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Assignment of purity to primary metal calibrants using pin-cell VG 9000 glow discharge mass spectrometry : a primary method with direct traceability to the SI international system of units?

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**ASSIGNMENT OF PURITY TO PRIMARY METAL CALIBRANTS USING
PIN-CELL VG 9000 GLOW DISCHARGE MASS SPECTROMETRY - A
PRIMARY METHOD WITH DIRECT TRACEABILITY TO THE SI
INTERNATIONAL SYSTEM OF UNITS**

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Abstract

A measurement model based on the use of pin-cell glow discharge source coupled to a VG 9000 sector field mass spectrometer (GD-MS) for the assignment of purity of high-purity metals, i.e., relative mass fraction of metal matrix, $w(M)$, is presented. A mass balance approach to the calculation requires the determination and summation of impurity mass fractions of all extraneous elements present, including non-metals and gases. It is argued that a primary method of measurement arises to yield *direct* traceability of results to the SI. The major source of uncertainty in the traceability chain stems from the need to adjust the initially estimated quantity values of each impurity element by a relative sensitivity factor "influence quantity" (RSF_M^e), potentially derived from *ab initio* calculations, but also validated through calibration with Certified Reference Materials. It is shown that the method is sufficiently well understood that a measurement equation can be written down in which the values of all parameters have dimensions in SI units, thereby conferring metrological traceability to these units; that all contributions to uncertainty of measurement can be quantitatively evaluated, underpinning the metrological traceability; and that the performance of GD-MS in CCQM key- and pilot-comparisons of trace elements in complex metal matrices is in conformance with claimed capabilities. The applicability of the approach to metals in the >3N range of purity shows that fit-for-purpose expanded uncertainties <0.005 % relative can be conservatively achieved for $w(M)$.

1. Introduction

Accreditation of testing and calibration laboratories to ISO/IEC 17025:2005 and reference material producers' compliance with ISO Guide 34 necessitates that reported results are accompanied by a statement of traceability [1]. The International Laboratory Accreditation Cooperation (ILAC) considers one criterion for confirming metrological traceability to be a demonstrated unbroken metrological traceability chain to an international measurement standard or a national measurement standard. Links to SI units may thus be achieved by reference to primary realizations of the SI units, or agreed representations of SI units based on fundamental physical constants, or secondary standards calibrated by a (another) National Metrology Institute.

Traceable to the SI ideally confers temporal and spatial comparability of measurement results. Traceability is defined as [2] "the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty". For measurements with more than one input quantity in the measurement model, each of the input quantity values must be metrologically traceable and the calibration hierarchy thus forms a branched structure or network [2]. As such, traceability can only be claimed if results are accompanied by an uncertainty statement based on traceability of all references, chemical and physical, as well as on contributions to procedural uncertainty. In the field of analytical chemistry, the purity of calibration standards is one such input variable to be considered when assessing an entire traceability chain [3], but it is often unavailable or overlooked because of the demand on resources needed for value assignment [4].

As exemplified by the recent reports of Zhou *et al.* [5] and Westwood *et al.* [6] (and references therein), there are two experimental approaches currently utilized for purity assessment: determination of the principal component by a direct (primary) method of measurement such as coulometry, titrimetry or gravimetry; or the determination of all possible impurities whose sum is subtracted from the ideal purity of 100 %. The latter approach is often preferred when dealing with high-purity materials, despite an enhanced investment of time, because primary methods too frequently lack the required

specificity or are unable to realize a desired target uncertainty of 10^{-4} relative [7]. This latter limitation for inorganic calibrants stems from a desire to achieve an uncertainty at least one order of magnitude lower than that available using the most precise comparator methods such as isotope dilution mass spectrometry and “high-performance” inductively coupled plasma optical emission spectrometry [8] for value assignments of measurands in real samples. Utilizing such mass balance methodology can achieve fit-for-purpose uncertainty targets for purity when the material to be characterized is initially of high purity because the relatively large uncertainties associated with the quantitation of individual impurity elements contribute negligibly to the overall result when they are present at mass fractions below 100 mg/kg. Thus, for mass fractions of the pure metal, $w(M)$, ranging from 0.999 to 0.999999 purity, calculated expanded uncertainties for assigned purity, based on a conservative semi-quantitative approach (i.e., a factor of two uncertainty) for the determination of each impurity element, lie in the range 0.02 % to 0.00002 % relative. In this vein, researchers at BAM (Federal Institute for Materials Research and Testing, Germany) [4, 9, 10], have successfully achieved purity assignments for 10 primary standards of pure metals and compounds over the past decade and are now involved with a number of European partner laboratories in a concerted EMRP project (SIB09) to achieve such objectives on an enhanced scale [11].

Primary methods for the measurement of amount of substance are considered to be an essential first link in the traceability chain because they do not require prior knowledge of any measurement of the same quantity [2, 12], allowing the value of an unknown to be measured in terms of a particular SI unit without reference to a standard or measurement already expressed in that unit. In the absence of *a priori* available primary calibrants for impurities of interest, it would appear from the above that a circular unresolvable problem arises with all subsequent attempts to establish purity assignments by instrumental analyses in that comprehensive traceability chains cannot be accomplished [4]. In the long-term, an iterative approach will serve to avoid this conundrum in that availability of a first generation of well-characterized primary calibrants can be used to establish traceability chains for quantitation of impurities in

second generation materials whose resultant combined uncertainties will be reduced and a “tighter”, more direct, SI traceability scheme ultimately established.

Glow discharge mass spectrometry (GD-MS) is one of the most comprehensive and sensitive techniques currently available for determination of the composition of solid materials [13]. Direct current GD sources are generally confined to use with conducting and semi-conducting materials whereas rf sources permit even non-conductors, such as glass and Teflon, to be interrogated with limits of detection of elemental impurities at the ng/g and lower range and with linear response over more than 10 orders of magnitude [13 - 16]. Independence of sample sputtering and ionization processes in these sources satisfies, to a first approximation, the requirements of a primary method of measurement in that semi-quantitative mass fractions for each impurity element are directly derived from ion beam ratio data (i.e., ion beam *currents* generated at the detectors for impurity isotope:metal matrix isotope) without the need for any instrument calibration using external standards [17, 18]. Results are thus *directly* traceable to the SI. Currently, quantitative analysis is typically and conveniently achieved following calibration of the instrument with Certified Reference Materials (CRMs) matched to the sample matrix whereby elemental response factors (frequently termed relative sensitivity factors, RSFs) are derived and used to make minor adjustments of the initial results for mass fractions obtained from the ratios of raw current data. The RSF is simply the reciprocal slope of a virtual calibration curve, based on the assumption that the curve is linear and does not have an intercept. It is defined as follows:

$$\text{RSF}_M^e = I_M / I_e \times w_M^e \quad (1)$$

where I_M and I_e are the ion beam intensities (corrected for isotopic abundance) generated for the impurity element (measurand “e”) within “M” as the metal matrix and w_M^e is the mass fraction of “e” present in metal matrix “M”. For the purpose herein of advancing arguments relating to traceability, such RSF values will also be referred to as “influence quantities”. These concepts are delineated in more detail below (see section 2.2.3).

The GD-MS facility at the National Research Council of Canada (NRC) has been accredited (as a testing laboratory) by the Standards Council of Canada (Canada's National Accreditation Body under ILAC) to ISO/IEC 17025 for more than a decade. Using the RSF approach, the NRC has established calibration and measurement capability claims (CMCs) for purity assessment in Appendix C of the BIPM key comparison database (KCDB) for 22 high-purity metals [19]. The capabilities document characterization of pure metals (3N to 7N) yielding very conservative expanded uncertainties ($k=2$) of 0.005 to 0.0000005 kg/kg, respectively. Currently, coverage is limited by the availability of SI traceable CRMs from which RSFs can be calculated (or validated). It has been demonstrated that, in principle, this shortcoming can be overcome by gravimetrically preparing pressed pure metal matrix powders quantitatively doped with known amounts of pure solutions of all relevant trace impurities to be determined in the matrix [20 - 22]. Such procedures are technically challenging, but have been specified in detail for both flat-cell [20, 21] and pin-cell source geometries [22], with measurements being made using both Element GD [20] and VG 9000 [21, 22] mass spectrometers.

Herein, we report on the methodology adopted by the NRC to assess and assign purity of high-purity metals (>3N) using a VG 9000 GD-MS operating with a pin-cell cathode, realizing fit-for-purpose characterization of such materials to yield *primary transfer standards* with *direct* traceability to the SI. In deference to the title of this article, two routes are explored and discussed for achievement of this objective: the first, based on a proposed primary (direct) reference measurement procedure which provides *direct* traceability of results through the shortest measurement chain and a second, based on calibration of the instrument with available CRMs, yielding an *indirect* traceability chain to the SI through such international standards.

Although arguments may be advanced to place other atomic spectroscopic techniques on a similar basis to (conceptually) provide results which are directly traceable to the SI [23], they are significantly weaker. Almost all require prior calibration that links response either *directly* to "pure" substances of known composition (i.e., purity), such as ICP-OES and -MS, or *indirectly* (such as spark-OES) to matrix CRMs, which

themselves have been certified using analytical methods calibrated *via* linkages to the same such "pure" substances. Availability of fast, simultaneous multi-element acquisition platforms for ICP-OES and -MS, such as those based on time-of-flight techniques or CCD/CID devices, can likewise take advantage of a ratio of detector response, as argued herein for GD-MS [24], abrogating these drawbacks. However, it is the influence quantities required to adjust initial estimates of primary raw data that are not yet reliably available for these techniques, despite their historically lengthy usage in the laboratory. Moreover, the majority of other techniques require extensive sample preparation and processing, introducing potentially non-quantitative steps into a lengthened traceability chain and are typically unable to provide comprehensive elemental coverage to include non-metals and gases, as does the GD-MS approach.

2. Experimental

2.1. GD-MS instrumentation

Measurements were performed on a VG 9000 (VG Microtrace, Windford, UK, subsequently supported by Thermo Fisher Scientific) reverse Nier Johnson magnetic sector high resolution mass spectrometer fitted with a pin-source tantalum cell that is cooled to near liquid nitrogen temperature (to minimize out-gassing as the discharge heats). Mass resolution up to 10,000 is available to minimize molecular interferences arising from atmospheric background gases as well as sample matrix-derived species. Thus, determination of C, N and O amount content at sub-mg/kg levels is readily achievable. The instrument is routinely operated at 4000 resolution. A combination of Faraday and Daly detector systems that are conveniently cross-calibrated through use of Ar (^{38}Ar and ^{40}Ar) isotopes from the discharge gas permits impurity elements to be quantitated at ng/g mass fractions. In our laboratory, the Faraday ion currents lie in the range 1×10^{-14} A to 10^{-9} A, whereas the Daly is operated between 5×10^{-19} A and 5×10^{-13} A, yielding some 10 orders of magnitude of linear range. All calculations performed on raw data generated during operation are conducted by the spectrometer operating system and, thereafter, results are exported to a laboratory information management

system (LIMS) for report generation, obviating human intervention and potential transcription errors.

2.2.2. *Sample preparation*

Samples comprise high-purity (>3N) solid metals which have been machined to dimensions of 2.5 x 2.5 x 18 mm. Once rendered to such shape, they are chemically etched to remove any traces of contamination which may have been adventitiously introduced; this is achieved in a clean hood using dilute solutions of ultrapure (sub-boiling distilled) mineral acids followed by a rinse with ultrapure (18.2 MΩ-cm resistivity) water. The sample is allowed to dry under a flow of class 100 clean air, mounted in a cleaned Ta chuck and translated into the Ta discharge cell (Megacell). A “pre-burn” sputtering of the sample is then undertaken using the plasma to etch the outer surface layers of the material and achieve a final cleaning of the surface prior to data acquisition. This typically requires about 20 min in a 5 mA, 1.1 kV discharge in a 1-2 ml/min flow of high-purity Ar. The pressure in the discharge chamber is approximately 10^{-2} Pa. The operating pressure of the mass spectrometer is typically 10^{-5} Pa with a base pressure of 2×10^{-6} Pa. During this period, the entire mass spectrum is interrogated to ensure that steady-state response has been achieved for each element (isotope) of interest, indicating that all surface contamination from the sample and the surrounding chuck holding the sample has been removed and bulk composition of the sample is being examined. After this time, the analytical data are acquired. These processes typically require 90 min at discharge conditions of 3.5 mA and 1.1 kV.

2.2.3. *Instrument calibration and traceability*

As recently demonstrated for neutron activation analysis (NAA) [25], GD-MS pin-cell techniques also have the potential to fulfill the requirements of a primary (direct) method as defined by the Comité Consultatif pour la Quantité de Matière - Métrologie en Chimie in 1998 [12, 26], i.e., a method having the highest metrological properties, whose

operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units". More specifically, a primary direct method was defined as "a primary method of measurement that measures the value of an unknown without reference to a standard of the same quantity" [2]; its operation must be completely described by a measurement equation.

In accordance with the above, we demonstrate herein that the coupling of a pin-cell GD-MS source with the VG 9000 spectrometer is sufficiently well understood that a measurement equation can be written down in which the values of all parameters have dimensions in SI units, thereby conferring metrological traceability to these units, and that all contributions to uncertainty of measurement can be quantitatively evaluated, underpinning the metrological traceability. Furthermore, the performance of GD-MS in CCQM key- and pilot-comparisons of trace elements in complex matrices is in conformance with claimed capabilities. Despite the substantial expanded uncertainties associated with mass fractions determined by GD-MS for each impurity element, a fit-for-purpose "determination" of the measurand, i.e., the purity, is shown to be achieved.

Response in GD-MS is influenced by a number of factors, many of which are under the direct control of the analyst. Thus, sample geometry (sample dimension and shape interrogated by the discharge) and discharge conditions (ambient gas composition and flow rate, discharge current, voltage and pressure) influence absolute ion intensities. These also can be readily controlled by adopting standard operating conditions. Detector efficiencies are conveniently cross-calibrated (daily) using two different Ar^+ isotopes from the discharge gas (^{38}Ar and ^{40}Ar) to ensure that their relative response is accounted for. Finally, it is well-recognized that pin-cell GD-MS is relatively free of matrix effects, i.e., the slope of a calibration plot of amount content of an isotope of an impurity element present in *different* host matrices *versus* its detected ion beam intensity typically varies by no more than 30 - 100 % and is thus, to a first approximation, independent of the host sample matrix [27]. Even smaller variations in such relative sensitivity factors can be achieved through judicious selection of discharge gas composition [28]. Such a favorable situation is questionable with newer generation GD-MS instrumentation based on a less well understood aggressive Ar jet-assisted

sputtering of the sample (such as the ELEMENT GD). It remains for users of this source to determine whether RSF values for a given measurand are as commutable (with relatively small variability) from matrix-to-matrix as is presently the case with the VG 9000 and to ultimately model the response from fundamental physical principles. Interestingly, traditional DC pin-cell GD-MS sources mated to newer generations of mass spectrometers (such as the Astrum produced by Nu instruments) are also able to make use of commutable RSF values [29].

Gusarova *et al.* [21] have succinctly summarized the various approaches to quantitation with GD-MS. All have as their basis the initial acquisition of an ion beam intensity ratio – the ratio of the ion beam intensity of a selected isotope of an elemental impurity in a given metal matrix M acquired by the Daly detector (I_e , in A) to that of the intensity of the selected host metal matrix ion isotope beam captured by the Faraday detector (I_M , in A). Here it is assumed that for high-purity metals, $I_M \sim (I_M + I_e)$, which introduces an error of not larger than 0.001 % relative for the least pure metals examined. These are subsequently corrected for abundances of the two isotopes, $x(^eE)_M$ and $x(^ME)_M$, respectively, and relative detector efficiencies, $\mathcal{E}_D/\mathcal{E}_F$. The former two are taken from their most recent IUPAC compilations [30, 31] and the latter, as noted, is experimentally determined prior to analysis. Note that in using a ratio technique such as this, advantage is inherently also made of the use of the matrix response as an internal standard for the correction of signal fluctuations during the measurement arising from any instrument/plasma instabilities. Moreover, it also becomes the principal source of traceability of the determination of the amount fraction of the impurity element as a consequence of a direct primary method of measurement being employed – a measurement of current (or voltage output across a load resistor in the detector circuit). This arises because the ion beam ratio, once corrected for isotopic abundances, can then be converted to the mass fraction of impurity element (w^e_M) by simple correction for relative standard atomic weights of the impurity element $A_r(^eE)$ and the metal matrix element $A_r(^ME)$.

To a first approximation, the mathematical model for the measurement process is as expressed by equation 2:

$$(w_M^e)' = [I_e / I_M] \times [\mathcal{E}_F / \mathcal{E}_D] \times [x(^M E)_M / x(^e E)_M] \times [A_r(^e E) / A_r(^M E)] \times [^e f / ^M f] \quad (2)$$

Note that an additional correction factor ($^e f / ^M f$) has been added to equation 2 to account for the relative transmission efficiencies of the two measured isotopes through the spectrometer – the so-called mass bias or mass discrimination factor [32]. This is generally a minor correction, but may be as large as 10-15 % when a combination of low m/z element impurity is of interest in a heavier m/z matrix.

A final consideration is to account for the relative sensitivity factor (RSF_M^e) for element “e” in matrix “M”, which represents the impact of the presence of the host matrix on the efficiencies of sample sputtering, ionization and diffusional transport of the respective ions in the GD cell such that:

$$w_M^e = (w_M^e)' \times RSF_M^e \quad (3)$$

It is significant that the RSF concept enjoys a sound theoretical footing with pin-cell GD-MS instrumentation in that these values ($RSF_{M,th}^e$) can be *a priori* mathematically calculated [17, 33] from first principles and subsequently validated with use of CRMs. RSFs are calculated by accounting for (diffusional) transport of the sputtered atoms in the glow discharge as well as by Penning, electron impact and asymmetric charge transfer ionization processes. A detailed modelling approach [17, 33] based on physicochemical first principles provides for a coherent rationalization of the experimental RSFs used with the VG 9000 GD-MS instrument. An excellent correlation between predicted and experimental values is reported by Bogaerts *et al.* [33] for which an average difference of only 25 % is evident for the ratios of experimentally measured to theoretically calculated RSF values for 38 tested elements. Thus, there is a clear basis for the concept of “influence factors” (i.e., RSFs) being applied to adjust initially estimated *direct* SI traceable primary measurement data. This concept is consistent with ISO Guide 34 [34], which notes that a primary method is one for which a property value “is either directly measured in terms of the base units of measurement or indirectly related to the base units through physical or chemical theory expressed in exact mathematical equations”. Such conditions are satisfied using the above approach and, by extension, one could argue that RSF values established or validated with the

use of CRMs yield an approximate expression of existing (but not yet calculated) theoretical RSF values; hence the method used is, in principle, free of calibration and obtains its *direct* traceability to the SI *via* physical properties inherent to the GD-MS instrument. Uncertainties associated with such computations have not yet been evaluated and in their absence, the use of CRMs for validation of RSFs will carry inherent uncertainties associated with this process, as highlighted below. Note that use of equation 3 with reliance on experimental RSF values obtained by calibration with CRMs does not then need further explicit correction for the $\mathcal{E}_D/\mathcal{E}_F$ and $[^ef / ^Mf]$ terms shown in equation 2, as these would already be convolved with an experimentally determined RSF value.

From the above, it is evident that the theoretical RSF value, $\text{RSF}_{M,\text{th}}^e$, is linked to the “real” RSF_M^e used in equation 3 by a correction factor, $\text{CF}_{M;r/\text{th}}^e$ (the ratio of real to theoretical value):

$$\text{RSF}_M^e = \text{RSF}_{M,\text{th}}^e \times [\mathcal{E}_F/\mathcal{E}_D] \times [^ef / ^Mf] \times \text{CF}_{M;r/\text{th}}^e \quad (4)$$

which does not deviate significantly from unity. Thus, only small corrections to theoretically calculated RSF values would be necessary if they were to be used in equation 3 instead of “real” RSF_M^e values.

The resulting expression relating mass fraction to experimental parameters is:

$$w_M^e = [I_e / I_M] \times [\mathcal{E}_F/\mathcal{E}_D] \times [X(^ME)_M / X(^eE)_M] \times [A_r(^eE) / A_r(^ME)] \times [^ef / ^Mf] \times \text{RSF}_{M,\text{th}}^e \times \text{CF}_{M;r/\text{th}}^e \quad (5)$$

containing only a single term, $\text{CF}_{M;\text{exp}/\text{th}}^e$, which is based on measurements of known mass fractions (*via* instrument calibration with CRMs). This correction factor could be omitted from equation 5 provided its impact on w_M^e is suitably accounted for as a simple contribution to the uncertainty of the $\text{RSF}_{M,\text{th}}^e$ term, yielding:

$$w_M^e = [I_e / I_M] \times [\mathcal{E}_F/\mathcal{E}_D] \times [X(^ME)_M / X(^eE)_M] \times [A_r(^eE) / A_r(^ME)] \times [^ef / ^Mf] \times \text{RSF}_{M,\text{th}}^e \quad (6)$$

devoid of any term based on measurements of known mass fractions. Clearly, $RSF_{M,th}^e$ incorporates such information in the form of an uncertainty, demonstrating that GD-MS determinations of mass fractions of trace elements in pure matrices can be based solely on measurements of ion beam ratios (trace elements to matrix) corrected by several factors inherent to the method and the instrumentation.

For practical measurements, corrections to $(w_M^e)'$ can be made when CRMs of the metal matrix under study are available with which to validate theoretical RSFs (to yield quantitative results). Unfortunately, as in other fields of chemical analysis, there is a paucity of CRMs available for this purpose and all elements certified in CRMs representing all metal matrices are lacking. In such situation, a sense of commutability of CRMs is derived from the use of the concept of *Standard* RSF, wherein RSF_{Fe}^M is used as a normalization factor to derive RSF_M^e values for a specific measurand in a different matrix in accordance with:

$$StdRSF_M^e = RSF_{Fe}^e / RSF_{Fe}^M \quad (7)$$

Normalizing RSF values for GD-MS response to iron (wherein $StdRSF_M^e = 1$, with $e = M$ in such case) is an historical practice that evolved due to the relatively larger number of CRMs available in iron (and steel) matrices. Note that any other CRM of matrix M can also be used for the purpose of calculating RSF values for measurand “e” in matrix “M”; thus, *standard* RSFs provide for a set of universal values from which one RSF can be converted to the RSF for another elemental impurity in a different matrix.

The metrological traceability of w_M^e is directly conferred to the SI as dictated by the measurement model expressed through equations 2 and 6, irrespective of the availability of an applicable CRM for calibration of the instrument. Experimentally determined RSF values are based on calibration using samples (CRMs) of known mass fractions of impurity elements undertaken either concurrently within a given measurement cycle or at a remote time. Noteworthy is that equation 6 is not based on such additional calibration, but rather theoretically calculated RSFs. These factors can (but do not need to) be corrected by factors (not far from unity) based on calibrations which provide comparisons between measured and theoretically calculated RSFs.

However, in view of the tolerable uncertainties of the determined mass fractions of impurity elements, this procedure is in principle not necessary. The fact that in most, or at least in many of the cases occurring in real analytical praxis, such theoretically calculated RSFs do not yet exist, provides no argument against the thesis that the method satisfies the requirements of a primary one, especially since additional theoretical RSFs could yet be determined. Correction of $(w_M^e)'$ for the *influence quantity* [3] constituting the RSF value to yield w_M^e can be viewed as introducing an operation equivalent to a unitless correction for “recovery”. De Bièvre and colleagues [3] have discussed those cases wherein the “initially estimated quantity value” must be adjusted for systematic effects by corrections applied to the initially estimated quantity value itself. As such, the measurement uncertainty in the final result is the combination of the measurement uncertainty associated with the initially estimated quantity value (from equation 2) and the measurement uncertainties of all corrections for the systematic effects or influence quantities. As noted below, the use of such “influence quantities” introduces a relatively enormous uncertainty on the mass fraction of each impurity. However, this is of no consequence to the establishment of metrological traceability for purity, as evident from the VIM [2, Note 4], i.e., “...the effort involved in establishing metrological traceability for each input quantity value should be commensurate with its relative contribution to the measurement result”, since it is clear that provided the mass fraction of the impurity is <100 mg/kg, a completely fit-for-purpose uncertainty in the assigned mass fraction $w(M)$ of the matrix is achieved.

RSF values experimentally determined in the NRC laboratories over the past three decades, along with compilations of published RSF values [e.g., 17, 18, 27, 28], reveal that averaged values of RSF_M^e calculated in accordance with equation 7 are characterized by a standard uncertainty of 30-100 % for metals and up to 250 % for C, N and O. The larger figure associated with the latter elements arises because they can only be ionized *via* electron impact (along with some specific interactions of O with certain metals that serve as getters, especially once they are activated on the atomic scale by the sputtering process, e.g., Zr) and there are much fewer CRMs available for various matrices that are certified for their C, N and O mass fractions. As a caveat to this general method of calibration, it is obviously necessary to process any CRM

primary calibrants using the same sample pin geometry and identical discharge conditions as for the samples. Clearly, when CRMs are available which have the same or similar matrix compositions as those of the samples to be analyzed, (i.e., a one-to-one match) much smaller calibration uncertainties can be realized as the broad assumptions used above for averaged RSF values no longer constrain the measurement uncertainty, yielding quantitative results. Unfortunately, as noted, an insufficient number of CRMs is currently available to cover the broad range of matrices of interest and, moreover, from the perspective of traceability and desire to minimize the “length of the chain” connecting the final result to SI units of measurement, it must be recognized that any CRM itself is linked to the SI *via* its own calibration chain(s) and characterization methodologies.

The enlarged uncertainties propagated in this manner could, in principle, be avoided through use of “doped” calibration standards, as espoused by Matschat and colleagues [20 - 22].

2.2.4. *Validation of methodology*

The GD-MS laboratory at the NRC has been accredited to ISO/IEC 17025 (as a test facility) through the Standards Council of Canada since October, 2002. The acceptance of CMC claims by the KCDB in 2012 was predicated on the confirmation of validation of non-standard methods developed within the GD-MS laboratory for assignment of purity. Several tools were used to demonstrate validation (as per ISO/IEC 17025 section 5.4.5), including: calibration of the instrumentation using international CRMs; quality control charting (using BCR Cu CRM 075B for some 11 years); participation in appropriate CCQM comparisons; inter-comparisons of data with other NMIs (CENAM, BAM); in-house confirmation of mass fractions of major impurities by the use of ICP-MS, and assessment of uncertainties of results based on model equations and the generation of fit-for-purpose purity assessments.

The mass balance equation for the assignment of purity [mass fraction of the matrix, $w(M)$] is given as:

$$w(M) = 1 - \sum_{i,j} [(w_M^e)_i + (0.5LOD)_j] \quad (8)$$

where $w(M)$ is the assigned purity of the matrix sample M (kg/kg); $(w_M^e)_i$ are the individual mass fractions of each impurity element “i” present at concentrations greater than their limits of detection (LODs). For each impurity element “j” deemed present at a mass fraction at or below the estimated LOD, a rectangular distribution of values between 0 and the LOD (i.e., averaged value = LOD/2) is assumed to hold. In our laboratory, a manually selected discriminator is used to limit current values above 5×10^{-19} A generated with the Daly detector. The instrument software is used to convert this current to an equivalent counts per second (cps). Assuming that the LOD is determined by Poisson statistics, the equivalent relative noise is estimated as $(cps)^{1/2}$. The LOD for the mass fraction of the isotope of interest is then calculated [35] as $3.3 (cps)^{1/2}$ divided by the slope of the calibration function (cps / kg/kg) resulting in an output of a “< value” by the LIMS system.

2.2.5. *Uncertainty assessment*

Uncertainty calculations are based on measurement model equations 6 and 8 to generate standard uncertainties w_M^e for each elemental impurity and for $w(M)$. Table 1 summarizes a typical set of assignments for the experimental variables. Measurements of current developed on the Faraday detector arising from the ion beam characterizing the major matrix element can be achieved with relative uncertainties below 0.01 % whereas that for the impurity elements measured with the Daly detector are in the range 1 – 15 %, depending on the mass fraction of the impurity (e.g., 15 % at 3 ng/g, 1.3 % at 160 ng/g); a conservative limit of 15 % is shown in Table 1. Daily cross-calibration of the relative detector efficiencies over the course of 2013 yields a relative standard uncertainty of 2.5 %. Relative standard uncertainties associated with fluctuations in the mass bias of the instrument are assumed to be 1 % but are likely far less than this. With the exceptions of C, N and O, the standard uncertainty assigned each w_M^e is thus very conservatively estimated to be 100 % relative and is dominated by the uncertainty assigned the $RSF_{M,th}^e$ values (surrogate for experimental RSF_M^e influence quantity). For

the former three elements, relative standard uncertainty is estimated to be 250 % due to the fewer and more widely spread RSF_M^e values available for these elements with which to validate their theoretical RSF values. Standard uncertainties for impurity mass fractions reported as “< values” i.e., the LOD, require further consideration. Although still based on equation 6, the term I_e is, in such a case, now equated to the value of $\sim 3 \times$ the standard deviation of the noise in the background current from the Daly detector (s_D) over the m/z mass windows of interest [35], i.e.:

$$(I_e)_{LOD} = 3.3s_D \quad (9)$$

The standard uncertainty of the resultant $(w_M^e)'_{LOD}$ value (i.e., the “< value”) can be considered to be 30 % relative (by definition of LOD) or computed as the standard uncertainty arising from a rectangular distribution assumed to describe such data (mass fraction assumed to lie in the range zero to the LOD), calculated as $LOD/(2\sqrt{3})$, or 35 % relative. Thus, for those elemental impurities assigned a “<” result, their associated uncertainties are based on the following equation which convolutes uncertainty components from both $(w_M^e)_{iLOD}$ and $(RSF_M^e)_i$:

$$u^2[\Sigma(w_M^e)_{jLOD}] = \Sigma [u^2 (w_M^e)'_{LOD} + u^2 (RSF_M^e)_j] \quad (10)$$

Purity, calculated from the mass balance equation 8, is then assigned an uncertainty in accordance with equation 11:

$$u^2[(w(M))] = \Sigma_{i,j} [u^2(w_M^e)_i + u^2(w_M^e)_{jLOD}] \quad (11)$$

A coverage factor, $k = 2$, is used to characterize the expanded uncertainty. It is noteworthy that the worst case scenario encountered for such an assignment of uncertainty occurs when only C, N, O or a combination of these elements is present as impurities. In such case as this, a 3N pure material will be associated with a relative expanded uncertainty in purity of 0.5 % whereas that of a 6N material will be 5×10^{-4} %. This is the source of the information presented in the CMC capabilities from the NRC [19].

3. Results and Discussion

The wide elemental coverage of GD-MS (potentially all elements with the current exception of H, but with radioactive elements and Ar or other noble gases being considered as "not relevant")), high detection power (ng/g and below), rapid throughput, and ease of sample preparation, make this approach to the characterization of high-purity metals (purity >3N) very attractive. There is no blank component requiring compensation except for spectroscopic background generated by the instrument and correction for any isobaric overlaps, which are all well-recognized and most are alleviated with a standard 4000 resolution. Indeed, the only matters of concern are the homogeneity of the sample and the availability of RSF values. Moreover, surface contamination, potentially introduced during sample preparation, is conveniently removed during the pre-analytical sputtering phase by monitoring output until a steady-state response is achieved, indicative of bulk properties.

Confidence in the analytical results is enhanced through use of a number of tools that serve to validate methodology as well as to ensure that long-term operation of the GD-MS facility is under strict control. Examples of these are presented below.

3.1. *Control charting*

BCR-075B copper CRM has been used as a control charting material for the past 11 years in the GD-MS facility; the sample is run approximately twice per month to assess whether the measurement process remains under control for 18 representative impurity elements (O, Al, P, S, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Ag, Cd, Sn, Sb, Pb and Bi). After some 20 initial results, 2s and 3s control and action limits, respectively, were established. Figure 1 illustrates charts for oxygen (non-certified) and chromium in this CRM. An 11 year average mass fraction for oxygen is 2.63 ± 0.83 mg/kg (U expressed as one standard deviation) whereas that for Cr is 0.90 ± 0.06 mg/kg (certified at 0.89 ± 0.10 mg/kg), exemplifying the stability of the system over more than a decade of operation (i.e., no change in initial RSF value assignment over 10 years!).

3.2. *Participation in CCQM comparisons*

There are few possibilities to engage the GD-MS facility in inter-laboratory comparisons because of the nature of the available samples (liquids or mostly non-conducting powders or metals of inappropriate geometry that comprise these exercises); fortunately, participation in several Key and Pilot comparisons organized by the Inorganic Analysis Working Group under the auspices of the Comité consultatif pour la quantité de matière – métrologie en chimie (CCQM) has served to illustrate the analytical capabilities of GD-MS when working with blind samples. During the past 8 years, the Chemical Metrology Group of NRC has participated in CCQM-P62 (Purity of nickel with respect to six defined metallic analytes); CCQM-P107 (Measurement of the purity of zinc with respect to six metallic impurities); CCQM-K72 (Measurement of the purity of zinc with respect to six metallic impurities); CCQM-K88 (Determination of lead in lead-free solder containing silver and copper), and has registered for the recent CCQM-P149 exercise (Purity determination of zinc to be used as primary standard for zinc determination). In each case, results contributed by GD-MS have been in agreement with those generated by other participants using more classical instrumental analysis techniques and well within the conservative expanded uncertainties attributed to the measurement results. As an example, CCQM-K88 reported on the determination of lead in lead-free solder. Using an exact matrix-matched CRM from NMIJ for calibration purposes (i.e., NMIJ 8203) to derive the appropriate $RSF^{Pb}_{Sn/Ag/Cu}$, an amount content of 202 mg/kg with an expanded ($k = 2$) uncertainty of 19 mg/kg was reported, in good agreement with reference values of 197.2 mg/kg and 0.93 mg/kg for the median and expanded uncertainty ($k = 2$) [36]. The major component of uncertainty was that associated with the certified value for Pb in the calibration CRM (hence RSF influence quantity). Whereas this serves to illustrate the capabilities of GD-MS for quantitative measurements when an exact matrix matched CRM is available for calibration (a bias of only 2.6 %), CCQM-P107 [37] presented a situation wherein averaged $StdRSF^e_{Zn}$ values for $e = Ag, Al, Cd, Cr, Ni$ and Tl in a zinc matrix were used to determine the mass fractions of these impurities. With the exception of Cr, the mass fractions of these targeted impurities were all within 10 % of the median of the other participant's values and for Cr this discrepancy was 28 % low, well within its associated relative expanded

uncertainty ($k = 2$) of 200 %, providing a fit-for-purpose sum of impurities (target uncertainty of 30 % relative) and demonstrating comparability of results with other laboratory methodologies. An identical situation arises with CCQM-K72 (Purity of Zinc with respect to six defined metallic analytes), wherein results submitted by NRC for the sum of Al, Cr, Ni, Ag, Cd and Tl impurities (10.6 ± 3.2) mg/kg ($k = 2$) are in excellent agreement with the calculated value of the KCRV (10.88 ± 1.2) mg/kg derived from results submitted by nine participants.

3.3. *Intercomparisons with other techniques*

Although several other complimentary techniques are available having a capability of quantifying metallic impurities in high-purity metals (ICP-MS, GF-AAS), those for such measurands as C, S and the halogens as well as dissolved or bound gases (noble gases as well as N, O and H) are less common. Unfortunately, this means these measurands are often overlooked when purity statements are issued, but in reality they often constitute the major sources of impurities in high-purity metals [5, 7, Table 2]. As noted earlier, the dearth of CRMs certified for C, N and O has resulted in an elevated uncertainty in the $StdRSF_M^e$ values used for these measurands. In an effort to alleviate this dilemma, our laboratory has undertaken several informal bilateral comparisons with CENAM which has expertise with carrier gas hot extraction (CGHE) techniques for determination of N and O as well as high temperature combustion approaches to determine C. Tables 3 and 4 summarize data for determinations of these elements in high-purity vanadium and aluminum [38]. Data generated by GD-MS is corroborated by that available from CENAM in that there is overlap of results within the stated uncertainties. A concerted effort is needed to enhance the reliability of C, N and O determinations through activities such as this and the production of more CRMs certified for these measurands. This will enable a significant reduction in the uncertainties associated with the RSF_M^e values for these elements. Accordingly, our laboratory has recently launched a program for development of methodologies for the determination of C, N, O and H in metals using CGHE and combustion methodologies.

3.4. *In-house confirmation*

ICP-MS is a versatile tool for rapid semi-quantitative analysis of solutions of dissolved metals for their impurity content as virtually all metallic impurities can be rapidly accessed in a typical “total-quant” scan. Unfortunately, significant “dilution” of the impurities by up to 100-fold arise as a consequence of the dissolution process and subsequent need to accommodate sample introduction systems that typically tolerate only a 1 % dissolved solids content solution. Nevertheless, with detection power typically in the sub-ng/g range, the *major* metallic impurities can be identified and selected for in-depth quantitation and full uncertainty assignment by the method of additions or isotope dilution, if desired, to yield SI traceable amount contents. In this manner, GD-MS results have been corroborated for the major (top 5-10) metallic impurities identified by this technique. Examples of such comparisons are presented in Tables 5 and 6 for samples of high-purity Mo and V, respectively. In these cases, the metals were sourced from Alfa Aesar, which provided certificates of analysis for the particular lot numbers in question. It is gratifying that, in these cases, an independent assessment of the impurity mass fractions shows substantive agreement from all three sources.

3.5. *Purity assignment*

Sample purity is estimated using equation 8, with equation 11 providing the standard uncertainty. Using as a worst case example of a 3N type of material, the GD-MS analytical report for Mo is shown in Table 2. A mass fraction of Mo, $w(\text{Mo})$, or purity of this sample, is calculated to be 0.99987 kg/kg with an expanded uncertainty ($k = 2$) of 0.00034 kg/kg. The sum of all quantified impurity elements is 130 mg/kg whereas half the sum of all the “<” values (assuming rectangular distributions) is 3.6 mg/kg, yielding a total mass fraction of impurities of 134 mg/kg. The standard uncertainty associated with the sum of all elements is 162 mg/kg which is expanded to yield $U = 324 \text{ mg/kg}$ ($k = 2$). As noted by Zhou *et al.* [5], the measurement distribution about the calculated uncertainty may not turn out to be symmetrical (i.e., $w(\text{Mo}) = 1.00019 \text{ kg/kg}$ arises as

the upper limit in this case). This issue has been ignored in the present work and a normal distribution accepted as an approximation, but truncating the upper limit at 1.00 kg/kg is logical.

As pointed out by Zhou *et al.* [5], the noble gases (He, Ne, Ar, Kr and Xe) as well as several radioactive elements (Tc, Pm, Po, At, Rn, Fr, Ra, Ac and Pa) are typically not accounted for even in aggressive purity characterization scenarios. The solubility of the gases in metals is low and often the zone refining melting process undertaken for purification serves to degas the melt (when done under vacuum). As for the radioactive elements, most metals of interest to the analytical community are of natural origin and these elements are unlikely to be encountered. Nevertheless, such elements can, in principle, be accommodated by MS measurements and assessed for their contribution to the impurity load.

4. Conclusions

The VG 9000 GD-MS instrument with pin-cell source is well-suited to the determination of *direct* SI traceable mass fractions for metals of 3N and greater purity, generating fit-for-purpose expanded uncertainties demanded for the characterization of primary calibration standards. It is argued herein that the methodology fundamentally provides a direct primary method of measurement since it is current that is used in the measurement model to obtain initial estimates, w_M^e , of impurity mass fractions. Subsequently, correction of w_M^e by the RSF_M^e influence quantity (equations 3 - 6) using values derived from first principles [33] (subsequently “validated” against CRMs when possible) further substantiates the primary measurement methodology. As noted in the GUM [39], the influence quantities used to correct the initial estimates of the amount fraction of each impurity element may be obtained from measurements with an appropriate CRM using the GD-MS procedure or by comparison of results obtained with the measurement procedure and those using a reference measurement procedure. The excellent agreement reported between GD-MS data and that generated using ICP-MS (Tables 5 and 6) as well as from performance in blind CCQM Key and Pilot comparison

exercises supports the belief that RSF values can be calculated in accordance with equation 7 when a one-to-one matrix-matched CRM is unavailable for this purpose.

Several means can be envisioned to reduce standard uncertainties associated with $(w_M^e)'$ and, more significantly, RSF_M^e influence quantities. Use of a simultaneous multi-element detection platform, such as a time-of-flight device, would serve to allow real-time ratio measurements of I_e and I_M rather than the sequential ones now achieved. With the VG 9000, availability of CRMs certified for a *complete* spectrum of impurities in only a few matrices would permit calculation of RSF_M^e values in all other matrices (note, a high-purity matrix is not required; it is actually more beneficial to have a broad range of impurity elements present at the mg/kg level for this purpose). Member laboratories of the IAWG of the CCQM should be able to contribute to this by employing multi-element detection schemes and techniques such as NAA for the characterization of select matrix metals with corroboration of results by independent measurements; this is the aim of the current CCQM-P149 broad-spectrum elemental analysis of impurities in zinc. There is a clear need for additional SI traceable calibration standards for C, N and O as their presence currently contributes significantly to the combined uncertainty. The work underway with the EU program [11] will hopefully be able to address these issues as will activities in individual laboratories having capabilities for CGHE and combustion techniques for metals.

Although the vast majority of analytical measurements generate data for which the uncertainty in purity of primary calibration standards has no impact on the combined uncertainty of the result, SI traceable primary standards are nevertheless required for the establishment of comprehensive traceable measurement chains. A potential exception to this generalization is clearly present for those organizations providing traceable certified primary calibration standards, such as the NIST 3100 series of solutions, for which expanded uncertainties lie in the domain of 0.1 % - 0.3 % relative. At these levels, major contributors to uncertainty become considerations of purity of the primary elemental starting materials, gravimetric preparation procedures, sample solubilization and solution stability issues. Fortunately, (or unfortunately!) the current state of capability for laboratories preparing their primary elemental calibration solutions

(at mass fractions of 1 g/kg), upon which rest their measurement claims in this domain, reveal expanded uncertainties in the range of 0.3 % to 0.5 % relative ($k = 2$) [40].

It remains for users of more modern GD-MS platforms (such as the ELEMENT GD which functions very differently from the essentially static discharge established with the VG 9000), to determine whether the principles outlined here can be successfully implemented; specifically, whether the commutability of RSF values determined from one matrix can be calculated for use with another host matrix without incurring significant measurement bias. Significantly more work is required to model and understand operation of such sources to the point where relevant $RSF_{M,th}^e$ values can be mathematically calculated from first principles and the resulting “influence quantities” can be applied to correct the initially estimated SI traceable primary measurement data.

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Table 1. Components of uncertainty associated with Equations 4-6*.

parameter	I_e	I_M	$\varepsilon_F/\varepsilon_D$	e_f	M_f	RSF_M^{e**}
relative u, %	15	0.01	2.5	1	1	100

*Conservative estimates.

** 250 % relative for values relating to C, N and O.

Table 2. Analytical report for high-purity Mo by GD-MS, mass fractions in ng/g.

	Lot#K27R052		Lot#K27R052
H		Rh	<4
Li	17	Pd	<5
Be	<0.4	Ag	<210
B	14	Cd	<490
C	310	In	<10
N	1600	Sn	22
O	18000	Sb	440
F	<9	Te	<10
Na	180	I	<3
Mg	34	Cs	<9
Al	780	Ba	<240
Si	670	La	860
P	840	Ce	<45
S	30	Pr	<3
Cl	43	Nd	<17
K	6300	Sm	<10
Ca	120	Eu	<3
Sc	<0.3	Gd	<6
Ti	<4100	Tb	<1
V	1100	Dy	<7
Cr	13000	Ho	<1
Mn	420	Er	<6
Fe	12000	Tm	<1
Co	57	Yb	<9
Ni	14000	Lu	<10
Cu	610	Hf	<2
Zn	<940	Ta	<470
Ga	<7	W	54000
Ge	<5	Re	320
As	280	Os	<6
Se	<17	Ir	<6
Br	<5	Pt	<20
Rb	<60	Au	<260
Sr	<60	Hg	<12
Y	<80	Tl	<3
Zr	<60	Pb	<1
Nb	4200	Bi	<2
Mo	Matrix	Th	20
Ru	<10	U	36

Table 3. Comparison of results from GD-MS and CGHE / combustion for analysis of V.

	CGHE / combustion		GD-MS
	mass fraction, mg/kg	U ($k=2$)	mass fraction, mg/kg*
oxygen	400	37	160
nitrogen	27.5	5.0	15
carbon	94	22	97
sulfur	<10.6	----	2

*As $U(w_M^e) = 500$ % relative (for $e = C, N$ and $O, k = 2$), the mass fractions of these impurities lie in the range of one-fifth to five-fold reported values.

Table 4. Comparison of results from GD-MS and CGHE / combustion for analysis of Al.

	CGHE / combustion		GD-MS
	mass fraction, mg/kg	U (k=2)	mass fraction, mg/kg*
oxygen	7.2	2.3	15
nitrogen	ND	---	0.5
carbon	167	71	22

*As $U(w_M^e) = 250\%$ relative (for $e = \text{C, N and O, } k = 2$), the mass fractions of these impurities lie in the range of one-fifth to five-fold reported values.

Table 5. Validation of GD-MS data by ICP-MS for characterization of high-purity Mo.

Impurity	Mass fraction, ng/g		
	GD-MS ^a	ICP-MS ^b	Alfa Aesar C of A ^c
Al	780	1050 ± 230	< 8000
Ni	14000	14500 ± 220	16000
Fe	12000	14200 ± 3200	15000
Cr	13000	11580 ± 380	----
K	6300	8890 ± 1900	23000
As	280	< 800 ^d	----

^a mass fractions lie in the range of one-half to two-fold reported values; i.e., $U(w_M^e) = 200\%$ relative ($k = 2$).

^b mean and expanded uncertainty ($k = 2$; $n = 3$).

^c certificate of analysis from supplier for lot No. K27R052.

^d results obtained using GF-AAS.

Table 6. Validation of GD-MS data by ICP-MS for characterization of V.

Impurity	Mass fraction, ng/g		
	GD-MS ^a	ICP-MS ^b	Alfa Aesar C of A ^c
Al	94000	120380 ± 880	180000
Ni	13000	11900 ± 300	13000
Fe	24000	27600 ± 4450	24000
Si	290000	231200 ± 4000	340000
Mo	32000	28120 ± 560	----
As	1100	760 ± 140	----

^a mass fractions lie in the range of one-half to two-fold reported values;, i.e., $U(w_M^e) = 200\%$ relative ($k = 2$).

^b mean and expanded uncertainty ($k = 2$; $n = 3$).

^ccertificate of analysis from supplier for lot No. A14W021

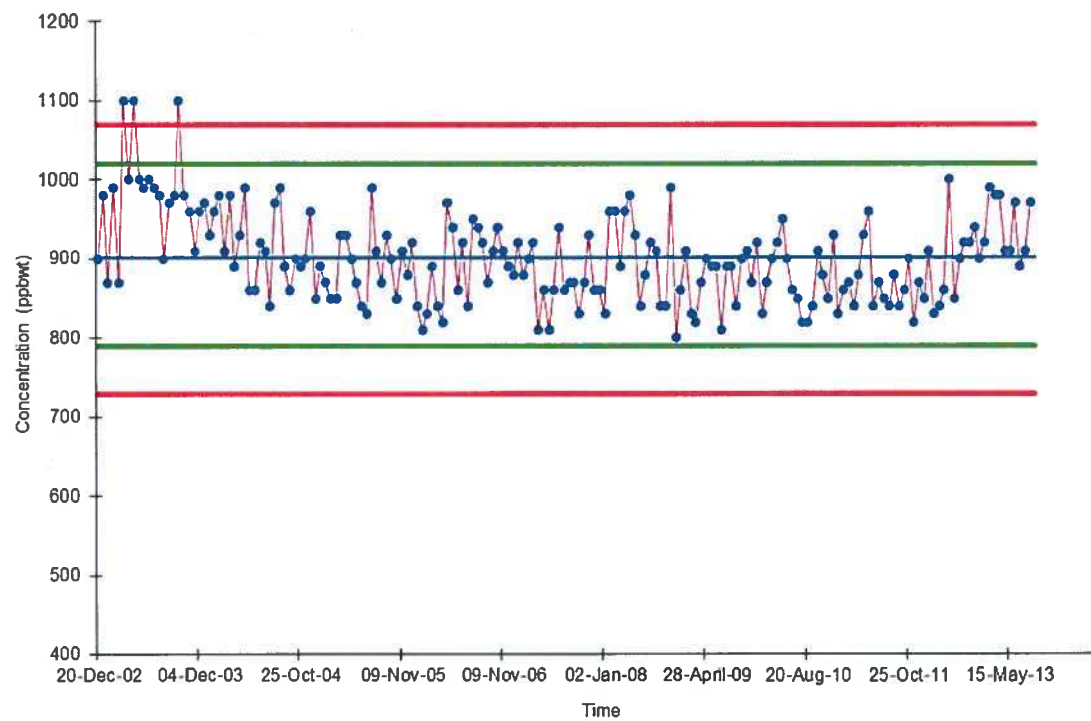
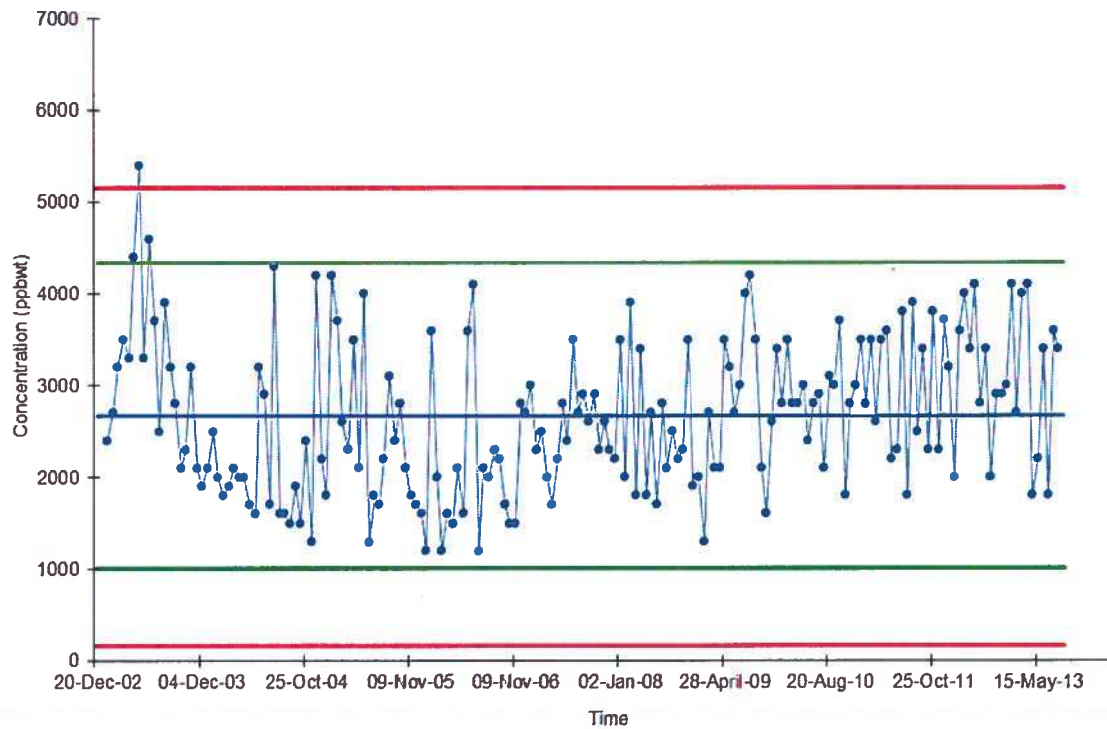


Figure 1: Control charts for BCR 075B CRM: oxygen (top panel), chromium (bottom panel). Control limits ($\bar{x} \pm 2s$) are represented by the green horizontal lines with action limits ($\bar{x} \pm 3s$) illustrated by the horizontal red lines.