fluorescence de rayons X pour l'industrie du minerais de fer

Reference number
ISO/TR 18336:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

Introduction

This Technical Report is intended for use in conjunction with other International Standards for the chemical analysis of iron ores. Although it was written for a high through-put iron ore laboratory, the procedures described can be modified to suit other industry or laboratory requirements. Some laboratories may find the recommended frequency of testing recommended by this Technical Report to be excessive for their situation or the precision required by them. In this case, the operator may use their informed discretion to adapt the recommendations of the guidelines to their situation.

Guidelines for good XRF laboratory practice for the iron ore industry

1 Scope

This Technical Report specifies recommended quality control procedures for XRF laboratories operating within the iron ore industry.

2 Reagents

All reagents (including fusion fluxes and calibration reagents) should be purchased from reputable suppliers and should meet the minimum requirements for purity as listed in ISO 9516-1. All reagents should have a batch number and, where available, a certificate of analysis. Details of purchased reagents (supplier, amount purchased, quality, and batch number) should be recorded. These records should include what the reagents are used for. For batches of flux, the records should indicate which samples were analysed with a particular batch.

2.1 Fusion flux

As the levels of contamination may vary from batch to batch of flux, the purity of fusion fluxes should be checked prior to use. This can be achieved by fusing duplicate beads of pure silica and iron with the new flux, and analysing these along with beads prepared using a previously tested (certified) flux. Background concentrations should not exceed 10 ppm to 20 ppm (as compared to a certified batch of flux) for each of the following oxides Mn_3O_4, SnO_2, V_2O_5, Cr_2O_3, Co_3O_4, NiO, CuO, ZnO, As_2O_3, PbO, BaO, Na_2O and Cl and the sum of the positive differences should not exceed 40 ppm to 50 ppm.

The concentrations of the oxides should not exceed 0,01 % for each of the following oxides Fe_2O_3, SiO_2, CaO, Al_2O_3, TiO_2, MgO, K_2O and P_2O_5 (the absolute sum of the differences should not exceed 0,02 %), while backgrounds should not differ by more than 0,01 %. Sulfur (reported as SO_3) can frequently vary by 0,05 %. Where flux does not conform to specifications, a second duplicate set of beads (made with old and new flux) should be prepared by a different operator on the same day, or by the same operator on a different day. If the material fails to meet the minimum specifications, the supplier of non-conforming flux should be contacted and a replacement batch obtained and tested.

Where non-significant deviations are observed for major and trace elements between flux batches, these beads can be used to update calibration intercepts. In all cases, records of calibration prior and after amendment should be kept.

Prior to calibration amendment, the concentration levels of all previously analysed blank beads (prior to calibration amendment) should be plotted, and trends noted. If consecutive sets of duplicate beads show consistent positive concentration increases, previous beads should be refused and re-run, and the trends confirmed or negated.

Where laboratories elect to use additive fluxes (oxidizing, release agents or internal standard compounds), the homogeneity of the flux should be tested, assessed and compared against the quoted quality or against a flux batch that is known to be homogenous. Testing methods include direct measurement of added analytes, or indirect measurement of a quality parameter (ignition loss). An example of flux testing results can be found in Annex A.

As calibrations would have been amended, trends will be seen as negative values progressing towards a more positive result. If past expected trends cannot be replicated, the XRF instrument (calibration, monitor) should be inspected. If previously seen trends are repeated, flux suppliers should be contacted, and the problem discussed.

2.2 Calibration reagents

Reagents used for XRF recalibration should be checked in a similar manner to that used to check flux (by preparing both the old reagent and the new reagent in the same type of flux). Here the level of contaminants should not exceed those reported on the reagent supplier's certificate of analysis. Please note that it is common for reagent suppliers to report reagent purity based on an "as difference" basis. Consequently, a 99,999 % reagent may have only been analysed for a single contaminant whose content is less than 1 ppm. However, this reagent may contain other contaminants which have not been analysed whose concentration may be significant.

Alternatively, if no in-house high purity reagent is available, small quantities of analysed reagents may be obtained from reputable laboratories. In addition, where reagents are suspected of contamination, they can be externally analysed.

3 Apparatus

All equipment used to prepare and measure fused glass beads should be checked on a regular basis in accordance with the schedule set out in Table 1. The frequencies defined in Table 1 are those required by a high through-put iron ore laboratory. As this Technical Report is a guideline rather than a prescriptive standard, laboratories with lesser demands can modify the figures accordingly.

3.1 Bead preparation equipment

All equipment used for the production of fused glass beads (such as balances, fusion ware, fusion furnaces and sample drying equipment) should be installed, maintained and operated in accordance to the manufacturer's recommendations. The external surfaces of all fusion furnaces should be inspected at the commencement of each shift for excessive dust and glass fragments or glass spills. If any spillage is detected it should be cleaned up before further use. On a weekly basis, or if spillage has occurred, fusion furnaces should be allowed to cool and the interior should be inspected for faults (broken or loose furnace linings that may contaminate samples) and cleaned (and repaired if necessary). Fusion furnace temperatures should be checked weekly for accuracy and uniformity of temperature using a calibrated reference thermocouple. As a general rule, an independent performance audit of bead making equipment (including any environmental factors) should be performed yearly.

Table 1 — Summary of frequency of tests and procedures

Frequency	Test
Each shift	Run Monitors[a]. Monitor data should be checked for drift (3.2.4). If problems/issues are suspected within the instrument, then increased monitor samples should be run throughout the day. At the commencement of every shift, all laboratory personnel involved in the production of XRF fusion beads should prepare at least one quality control sample (reference or certified reference material) in duplicate (5.1).
	At the commencement of every shift, all laboratory personnel involved in the production of XRF fusion beads should prepare at least one quality control sample (reference or certified reference material) in duplicate (5.1). These specimens should be measured and the results evaluated before any unknown specimens are validated.
	Monitor chilled water flow rate and temperature (3.2.2). Monitor compressed air pressure (3.2.2). Monitor detector gas flow rate and pressure (3.2.2). Monitor instrument error logs (3.2.2). Inspect fusion furnaces and clean if necessary (3.1).

[a] Monitor is used exclusively for drift correction. Where the power settings have not changed more than 1 kW from the nominal operating power and the spectrometer has been shown to have achieved stability over a desired time frame (3.2). Monitor updates can be performed for the corresponding time frame.

Table 1 *(continued)*

Frequency	Test
Weekly	Check resolution and pulse shift for flow detectors (3.2.2). Perform disc making precision tests for new operators. Once competent, perform checks monthly (4.3). Clean interior and exterior of fusion furnaces (3.1). Check furnace temperature and uniformity of temperature (3.1).
Fortnightly	Back up spectrometer data files, calibrations and configurations (3.2.3). Measure flatness of moulds and casting dishes (4.4).
Monthly	Perform disc making precision tests for competent operators (4.3) or automated equipment. Clean monitors (3.2.4).
Three-monthly	Prepare synthetic calibration standards (SynCals) in quadruplicate and compare results to calibration data (5.3).
Half-yearly and prior to calibration or after major repairs	Perform precision tests in ISO/TR 18231. Perform long-term stability tests in ISO/TR 18231. Perform detector linearity tests in ISO/TR 18231.
Yearly	Check all bead preparation equipment (balances, fusion ware, fusion furnaces and environmental conditions) (3.1).

[a] Monitor is used exclusively for drift correction. Where the power settings have not changed more than 1 kW from the nominal operating power and the spectrometer has been shown to have achieved stability over a desired time frame (3.2). Monitor updates can be performed for the corresponding time frame.

3.2 XRF Spectrometer

3.2.1 General

All XRF instruments should be tested to ensure conformance to ISO/TR 18231 for instrument precision and detector linearity. Precision testing should be performed twice yearly, or whenever major repairs to an XRF (replacement of detector, X-ray tube, generator or measurement electronics) or to the chilled water circuit has been performed.

For all instrument tests, a relative precision of better than 0,03 % coefficient of variation is required for the analysis of Fe in iron ores, and so spectrometer precision and linearity tests should be carried out using accumulated count rates of 2×10^7 counts for each measurement. Where separate counting channels are used for the different elements (simultaneous instruments), or where the detector is changed, the dead time of each channel and each detector should be determined independently, using an appropriate wavelength for the detector/crystal combination.

Long term (24 h) XRF stability tests should be performed using various kV and mA settings, detector, collimator, and crystal combinations. All tests should be conducted biannually at a significance level of 0,03 % (2×10^7 counts), and immediately prior to performing an XRF calibration. Instruments should exhibit short-term stability in the order of 0,03 % over a 6 h to 12 h period. If an XRF fails to meet desired precisions, instrument manufacturers should be consulted and the cause of poor instrument stability rectified.

Additional spectrometer tests can be found in Annexes I, J and L.

3.2.2 Each shift/weekly spectrometer checks

As the operation and performance of an XRF spectrometer is highly dependent on the quality of external services such as chilled water (flow rate and temperature), compressed air (pressure) and detector gas (flow rate and pressure), the status of these supplies should be monitored on a daily basis and the results recorded in a check sheet. In addition, error logs should be checked daily and corrective action taken when faults are reported. As spectrometers possess internal services (such as chilled water flow, temperature and conductivity, internal spectrometer temperature and instrument vacuum levels), the status of these should be monitored. Note that as all modern XRF software possesses spectrometer status screens, these should be configured to be open in a minimised window so that the status of spectrometer services can be monitored.

As the performance and condition of spectrometer flow detectors are highly dependent on the quality of detector gas, the resolution and pulse shift should be checked on a weekly basis. Checks should be performed with regard to the manufacturer's recommended procedure. Minor changes in pulse shift (≥2, ≤5) should be corrected (note as spectrometers typically have different detector voltage settings for each crystal, all should be checked when tests and amendments are performed). Significant changes in detector resolution or pulse shift position should be investigated as these may be caused by window failure or gas contamination (leaks).

3.2.3 Hardware and software backup

A backup of spectrometer data files, calibrations and configurations should be performed every two weeks. This backup should be stored on a remote computer or shared data storage area. XRF software can be stored in a secure area within the laboratory.

It is also highly recommended that XRF software and spectrometer data (calibration files and configuration settings) be loaded on several computers (laptops preferred) which possess the necessary hardware (serial ports) required to connect and communicate with the spectrometer. These computers will serve as a hardware and software backup.

3.2.4 Instrument monitors

To compensate for drifts in X-ray tube output intensity, all X-ray measurements should be made relative to a monitor disc. Although different monitor discs could be used for each component, it is most convenient to use a single disc, containing all components to be measured. The requirement of the monitor disc is that it be stable over a long period. Also, the monitor should contain sufficient of each element to ensure that the intensity of each analytical line is much higher than the intensity of the background and can be measured with the required precision in a reasonable time. Suitable stable monitor discs made for the analysis of iron ore are available commercially.

The essential property of the monitor is its long-term stability. It should be flat so that it can be placed reproducibly in the sample holder of the XRF, and the analytical surface should be polished for easy cleaning. Monitors should be cleaned in accordance with manufacturer's specifications or every two months with ethanol or acetone. In-house prepared borate monitors are not recommended as they are unstable and deteriorate over time.

The accumulated counts for the various elements should be such that they are higher than those from iron ores, so that precision is not limited by the monitor. For the major elements, including Fe, the count rate may be less than observed from iron ores, but it should be high enough that, in a short counting time, the counting error is sufficiently small. Monitors should be run every 4 h to 6 h during, and prior to the commencement of routine analyses.

Monitor count times can be determined at the time of calibration using the formula below.

The monitor count time TM (in seconds) for each element is given by Formula (1):

$$TM = 2 \times \frac{RS \times T}{RM} \tag{1}$$

where

RS is the intensity, c/s, from the calibration standard SynCal, measured for 10 s (see ISO 9516-1);

For Fe, the intensity should be measured using 100 % Fe_2O_3.

T is the required counting time (in seconds), for each element as derived in ISO 9516-1:2003, 7.2.6;

RM is the intensity, c/s, from the monitor for each analyte, measured for 10 s.

Whenever XRF spectrometer power settings are changed more than 1 kW, instrument tube instability may occur. Depending on the type of spectrometer and X-ray tube design, this instability may persist for 30 min to 60 min. Consequently, prior to measurement, X-ray equipment should be powered up for a suitable time and allowed to stabilise.

Where spectrometers are maintained at a standby setting that is less than 0,5 kW of the nominal operating power, monitors need not be run prior to the commencement of analysis. Monitor acceptance control charts should be plotted on Shewhart charts using the limits specified in the control chart section of this Technical Report.

3.2.5 Calibration validation

Once a calibration has been performed in accordance to ISO 9516-1, the method should be validated (trueness testing and conformance to method precision) using appropriate reference standards. The certified reference and other reference materials used to validate a calibration should be chosen using ISO 16042 for concentration and matrix elements.

In addition to validating a calibration using reference materials, silicon dioxide and iron oxide, pure and binary calibration standards and synthetic calibration standards (SynCals) should be analysed as unknowns to validate the calibration. Note, as the calibration and calculation algorithms are different, a slight bias between the regressed and measured chemical concentrations may occur. This bias should be not more than 1,5 times the counting statistical error (measurement precision) for 10 % of the analysed samples.

4 Fused glass beads

4.1 General

All samples, regardless if they are calibration, quality control or for routine analysis should be prepared with equal care and consideration. Consequently, all samples should be prepared using the procedures listed in ISO 9516-1:2003, 7.1.2 to 7.1.7 using competent operators. To ensure that the quality of analyses are not operator compromised or biased, all bead preparations should be operator traceable.

4.2 Storage

Beads should not be stored in desiccators containing any drying agents (such as silica gel) or in drying ovens as erroneous dust particles will contaminate the analytical surface. It is recommended that beads be clearly labelled and placed in clean re-sealable PVC bags prior to analysis and for long term storage. Where beads are to be analysed within 30 min of preparation, cooled beads should be transferred directly from the casting dish/mouldable into a clean spectrometer sample tray.

4.3 Disc making precision

All personnel/equipment involved in the production of XRF samples should be tested for disc making precision. Initially, operators should be taught by an operator who has proven experience in the preparation of fused beads. Disc making should be checked weekly, until such a time as beads can be made consistently to conform to required laboratory precisions (normally, three consecutive runs). Thereafter, disc making precision should be checked monthly. A general procedure for checking disc making can be found in Annex B, with a calculation program for measurement precision in Annex G. Where automated bead making facilities are used (weigh stations and fusion lines), all preparation lines should be tested.

As a general guide, reading errors should not exceed statistical counting errors, while disc making errors should not exceed reading errors by more than 1,5 % of the theoretical counting error. If reading errors (measurement precision) exceed those expected for counting times, this is indicative of instrument precision errors (non-stability of detectors, tube, collimators, loading errors). Alternatively, this could indicate insufficient instrument warm up time (stabilisation time). If consecutive runs (performed at longer instrument warm up periods) fail to meet desired instrument precisions, instrument manufacturers should be consulted and the cause of poor instrument stability rectified.

If disc making errors (precision) are in excess of read errors by 1,5 %, beads should be broken and refused/re-poured using exactly the same fusion ware (moulds and mouldables) used to prepare the beads. If individual re analysed bead error trends correlate previously analysed beads, this is indicative of an inherent problem in the composition of the bead. This could be due to incomplete drying of flux or oxidant or incomplete ignition of sample. Alternatively, operators may have balance problems, poor weighing technique, bead curvature problems or quantitative loss of material during transfer operations.

If disc making is found to improve following refusion and reanalysis (XRF reading errors are constant) this is indicative that the originally cast beads were not homogeneous or were poorly prepared beads (cracked, undissolved material crystallisation). If this occurs, the operation of the fusion equipment should be checked to ensure that the temperature within the furnace, the agitation and the bead cooling operation are all uniform. Where a significant loss in the ability to cast beads is encountered, inspections and tests of weighing and casting equipment should be performed (see Annex K). If these are found to be in order, the fusion parameters (agitation time, speed etc.) should be adjusted and the bead making precision rechecked using freshly weighed samples. Note that when manually operated fusion equipment is used, differences in the pouring time and cooling rates have been found to affect precision.

The results of all precision beads (including the operator name, date, equipment used and the results of any corrective actions used to improve bead precision) should be tabulated and stored.

4.4 Bead distortion (curvature and flatness)

As the X-ray intensity (and hence concentration) generated from an analytical sample is dependent on its relative geometry from the detector and X-ray excitation source, imperfections in the curvature and flatness of XRF beads (distortion) will directly affect the accuracy of analytical determinations. As the relationship between bead distortion and measurement accuracy (measured concentration) is unique for each spectrometer configuration and bead preparation technique (dilution and bead size), this relationship should be determined for each specific combination. Annex C describes a method to determine the relationship between bead distortion and concentration, while Annex D depicts modifications to test equipment. Once a relationship has been determined, bead distortion (imperfections in casting apparatus) should be assessed and rectified using the equipment and procedure described in Annex E and Annex F. Fusion ware-specific reforming tools can be purchased from the appropriate vendors.

Alternatively, moulds and casting dishes should be reformed on a weekly or monthly basis, or whenever flatness is suspected as a source of analytical error.

5 Quality control

5.1 Selection of QC samples and frequency of preparation

At the commencement of every shift, all laboratory personnel involved in the production of XRF fusion beads should prepare at least one quality control sample (reference or certified reference material) in duplicate 5.1. These specimens should be measured and the results evaluated before any unknown specimens are validated.

Quality control samples should be chosen in accordance with ISO 16042 for the reported elements. Note that any reference material that has been made to conform to ISO Guide 35 is acceptable for in-house use. Where possible, the same standards that were used to validate the calibration should be used as QC standards.

The use of duplicate beads is highly recommended as they can be used to assess operator disc making proficiency and short-term precision.

Pure silicon dioxide (99,999 % containing less than 3 µg/g of each of the other oxides listed in ISO 9516-1:2003, Table 1) should be used as a quality control sample to monitor contamination of reagents and deviations in background equivalent concentrations. Duplicate beads should be prepared at the commencement of each shift and the results plotted. Every three months, quadruplicate synthetic calibration standards (SynCals), as described in ISO 9516-1, should be prepared and the results compared to those of the calibration data.

Results for QC samples should be statistically analysed using the trueness test specified in ISO 9516-1:2003, 9.6 and the results plotted in an appropriate control chart containing Z scores. Fused bead samples which fail to pass the trueness or precision tests should be rerun or refused. If a difference between subsequent XRF analyses is greater than four times the iron analytical error (typically 0,02 % to 0,03 %), the stability or loading mechanics of the spectrometer should be tested in accordance with ISO/TR 18231.

Reanalysed beads which still fail trueness or precision tests should be refused and analysed. Samples which fail subsequent refusing and analysis should be reanalysed as an independent duplicate pair. Where consecutive duplicate beads fail trueness tests, the spectrometer and analytical balance precision should be assessed. In addition, the operation of the fusion equipment (mixing, fusion time and temperature) and condition of the fusion ware (bead curvature and contamination) should be checked and appropriate corrective action taken.

5.2 Analysis of QC and analytical samples

The accuracy and precision of routine analyses are dependent on sampling and preparation procedures. Consequently, analytical samples should be prepared in accordance with ISO 3082.

Without undertaking multiple sample analyses it is impossible to ascertain what percentage of the overall precision can be attributed to sample preparation and what can be attributed to measurement precision. With respect to analytical data, although it is desirable to analyse routine samples in duplicate, in many circumstances this is impractical due to operational limitations. Nevertheless, a proportion of analytical samples (5 % to 10 %) should be measured in duplicate.

In an ideal situation, the precision of sample preparation should be equal for both routine samples and certified reference materials used for quality control data. Therefore, where a significant precision difference is observed between quality and routine analyses, this can be attributed to poor sample preparation. In this case, the problem should be investigated and corrected.

5.3 Control charts

Charts should be constructed in accordance with ISO 7870-2 for each quality control standard and for each XRF monitor. Charts should be constructed for every laboratory technician and XRF instrument. Where multiple analytical balances and fusion equipment (furnace and fusion ware) are used in a laboratory, samples should be prepared in a way that all equipment is utilized. The Shewhart chart should be updated every time a QC sample/CRM is analysed. Significant long term trends (three consecutive biased results) should be investigated and appropriate corrective measures taken to correct this bias. Preferably, a single chart for each XRF instrument should be constructed where the technician and permutations of fusion furnaces and balances are clearly identified.

While the trueness test for each use of the CRM still applies (see ISO 9516-1:2003, 9.4), the use of the Shewhart chart is recommended to identify outliers, trends and runs, following the principles outlined in ISO 7870-2, using "tests for assignable causes". Statistical evaluations should include information pertaining to short (bead duplicate) and long term bead making precision of operators and bead making equipment. In addition, the short and long term spectrometer precision should be assessed on a weekly basis.

For pure silicon dioxide, the mean trace element concentrations should be not more than two times the measured background concentration (obtained during calibration). For a correctly calibrated XRF instrument, this should be approximately equal to half the quantification limit derived from ISO 9516-1:2003, Table 7 (using S = standard deviation). Excessive background concentrations (in the order of 10 times the measured XRF value) are indicative of gross contamination from fusion ware or fusion furnaces.

Short-term monitor drift should be not more than 0,10 % variation in counts between monitor measurements for iron, silica, calcium, manganese, aluminium, titanium, magnesium, phosphorous, sulfur and potassium. If this limit is exceeded, all measurements should be repeated. Sudden erratic changes in monitor counts should be corrected prior to analysis. Long term monitor drift should not change more than 0,5 % per year for atomic masses greater than potassium. For atomic numbers less than potassium, long term drift should not vary more than 2 % per year. Due to tube ageing, monitor values may either decrease (light elements) or increase over time.

If drift exceeds these figures, operators should investigate the cause of the drift.

5.4 Participation in proficiency test programs

All laboratories should participate in round robin proficiency test (inter-laboratory comparison) programs which conform to the guidelines stipulated in ISO/IEC 17043. These proficiency programs should be used to evaluate the laboratory's accuracy and the short-term (replicate error) and long term analysis precision. Individual laboratories results should be ranked to the overall laboratory performance by means of Z scores.

The results of proficiency programs should be made readily available to all laboratory staff. Preferentially, results should be reported graphically and should include a clear and concise interpretation of accuracy and precision of data.

Laboratories should ensure that sufficient resources are committed to maintaining records, including the outcomes of investigations of any unsatisfactory results and subsequent corrective or preventative actions. A laboratory should be able to draw its own conclusion about its performance from proficiency tests.

Annex A
(informative)

Results for flux loss on ignition testing

Table A.1 — Results for flux loss on ignition testing

Flux batch 1A				Flux batch 1B			
$w_{t,cruc}$	$w_{t,cruc}$ **plus flux**	**After furnace**	**% *LOI***	$w_{t,cruc}$	$w_{t,cruc}$ **plus flux**	**After furnace**	**% *LOI***
29,755 5	38,352 6	37,998 2	4,12	30,087 3	37,724 6	37,426 3	3,91
30,297 1	37,269 1	36,981 4	4,13	29,419 4	37,871 2	37,593 7	3,28
30,230 9	39,993 9	39,597 9	4,06	30,239 1	40,963 5	40,582 6	3,55
29,391 6	39,010 9	38,626 7	3,99	29,438 0	38,831 7	38,468 6	3,87
29,266 4	41,636 3	41,143 4	3,98	30,216 3	40,707 0	40,281 3	4,06
29,952 7	37,208 2	36,925 8	3,89	29,901 7	38,491 1	38,172 9	3,70
29,875 6	38,772 0	38,409 2	4,08	30,433 5	39,169 4	38,800 3	4,23
29,589 0	39,280 1	38,882 2	4,11	30,178 8	41,079 8	40,565 0	4,72
29,898 5	41,575 0	41,102 2	4,05	30,447 5	39,146 9	38,793 4	4,06
30,126 8	39,465 6	39,087 2	4,05	29,547 2	40,328 4	39,876 7	4,19
		Average	4,05			Average	3,96
		Std dev.	0,07			Std dev.	0,40
		% *RSD*	1,8			% *RSD*	10,1

Results of ignition trials indicate that the relative standard deviation (*RSD*) for 10 ignitions of flux batch 1B is higher than that observed for 1A. As the ignition loss is due to the decomposition of the added oxidizing agent, the percentage *RSD* and average ignition loss can be used as measure of additive homogeneity and quantity.

Annex B
(informative)

Procedure to check disc making precision

Make sure that moulds and casting dishes have been assessed to ensure flatness (4.4). Prepare between 8 and 12 beads of ignited spectroscopically pure Fe_2O_3 (99,995 % purity) using the normal dilution recipe (flux:sample:oxidant ratio) and fusion technique (fusion times and temperatures).

Using an existing iron ore analytical method as a base, create a new analytical procedure where only iron is measured and matrix corrected (all major and trace elements are removed from the calibration). Measurement times should be selected so that total accumulated counts of 2×10^7 are obtained for a precision bead.

Beads should be measured twice in succession, re-measuring the first bead at the end of each sample run. Data should be processed according to the sample calculation spreadsheet in Annex G and Annex H (a copy of the calculation program is available from CSIRO, Adelaide).

In all cases, Read error should be equal to the statistical counting error of the analytical method (≈ 0,03 % or 2×10^7 counts). Disc error should be less than 1,5 of the theoretical counting error, but preferably equal to the measurement error (when reported at 100 % Fe_2O_3 concentrations).

Annex C
(informative)

Method to determine relationship between height and concentration

The procedure to determine relationship between height and concentration is as follows:

a) Using bead measurement apparatus (Annex E) and an unmodified X-ray cup, set depth gauge reference point to zero using datum bead.

b) Using height adjustable cup (as described in Annex D), set bead height 0,50 mm lower than the datum bead height (plus 0,50 mm on depth gauge).

c) Using a flat 100 % Fe_2O_3 fusion bead, measure the iron concentration (in quadruplicate) utilizing a counting statistical error of 0,025.

NOTE A flat fusion bead can be prepared from a nominal fusion bead that has been dry lapped using 1 200 grit diamond polishing paper and machinist's surface plate.

d) Repeat measurement procedure (above) for datum heights at (−0,25, 0,00, +0,25 and +0,50) mm.

e) Plot average Fe_2O_3 concentration against difference from datum point (preparation of height/concentration relationship).

Annex D
(informative)

Production of a height adjustable cup

D.1 General

The procedure describes a method to modify an XRF sample cup and the manufacturer of shims. The principal of the described method relays on modifying an X-ray cup by a prescribed amount so that it is mounting location is offset. Shims of the appropriate thicknesses are prepared so that these can be inserted between the X-Ray cup and sample so that the mounting location can be offset. It is recommended that prior to modifying any XRF equipment the vendor (or agent) is consulted.

a) Using a standard specification spectrometer cup, reduce the thickness of the locating flange by approximately 0,50 mm. It is recommended that largest internal diameter spring loaded cup be used. Using an engraver of permanent means of marking the cup clearly identify that modified cup has been modified and that it is not to be used the analysis purposes.

b) Using (0,25, 0,50, 0,75 and 1,00) mm shim material, manufacturer spacers of appropriate size so that they can be mounted between the cup and the sample.

D.2 Guidelines for the production of a height adjustable cup

Guidelines for the production of a height adjustable cup are as follows.

a) Use an X-ray cup in which the internal proportion is approx. 10 mm larger than the fused bead size.

b) Remove lower bead locating lip from X-ray cup (tunnel bore cup).

c) Machine internal thread in cup (pitch).

d) Manufacture internal sleeve with corresponding external thread (allow provision for adjustment).

e) Manufacture datum bead from stainless steel (flatness ± 0,001 mm).

Annex E
(informative)

Bead measurement apparatus

E.1 **Plunge gauge,** measurement precision 0,001 mm, 10 mm plunge depth.

E.2 **Base,** materials and machine tolerance.

E.3 **Cup locator,** materials and machine tolerance.

E.4 **Illuminator**.

Annex F
(informative)

Flow sheet for fused bead quality

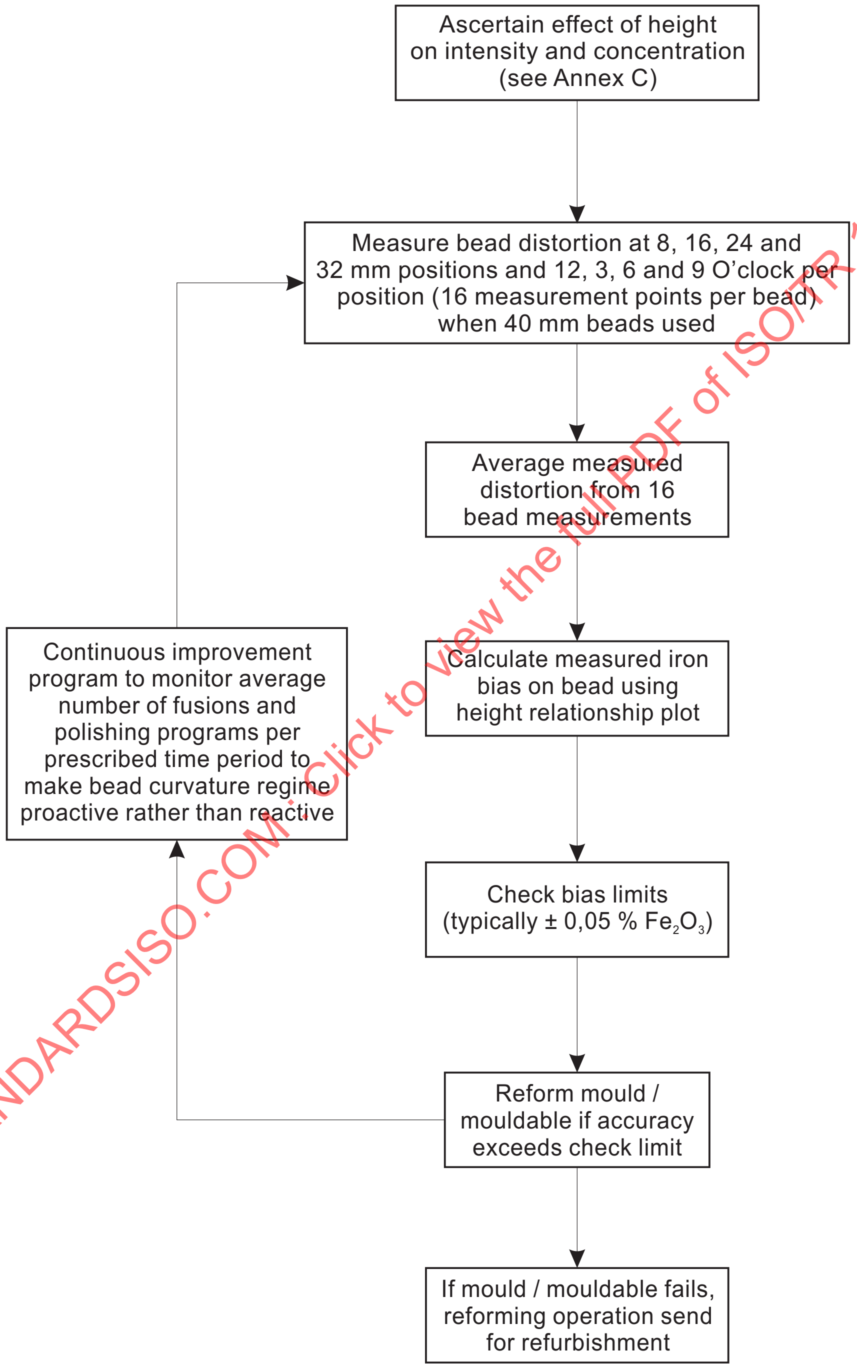


Figure F.1 — Flow sheet for fused bead quality

Annex G
(informative)

Microsoft Excel program for calculating disc precision

```
Sub Calculate()
'
' Calculate Macro
' Macro recorded 10/04/2002 by Minerals
'

Rem PROGRAM “MULTIDISCERRC” IS A MODIFIED VERSION OF PROGRAM “DISCERR” WRITTEN BY K.NORRISH, CSIRO DIVISION OF SOILS, 29.3.93
Rem “DISCERR” modified to “MULTIDISCERRC” by M.FRITZ, CSIRO DIVISION OF SOILS (3.12.98) so that the number of discs could be selected
Rem Modified by P.Fazey CSIRO Minerals to read csv files and send output to ‘inputname.TXT’.
Rem
Rem THIS BASIC PROGRAM IS FOR CALCULATING DISC ERRORS IN FE2O3 DISCS PREPARED USING CATCH WEIGHTS
Rem THE STANDARD DEVIATION FOR ALL DISCS PREPARED IS ALSO CALCULATED
Rem MOD FOR USE WITH IRON ORE WG27B-3 PROGRAM - READS ALPHAS FROM FILE
Rem CORRECTS FOR DRIFT IN MONITOR
PRG$ = “MULTIDISCERR”
'DefDbl S ****Moved to declaration section
Dim RESULT(2, 21), CS(20, 4), R(2, 21), SC(20), SWG(20), MAT(20), DIFF(20), RM(2), K(2)
Dim RowNum As Integer, W1 As Single, W2 As Single, W3 As Single, NameOfSheet As String

NameOfSheet = ActiveSheet.Name ‘Get the name of the current sheet being used.
'Worksheets(NameOfSheet).Range(“a1”).Value = NameOfSheet
Rem ************************************************************
Rem INPUT ASSAY IDENTIFICATION
'INPUT “ASSAY IDENTIFICATION (MAX 8 CHARACTERS) ”; NAM$
Rem NAM$ = NAM$
'Open NAM$ + “.CSV” For Input As #1
Rem ************************************************************
Rem INPUT NUMBER OF REPLICATE PLATES
'INPUT “NUMBER OF REPLICATE DISCS TO BE MEASURED ”, ITEMS%
Items% = Worksheets(NameOfSheet).Range(“d3”).Value
Titems% = Items% + 1
LITEMS% = Items% - 1
Rem ************************************************************
Rem INPUT STANDARD WEIGHTS
'INPUT “STD WEIGHTS OF FLUX, NaNO3, SAMPLE ”; WS1, WS2, WS3
WS1 = Worksheets(NameOfSheet).Range(“d4”).Value ‘flux
WS2 = Worksheets(NameOfSheet).Range(“d5”).Value ‘NaNO3
WS3 = Worksheets(NameOfSheet).Range(“d6”).Value ‘ sample
Rem ************************************************************
Rem INPUT DEADTIME AND SET BACKGROUND
'INPUT “INPUT DEADTIME IN MICROSECS ”; DTIM
Dtim = Worksheets(NameOfSheet).Range(“d7”).Value
Dtim = Dtim * 0.000001
b = −0.1 ‘SET APPROXIMATE BACKGROUND %
```

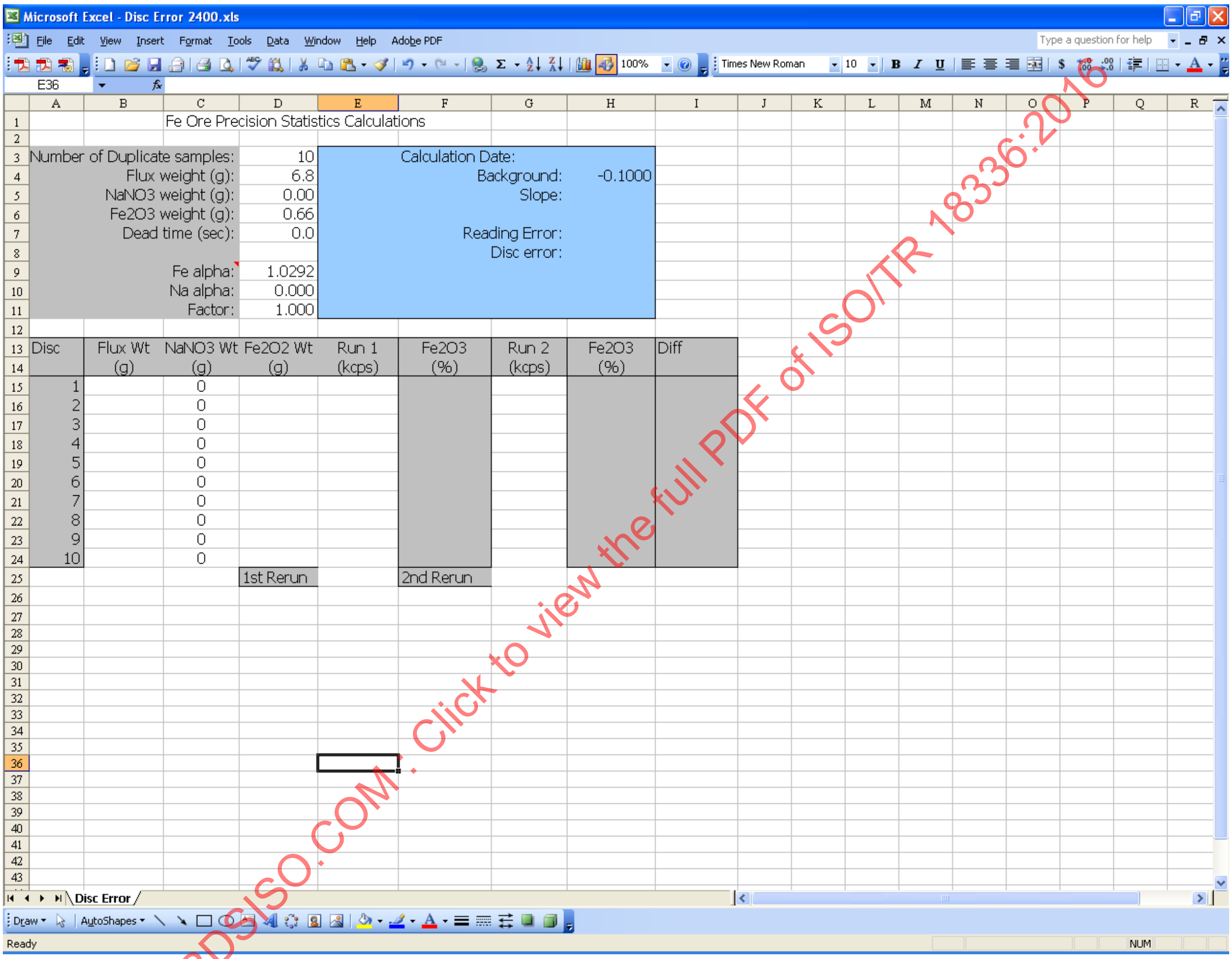
```
Rem ***************************************************************
Rem INPUT ALPHAS
'Input #1, ALPHA1, ALPHA2, T, Dummy1$, Dummy1$
Alpha1 = Worksheets(NameOfSheet).Range("d9").Value
Alpha2 = Worksheets(NameOfSheet).Range("d10").Value
T = Worksheets(NameOfSheet).Range("d11").Value
Rem ***************************************************************
Rem INPUT DATA
RM(1) = 0
RM(2) = 0
SWGx = 0
CS2x = 0
MATx = 0
For N = 1 To Items%
'Input #1, W1, W2, W3, R(1, N), R(2, N)
'MyRange = "B" + Chr$(14 + N)
RowNum = 14 + N
' this is just a test line W1 = Worksheets(NameOfSheet).Range("B15").Value
W1 = Worksheets(NameOfSheet).Cells(RowNum, 2).Value
'MyRange = "C" + Chr$(14 + N)
W2 = Worksheets(NameOfSheet).Cells(RowNum, 3).Value '3 = column C
'MyRange = "D" + Chr$(14 + N)
W3 = Worksheets(NameOfSheet).Cells(RowNum, 4).Value
'MyRange = "E" + Chr$(14 + N)
R(1, N) = Worksheets(NameOfSheet).Cells(RowNum, 5).Value
'MyRange = "G" + Chr$(14 + N)
R(2, N) = Worksheets(NameOfSheet).Cells(RowNum, 7).Value
Rem W1 = WT FLUX ; W2 = WT NANO3 ; W3 = WT SAMPLE ; R(1, N) = COUNTS,RUN 1 ; R(2, N) = COUNTS,RUN2
Rem ***************************************************************
Rem CALCULATE CONCENTRATIONS IN DISCS
SWG(N) = WS1 * W3 / W1 / WS3 'SAMPLE WT RELATIVE TO STANDARD WT
CS(N, 2) = (W2 * WS1 / W1 - WS2) * 36.46 / WS3 'NA2O EXCESS OR DEFICIT RELATIVE TO STANDARD SAMPLE WT
Rem ***************************************************************

Rem CALCULATE AVERAGE CONCENTRATION OF ITEMS% DISCS
SWGx = SWGx + SWG(N)
CS2x = CS2x + CS(N, 2)
Next N
CS2x = CS2x / Items% 'AVERAGE EXCESS NA2O
SWGx = SWGx / Items% 'AVERAGE SAMPLE MASS RELATIVE TO STANDARD SAMPLE MASS
CS1 = 100 * SWGx
Rem ***************************************************************

Rem CORRECT FOR DRIFT
'Input #1, R(1, TITEMS%), R(2, TITEMS%), Dummy1$, Dummy1$, Dummy1$ 'DISC#1 RERUN TO CHECK DRIFT
'MyRange = "E" + Chr$(15 + Items%)
RowNum = 15 + Items%
R(1, Titems%) = Worksheets(NameOfSheet).Cells(RowNum, 5).Value 'disc#1 1st rerun
'MyRange = "G" + Chr$(15 + Items%)
R(2, Titems%) = Worksheets(NameOfSheet).Cells(RowNum, 7).Value 'disc#1 2nd rerun
For l = 1 To 2
```

```
K(l) = (R(l, Titems%) - R(l, 1)) / Items%
For N = 2 To Items%
R(l, N) = R(l, N) * R(l, 1) / (R(l, 1) + (N - 1) * K(l))
Next N
Next l
Rem ********************************************************
Rem APPLY DEADTIME CORRECTION TO COUNTRATES
For l = 1 To 2
For N = 1 To Items%
R(l, N) = R(l, N) / (1 - R(l, N) * Dtim)
RM(l) = RM(l) + R(l, N)
Next N
RM(l) = RM(l) / Items% 'CALCULATE AVERAGE COUNTRATE FOR EACH RUN
Next l
Rem ********************************************************
Rem CALCULATE AVERAGE MATRIX CORRECTION
MATx = 1 + 0.01 * ((CS1 * Alpha1) + (CS2 * Alpha2))
Rem *******************************************************
Rem CALIBRATION
S = 0: SQ = 0
For l = 1 To 2
e = (100 - b) * SWGx / (RM(l) * MATx)
Rem ********************************************************
Rem CALCULATION OF RESULTS AND STATISTICS
For N = 1 To Items%
RESULT(l, N) = (e * R(l, N) * (1 + 0.01 * CS(N, 2) * Alpha2) + b) / (1 - e * 0.01 * R(l, N) * Alpha1) / SWG(N) 'MATRIX
CORRECTION
SC(N) = SC(N) + RESULT(l, N)
S = S + RESULT(l, N) ' SUM
SQ = SQ + (RESULT(l, N)) ^ 2 ' SUM OF SQUARES
Next N
Next l

Rem CALCULATE READING ERROR AND DISC ERROR
For N = 1 To Items%
SCQ = SCQ + SC(N) ^ 2
Next N
DISCSS = SCQ / 2 - S ^ 2 / (2 * Items%)
TOTALSS = SQ - S ^ 2 / (2 * Items%)
READSS = TOTALSS – DISCSS
ReadErr = Sqr(READSS / Items%)
DiscErr = Sqr(Abs((DISCSS / LITEMS% - READSS / Items%) / 2))
Rem DIFFERENCE BETWEEN RUNS
For N = 1 To Items%
DIFF(N) = RESULT(1, N) - RESULT(2, N)
Next N
Rem ********************************************************
'Open NAM$ + ".TXT" For Output As #99
Rem PRINT RESULTS
'Print #99, "FILENAME = "; NAM$; " "
'Print #99, "PROGRAM = "; PRG$; " "
'Print #99, "DATE = "; Date$; " "
Worksheets(NameOfSheet).Range("H3").Value = Date$
```

```
'Print #99, “DEADTIME = “; USING; ”#.###^^^^”; Dtim
'Print #99, “BACKGROUND = “; B; ” ”
Worksheets(NameOfSheet).Range(“H4”).Value = b
'Print #99, “ERROR =”; E; ” ”
Worksheets(NameOfSheet).Range(“H5”).Value = e
'Print #99,
'Print #99,
'Print #99, ” RUN 1 RUN 2 DIFF”
For N = 1 To Items%
'Print #99, “SAMPLE “; N; USING; ” ###.### ”; RESULT(1, N); RESULT(2, N);
'Print #99, USING; “#.###”; DIFF(N)
'MyRange = “F” + Chr$(14 + N)
RowNum = 14 + N
Worksheets(NameOfSheet).Cells(RowNum, 6).Value = RESULT(1, N)
'MyRange = “H” + Chr$(14 + N)
Worksheets(NameOfSheet).Cells(RowNum, 8).Value = RESULT(2, N)
'MyRange = “I” + Chr$(14 + N)
Worksheets(NameOfSheet).Cells(RowNum, 9).Value = DIFF(N)
Next N
'Print #99,
'Print #99,
'Print #99, “ READING ERROR = “; USING; ” #.##### ”; READERR
'Print #99, “ DISC ERROR = “; USING; ” #.##### ”; DISCERR
'Print #99,
Worksheets(NameOfSheet).Range(“H7”).Value = ReadErr
Worksheets(NameOfSheet).Range(“H8”).Value = DiscErr
'

End Sub
```

Annex H
(informative)

Data input screen for calculating disc precision



Fe Ore Precision Statistics Calculations

Number of Duplicate samples:	10
Flux weight (g):	6.8
NaNO3 weight (g):	0.00
Fe2O3 weight (g):	0.66
Dead time (sec):	0.0
Fe alpha:	1.0292
Na alpha:	0.000
Factor:	1.000

Calculation Date:
Background: -0.1000
Slope:
Reading Error:
Disc error:

Disc	Flux Wt (g)	NaNO3 Wt (g)	Fe2O2 Wt (g)	Run 1 (kcps)	Fe2O3 (%)	Run 2 (kcps)	Fe2O3 (%)	Diff
1		0						
2		0						
3		0						
4		0						
5		0						
6		0						
7		0						
8		0						
9		0						
10		0						
			1st Rerun		2nd Rerun			

Figure H.1 — Data input screen for calculating disc precision — Example

Annex I
(informative)

Loss of accuracy with no loss of precision

I.1 Major elements (no correction of drift)

a) Drift correction not updating (manually check correction) — Annex M.

b) Dirty/contaminated monitor (Na, Cl contamination or oil build up reducing low atomic number intensity).

c) Change in detector linearity — check dead time as given in ISO/TR 18231.

d) Preparation of samples (obvious measured Fe):

  1) Flux moisture content (results biased high/low);

  2) Bead curvature (results biased high/low);

  3) Sample drying (results biased high/low);

  4) Contaminated samples/standards.

e) Catastrophic failure of major XRF component — may or may not be seen in analytical results; obvious in monitor drift factors:

  1) Tube filter — certain wavelengths;

  2) Collimator — certain channels;

  3) Mask (Be) — certain wavelengths (low sensitive low atomic number elements);

  4) Detector electronics — loss of counts;

  5) Failure of specific turret position (test each position independently and compare results for each position).

I.2 Trace elements (change in backgrounds)

a) Results biased low (loss of counts):

  1) Crystal degradation — Loss of background intensity (common in Mg TlAP crystal);

  2) Loss of vacuum — Low atomic number elements more severely affected;

  3) Shift pulse height — check specific crystal combinations:

    i) Leaking detector windows (high gas flow, poor vacuum);

    ii) Change in gas pressure/temperature (bottle and / or ambient);

    iii) Leaks in flow gas lines;

   - iv) Change detector gas PHD never reset, or PHD reset with insufficient gas flush time.

b) Results biased high (increase of counts):

   1) Contamination of reagents (flux specific, split of standards);

   2) Backgrounds increase from tube impurities (Cr, Ni etc.);

   3) Contamination in spectrometer — broken beads;

   4) Change in sample to flux ratio — weighing errors (flux has absorbed moisture). This is particularly the case with fluxes containing pre weighed oxidising agents.