Methodologies for the estimation of uncertainties and the correction of fixed-point temperatures attributable to the influence of chemical impurities

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Abstract

Recent CCT Key Comparisons have exposed the fact that national metrology institutes use various means to estimate the uncertainty component of temperature fixed points that addresses the influence of impurities. Since this component often dominates the uncertainty budget, its importance cannot be understated. The lack of a common approach to the estimation of this component has created a situation whereby values for this single component may differ by orders of magnitude from lab to lab even though the materials and their treatment are generally very similar. We seek to standardize the methodology by proposing the Sum of Individual Estimates as the preferred method for estimating the change of the observed liquidus-point temperature relative to that of the chemically pure material where sufficient information is available to enable the required calculations. Where this is not possible, the Overall Maximum Estimate is an acceptable, though less desirable, alternative. The Estimate based on Representative Comparisons is specifically discouraged. The determination of the liquidus-point temperature from the freezing or melting curve is also discussed.

1. Introduction

The uncertainties of the reference temperatures realized by the defining fixed points of the International Temperature Scale of 1990 [ITS-90] are often dominated by the component attributable to the influence of impurities. Moreover, underestimation of this component may well be the root cause of temperature differences in excess of their combined uncertainties among the national metrology institutes, as demonstrated in recently reported CCT Key Comparisons [CCT-K3, CCT-K4]. The discussions that took place during the preparation of these Key Comparison reports, and that have continued subsequent to their publication, have delineated the fact that a variety of approaches are currently in use to estimate the magnitude of this uncertainty component. Clearly, the temperature metrology community would benefit from greater harmony of approach.

We propose a methodology that is based on the behaviour of impurities in the dilute limit, since the materials used to realize the ITS-90 are of a purity that approaches, and in some cases exceeds, a level of one part per million. (The crystallographic behaviour of impurities during freezing under different experimental conditions is briefly discussed in [CCT/99-11]). Methods based on chemical assays are recommended as the primary method, supplemented by thermal analysis (such as the slope of a melting curve) and comparisons between cells. Estimates of uncertainties based on representative comparisons are mainly useful as a validation tool to check for contamination during preparation. Sole reliance on thermal analysis should be avoided as a means of determining the cell uncertainty since some impurities can influence the melting temperature without broadening the melting range.

The document remains a work in progress as we develop the additional information required for its practical application and validation.

2. Methods

Three methods of differing significance were proposed in [CCT/01-02] with a view to obtaining a reliable estimate for the uncertainty component due to impurities. These methods are the "Sum of Individual Estimates" (SIE), the "Overall Maximum Estimate" (OME), and the "Estimate based on Representative Comparisons" (ERC). We proceed to discuss each of these in turn, in addition to a combined SIE/OME approach.

2.1 Sum of Individual Estimates (SIE)

The application of this method requires the determination of the concentrations of all relevant impurities using appropriate analysis techniques (an example of a state-of-the-art Glow Discharge Mass Spectrometry report is given in Appendix 1 that includes, as is usual at present, a very crude uncertainty estimate) and a knowledge of the concentration-dependence of the fixed-point temperature for the different impurities detected. The latter is simply the derivative, $m^{\mathrm{i}}_{\mathrm{l}}=\partial T_{\mathrm{l}}/\partial c^{i}_{\mathrm{l}}$, of the temperature of the liquidus line T_{l} in the phase diagram with regard to the concentration of impurity i, which must be deduced for each impurity from the corresponding equilibrium phase diagram at low concentrations, and c^{i}_{l} is the mole fraction concentration of the impurity i in the liquid equilibrium phase of the sample. It is the intention of WG1 to tabulate the required derivatives in appendices to this document for each of the fixed points of the ITS-90 in an effort to promote harmonization and to avoid duplication of analysis of the phase diagrams.

The SIE approach yields for the change in the observed fixed-point temperature T_{liq} relative to that of the chemically pure material T_{pure} at the liquidus point, where only an infinitesimal portion of the sample is frozen (F=1, where F is the fraction of sample melted):

$$\Delta T_{\mathrm{SIE}} = T_{\mathrm{pure}} - T_{\mathrm{liq}} = -\sum_{i} c^{i}_{\mathrm{l1}} \left(\partial T_{\mathrm{l}} / \partial c^{i}_{\mathrm{l}}\right). \tag{1}$$

In (1), $c^{\mathrm{i}}_{\mathrm{l1}}$ is the concentration of the impurity i at the liquidus point. The summation is over all impurities since, in the dilute limit, there is evidence that each impurity behaves independently, and the formation of ternary and higher order compounds exert a negligible influence. Thus, the SIE method is in explicit accordance with the notion that the temperature of the fixed point should be *corrected* for the influence of impurities by the amount calculated via (1). This is fully consistent with the directive in the ISO Guide to the Expression of Uncertainty in Measurement that calls for all measurements to be corrected for known bias or systematic effects. At present, the uncertainty estimates for chemical analyses are rarely expressed in a manner consistent with the GUM [ISO 1995] and the reliability of the estimates remains a concern. To improve the situation, it may be necessary to undertake a project to compare analyses obtained by different institutes for different analysis methods (e.g. Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Glow Discharge Mass Spectrometry (GDMS), Instrumental Neutron Activation Analysis (INAA), Carrier-Gas Hot Extraction, Electrothermal Evaporation Atomic Absorption Spectrometry (ETAAS)) for samples of the fixed-point materials that are of vital importance to the thermometry community.

The standard uncertainty of the estimate ΔT_{SIE} then results from the uncertainties of the analysis results $u(c^{\mathrm{i}}_{\mathrm{l1}})$ and of the data for the concentration dependencies $u(m^{\mathrm{i}}_{\mathrm{l}})$.

$$u^2(\Delta T_{\mathrm{SIE}}) = \Sigma_{\mathrm{i}}\, [u(c^{\mathrm{i}}_{\mathrm{l1}})\, m^{\mathrm{i}}_{\mathrm{l}}]^2 + [c^{\mathrm{i}}_{\mathrm{l1}}\, u(m^{\mathrm{i}}_{\mathrm{l}})]^2. \quad (2)$$

Until recently, the common practice in chemical testing was to use the repeatability or reproducibility of measurements as the basis for the uncertainty assessment. This may still be the practice in many laboratories. Other sources of uncertainty include sampling effects, segregation effects within a sample, contamination of the analysis equipment, and calibration. Thus, uncertainties in chemical analyses (if reported at all) may be low. The magnitude of $u(c^{\mathrm{i}}_{\mathrm{l1}})$ may be comparable to $c^{\mathrm{i}}_{\mathrm{l1}}$ itself. Based on our present knowledge of chemical analyses, uncertainties (k=2) for individual elements are normally within the range 20% to 300% of the nominal value. Where the uncertainty of the chemical analysis is large compared to other uncertainties, it is imperative to compute the degrees of freedom associated with the standard uncertainty of Eq. (2) to ensure that the expanded uncertainty can be properly computed.

Use of the SIE method is not recommended for materials of less than 99.999% purity since the assumptions of independent influence appropriate to the dilute limit may no longer apply.

2.2 Overall Maximum Estimate (OME)

The OME method must be applied if the concentrations of the impurities or their individual influence on the fixed-point temperature are unknown as accurately as necessary for the SIE method to be of use. All that is required is an accurate estimate of the overall impurity concentration, expressed as a mole fraction. With this, the maximum estimate for the liquidus-point temperature change is given by

$$\Delta T_{\mathrm{OME}} = c_{\mathrm{l1}} \,/\, A\,. \quad (3)$$

In (4), c_{l1} is the overall impurity concentration at the liquidus point and the first cryoscopic constant, A, is given by the relation

$$A = L/R[T_{\mathrm{pure}}]^2\,, \quad (4)$$

L is the molar heat of fusion, R is the molar gas constant, and T_{pure} is the phase transformation temperature of the ideally pure substance (see Table 1).

Even though the OME method provides an overall estimate for the expected temperature change, it should not be used to correct the fixed-point temperature because Eq. (3) yields only a bound. However, the value may be used to estimate the uncertainty component arising from the impurities present in the sample. Equation (5) is recommended for this purpose:

$$u^2(\Delta T_{\mathrm{OME}}) = [\Delta T_{\mathrm{OME}}]^2 / 3 = [c_{l1} / A]^2 / 3 \ . \qquad (5)$$

Where the uncertainty $u(\Delta T_{\mathrm{OME}})$ is large compared to other uncertainties, it is again necessary to determine the effective degrees of freedom. The finite degrees of freedom of this standard uncertainty arises principally from the uncertainty in the estimated impurity concentration, c_{l1}. Given that the uncertainty of the purity is likely to be in the range 100% to 300%, it is vital that the degrees of freedom be stated together with the standard uncertainty to ensure proper calculation of the coverage factor and expanded uncertainty for the desired confidence level.

Where supplier assays are incomplete, i.e. lacking uncertainties or detection limits, or an incomplete list of detected elements, often no further claim can be made beyond the nominal purity (e.g. 99.9999% by weight, metallic elements only). Note that purities derived via the expression (1 − Σ(detected impurities)) are unsupportable because manufacturer assays may indicate little more than "no impurities detected". For zone-refined fixed-point materials, the OME method yields a maximum estimate if the overall impurity content c_{l1} is estimated reliably because impurities having equilibrium distribution coefficients, $k^i_{\mathrm{o}} = c^{\mathrm{i}}_{\mathrm{s}}/c^{\mathrm{i}}_{\mathrm{l}}$ ($c^{\mathrm{i}}_{\mathrm{s}}$ mole fraction concentration of the impurity i in the solid phase), larger than 2 are very effectively removed by zone refining and, thus, are usually unimportant. (k^i_{o} describes the segregation of the impurity during slow freezing at very low concentrations.) Nevertheless, it is recommended that the concentration of such impurities be verified, as only a small number are relevant to each fixed-point substance.

If the uncertainties of the analysis results and the slopes, $m^{\mathrm{i}}_{\mathrm{l}}$, are sufficiently small, the SIE method generally yields smaller values than the OME method.

Chemical assays should include, as a minimum, all of the "common" elements that are normally found in a particular fixed-point material. It is the intention of WG1 to prepare Appendices/Addenda for a list of such elements for the respective ITS-90 fixed points. If the abundances of these elements are not specifically identified, then (half) the detection limit should be used. It is important to emphasize that the certificate of analysis must include an uncertainty statement as the chemists performing the analyses are in the best position to make such estimates. When such information is lacking, or when it is evident that the analysis is incomplete, use of the nominal purity (e.g. 99.9999%) is recommended with an estimated standard uncertainty equal to the purity (e.g. 10^{-6} mole fraction ± 10^{-6} mole fraction). A purity obtained by computing (1 – Σ(detected elements)) may be expected to underestimate the uncertainty component. Again, the degrees of freedom of the estimated uncertainty must be taken into account in the calculation of the expanded uncertainty appropriate to the desired confidence level.

Table 1. The latent heats of fusion (L) and the first cryoscopic constants (A) for the fixed point substances of the ITS-90.

Substance	T_{90} K	L J/mole	A K^{-1}	A^{-1} mK/10^{-6} mole fraction
e-H_2	13.8033	117	0.0739	0.014
Ne	24.5561	335	0.0668	0.015
O_2	54.3584	444	0.0181	0.055
Ar	83.8058	1188	0.0203	0.049
Hg	234.3156	2301	0.005041	0.198
H_2O	273.1600	6008	0.009684	0.103
Ga	302.9146	5885	0.007714	0.130
In	429.7485	3291	0.002143	0.467
Sn	505.078	7162	0.003377	0.296
Zn	692.677	7068	0.001772	0.564
Al	933.473	10789	0.001489	0.672
Ag	1234.93	11284	0.000890	1.124
Au	1337.33	12720	0.000855	1.170
Cu	1357.77	12928	0.000843	1.186

2.3 SIE/Modified-OME Combined Method

It is possible to combine the SIE method for the dominant impurities and the OME method for the remaining impurities. It is furthermore possible to apply a simpler, modified OME method if the equilibrium distribution coefficients of all relevant impurities are known. The change in the liquidus-point temperature by impurities with k^i_o less than 0.1, $T_{pure} - T_{liq,\le 0.1}$, can be reliably estimated by fitting the expression (6)

$$T_{pure} - T_{liq,\le 0.1} = c/FA \tag{6}$$

to the freezing or melting curve (measured with one liquid-solid interface, see CCT/99-11 and CCT/2000-13) in an appropriate F range. (The fitted coefficient c is a reliable estimate for the mole fraction concentration of all impurities with k^i_o less than 0.1. It is influenced by the other impurities present in the sample, but this usually leads to an acceptable overestimation.) Behaviour consistent with equation (6), with the assumption that all of the impurities behave independently, is said to obey Raoult's law. Thus, it is only necessary to determine the concentrations of the impurities with $k^i_o > 0.1$ and to combine the two estimates based on (6) ($k^i_o \le 0.1$) and (1) ($k^i_o > 0.1$).

We must stress that (6) should not be applied casually for all impurities since, strictly speaking, it is only valid for impurities that are insoluble in the solid phase ($k^i_o = 0$). A chemical analysis is required to ensure that the influence of impurities with significant solubility in the solid phase is first accounted for by the SIE method. For $k^i_o > 0.1$, the inappropriate application of Raoult's law will significantly underestimate the change in the melting temperature [CCT/03-12].

Caution is required in assessing the influence of impurities associated with so-called "zero-percent" systems, a term introduced by [Hume-Rothery, Anderson 1960] for systems having a very low solubility in the solid phase and a eutectic or peritectic formation temperature very close to the freezing temperature of the pure host metal. Zero percent systems are particularly insidious due to the fact that freezing at the eutectic or peritectic formation temperature may yield a very flat freezing curve. In [Connolly, McAllan 1980], the zero-percent system Sn-Fe is shown to form a eutectic at 10 ppm Fe at a temperature approximately 8 mK lower than the freezing temperature of pure tin. Fortunately, such cases can be easily detected and removed using state-of-the-art measuring techniques and high-purity materials. Furthermore, information regarding the behaviour of impurities present in the fixed-point materials as derived from the phase diagrams at low concentrations has improved significantly in recent years (see Section 3). It is the intention of WG1 to collect the relevant information in appendices to this document.

The uncertainty appropriate to this hybrid method may be calculated by combining in quadrature the result from (2) with that from (5) (with c from (6) replacing c_{l1} for the remaining impurities).

Since the method depends on fitting the freezing or melting curve over some range of liquid fraction, the results so obtained will be affected by other factors that influence the shape of the curve. Care must be taken that the realization follows good practice to minimize the effects of the thermal environment on the shape of the curve [CCT/96-8]. It has been suggested that the slope of the melting curve is influenced by the change in the hydrostatic head as the liquid-to-solid ratio changes during the process of freezing or melting. While the origin of the slope of the melting curve may be incorrectly attributed (when such effects are observable), the uncertainty arising from the analysis goes some way towards recognizing the fact that such curves are not ideally flat, and the likely consequence is a somewhat increased uncertainty estimate.

Melting and freezing curves may be expected to exhibit rate-dependence due to both thermal influences as well as the nature of the phase transformation process itself. If we consider a typical freezing process where an impurity is less soluble in the solid phase than in the liquid, then growth of solid at the solid-liquid interface leads to rejection of the impurity from the solid, generating a boundary layer of impurity-rich liquid at the interface. Under equilibrium freezing conditions, the impurity concentration in the liquid has adequate time to homogenize through diffusive and convective processes. Such equilibrium conditions are rarely achieved, and uniformity of the solid phase is seldom (if ever) reached due to the exceptionally slow rate of solid-solid diffusion. The distribution coefficient does not achieve its equilibrium value, k^i_o, but takes on an "effective" value k^i_eff between k^i_o and 1. If the condition $k^i_\mathrm{eff} \leq 0.1$ is not fulfilled, the application of equation (6) is no longer justified. While long freezing plateaux are preferred, investigations of the rate-dependence are encouraged as such influences ought to be part of the overall uncertainty budget. This investigation allows an estimate of how large the deviations from the behaviour corresponding to equation (6) may be. It has long been recognized that the shape of the melt is sensitive to the distribution of impurities. This is best demonstrated by comparing a melt following a very fast (quench) freeze that generally leads to a reasonably homogeneous sample with that following a very slow freeze that allows significant impurity segregation.

2.4 Determination of the liquidus-point temperature

For the freezing curves of the metallic fixed-point materials, the maximum should be taken as the best approximation of the liquidus-point temperature. Observation of the curves should be performed with inner and outer liquid-solid interfaces (see [CCT/2000-13]) and should extend past the maximum by 10 % to 20 % of the fraction frozen, to clearly establish the value of the maximum and the resolution of its determination.

For the melting curves used to realize the triple points of the cryogenic gases via adiabatic techniques, the liquidus-point temperature should be determined by extrapolating the dependence of the melting temperature on the fraction of sample melted to the liquidus point. This is done by fitting a function $T_{\mathrm{melt}}(F)$ to the experimental data, keeping in mind the following points:

- The fitting should be performed in an F range for which the melting temperature T_{melt} of the fixed-point sample can be determined with the lowest possible uncertainty. For example, the cryogenic gases have very small thermal conductivities. This causes the melting curves to become sensitive to the thermal surroundings as melting proceeds towards large F values. This influences the shape of the melting curve and increases the uncertainty in estimating the liquidus point. On the other hand, most physical effects influence the melting temperature at low F values where the solid phase dominates (i.e. effects arising from the influence of crystal defects, of the spin-conversion catalyst necessary to realize the triple-point of equilibrium hydrogen, etc.). Thus, the choice of the F range used for fitting should be considered very carefully after taking into account the properties and behaviour of the specific fixed-point material.
- To extrapolate the melting curve to the liquidus point, the melting curve is approximated by a function $T_{\mathrm{liq}}(F)$ whose form corresponds to the F-dependence of the effects influencing the melting curve. (The simplest approaches are to fit T_{melt} versus F or $1/F$.) The optimum function may prove different for the various fixed-point materials. The choice should be guided by selecting a form that minimizes the standard deviation of the experimental data from the fit function and maximizes the repeatability of the liquidus-point temperature.

Fortunately, these melting curves are in many cases sufficiently flat that detailed fitting is unnecessary. The value near 50% melted fraction is often an adequate estimate of the liquidus point that avoids the influences of crystal defects, etc. at low melted fraction and the thermal influences that manifest at large melted fraction. This approach is recommended for the very flat curves observed for mercury, water, and gallium—fixed points realizable at very high purity.

The uncertainty in determining the liquidus-point temperature from the observed freezing or melting curves must also be included in the overall uncertainty budget for the fixed-point realization. This component is in addition to the uncertainty component attributable to the influence of impurities on the liquidus-point temperature and estimated as discussed previously.

3. Phase Diagrams

For both the SIE method and the hybrid SIE/modified-OME method, it is necessary to have information regarding the behaviour of all relevant impurities present in the fixed-point material as derived from the phase diagrams at low concentrations. The data used to construct phase diagrams has improved significantly in recent years. In 1978, the ASM (American Society for Metals) International joined forces with the National Bureau of Standards (now the National Institute of Standards and Technology) in an effort to improve the reliability of phase diagrams by evaluating the existing data on a system-by-system basis. An international programme for alloy phase diagrams was carried out. The results are available in the ASM Handbook [Baker *et al.* 1992], in the three-volume set of "Binary Alloy Phase Diagrams" [Massalski *et al.*] and in the ten-volume set of "Handbook of Ternary Alloy Phase Diagrams" [Villars *et al.* 1995]. The available data are sufficient for systems with solubilities of a few per cent or more. For these systems, peculiarities should not exist at very low concentrations. Further investigations are necessary for systems referred to as degenerate or zero-percent systems, for which solubility has yet to be detected. Since the phase diagrams have typically been investigated at concentrations near and in excess of one per cent, a small solubility at very low concentrations cannot be ruled out. However, it appears likely that information regarding degenerate systems will improve in the near future. Computer programs for thermodynamic calculations are currently capable of computing phase diagrams using databases that quantify the thermodynamic properties of the materials [Eriksson, Hack 1990; Jansson et al. 1993]. Thus, the application of the SIE method and the SIE/modified-OME method for the temperature fixed points of the ITS-90 appears possible on the basis of current state-of-the-art material data and analysis techniques.

4. Validation of Fixed-Point Cells

The use of the SIE or OME methods assumes that the fixed-point material within the cell is substantially similar in composition to the starting material. In fact, fixed-point cells may be contaminated in the fabrication process, especially for fixed points at temperatures of 420 °C (zinc) and higher. Several methods are appropriate for verifying that the cell construction did not add appreciable impurities.

The thermal analysis of phase-transition plateaux should be performed with all new cells to check for consistency with results from SIE or OME methods, to make sure that no additional impurities were added to the fixed-point sample during fabrication of the fixed-point cell. Additionally, the ERC method (Estimate based on Representative Comparisons), while no longer considered acceptable as the basis for estimating the uncertainty attributed to chemical impurities as the method is somewhat dependent on chance, can assist in the validation of cell preparation. Differences in cell realization temperatures are best measured as a "direct comparison," where two cells are simultaneously realized in identical thermal enclosures. These comparisons need not be Key Comparisons. In fact, the comparisons can be direct comparisons of fixed-point cells within one laboratory. Advantages of single-laboratory comparisons are: 1) many effects other than cell variations are maintained constant and are not inappropriately interpreted as "cell impurities," and 2) because the cost is less, it is feasible to test many more cells. Where the ERC method is employed for these supplementary investigations, uncertainty budgets should identify the components that are encompassed in cell differences observed in ERCs.

If either an ERC using direct comparisons, or a thermal analysis of cell plateaux results in an estimated uncertainty larger than that obtained by the SIE or OME methods, then it is quite likely that the cell has been contaminated in fabrication, that the chemical analysis underestimates the impurities, or that the realization methods are not optimal.

5. Effective degrees of freedom, expanded uncertainties, and confidence levels

The approach to reporting uncertainties arising developed herein proposes a paradigm shift for thermometry. A review of the CCT-K3 report [CCT-K3] and subsequent analysis [Guthrie] either implicitly (by omission) or explicitly associate the Type B estimates for the impurity influences with infinite degrees of freedom. In the CCT-K3 exercise, the majority of the participants stated that the uncertainty estimate for the impurity influence was based on Raoult's Law. Given the relatively large relative uncertainty of the chemical analyses on which these estimates depend, a more realistic assessment of the degrees of freedom is in order. For ease of reference, we make use of an expression from the GUM [ISO 1995], with the equation numbering used therein. The approximation

$$\nu_i \approx \frac{1}{2}\left(\frac{\Delta u(x_i)}{u(x_i)}\right)^{-2} \tag{G.3}$$

provides a means to estimate the degrees of freedom given the relative uncertainty (the uncertainty in the uncertainty, if you will). The alternative expression [Douglas 2005]

$$\nu_S = \frac{1}{2}\left(\frac{\Delta u}{u}\right)^{-2}\left[1 + 3\left(\frac{\Delta u}{u}\right) + 1.2\left(\frac{\Delta u}{u}\right)^2\right] \tag{7}$$

focuses on the broadening of the asymmetric chi-squared distribution to choose a better Student distribution than G.3 for small ν.

Values of $\Delta u(x_i)$ are best obtained directly from reports of analysis, when the report gives uncertainties in the determination of x_i. In the absence of this information, the effective degrees of freedom may be estimated by examining the reproducibility of multiple, *independent* chemical analyses and other experimental evidence.

$(\Delta u/u)$	Eq. (G.3)	Eq. (7)
400%	0.0	1.0
300%	0.1	1.2
200%	0.1	1.5
100%	0.5	2.6
50%	2.0	5.6
20%	12.5	20.6
10%	50.0	65.6

Once the degrees of freedom have been calculated, the coverage factor can be determined for a given confidence level (usually 95%). Following the form of the GUM, we write for the expanded uncertainty

$$U_{95} = t_{95}(\nu)\, u \tag{8}$$

In Eq. (8), $t_{95}(\nu)$ is from Student's distribution (or t-distribution) where ν defines the interval from $-t_{95}(\nu)$ to $+t_{95}(\nu)$ that encompasses 95% of the distribution.

ν	t_{95}	ν	t_{95}	ν	t_{95}
1	12.71	11	2.20	25	2.06
2	4.30	12	2.18	30	2.04
3	3.18	13	2.16	35	2.03
4	2.78	14	2.14	40	2.02
5	2.57	15	2.13	45	2.01
6	2.45	16	2.12	50	2.01
7	2.36	17	2.11		
8	2.31	18	2.10	100	1.984
9	2.26	19	2.09		
10	2.23	20	2.09	∞	1.96

When ν is not an integer, the GUM advocates interpolating t_{95} from the table or truncating ν to the next lower integer. Given the procedural difficulties in estimating t_{95} when it is likely that the degrees of freedom from Eq. (G.3) will fall below 1, Eq. (7) is recommended instead. The treatment of the uncertainty of non-normal distributions or distributions with low effective degrees of freedom is a current area of research, and the statistical tools are not yet fully developed.

This discussion is merely a reminder of how finite degrees of freedom influence a single-component uncertainty. The reader is referred to the GUM [ISO 1995] for the procedure to be used when combining uncertainty components, each having their associated degrees of freedom, via the Welch-Sattherwaite formula.

6. Conclusions

With a goal to harmonize the approach used to estimate the component uncertainties attributed to the influence of impurities on fixed-point temperatures, we recommend the Sum of Individual Estimates (SIE) as the preferred means by which to estimate the change of the observed liquidus-point temperature relative to that of the chemically pure material. The SIE method requires that chemical analysis of the fixed-point material be combined with knowledge of the influence of the individual impurities on the fixed-point temperature. Clearly, practical application of the SIE method would benefit from lower uncertainties in the chemical analyses (and universal recognition that these uncertainties need to be included in the report). This is a topic that may need to be addressed through a joint CCT/CCQM Working Group if we are to ensure that the needs of the temperature metrology community [Hill, Rudtsch, 2005] are seriously considered. Tabulation of the sensitivity coefficients (the derivatives, $m^{\mathrm{i}}_{\mathrm{l}}=\partial T_{\mathrm{l}}/\partial c^{i}_{\mathrm{l}}$, of the temperature of the liquidus line T_{l} in the phase diagram with regard to the concentration of impurity i) for each point is required to ensure commonality in the calculations. Nonetheless, the first step towards our goal is to reach consensus regarding the method. We recognize that the temperatures ought to be corrected for the influence of impurities and that this will lead to a symmetric uncertainty about the corrected value. The current approach is undoubtedly biased since the effect of most impurities is to depress the melting temperature of the material in question. (In zone-refined materials, impurities increasing the melting temperature may also have an important influence. Their concentration and influence need to be checked individually.)

Where the information required to fully implement the SIE method is lacking, the OME method may be the only recourse. The OME method does not consider the individual behaviour of the various impurities present in the fixed-point material. It yields a maximum estimate if the influence of impurities with equilibrium distribution coefficients larger than 2 can be neglected, as is usually the case for zone-refined materials.

A hybrid SIE/modified-OME method may be of some utility in certain cases. This approach requires the same analytical information as the SIE method for only the most abundant impurities with equilibrium distribution coefficients $k^{i}_{\mathrm{o}} > 0.1$. The additional influence of impurities with $k^{i}_{\mathrm{o}} \leq 0.1$ can be reliably estimated by evaluating the freezing curves by applying Raoult's law.

The ERC method, currently used by some national metrology institutes, is discouraged as a means to estimate the uncertainty attributable to the influence of impurities for an individual fixed point. The method relies on chance rather than an understanding of the science and cannot be considered reliable. Nonetheless, the direct comparison of cells is a useful check of SIE/OME-based estimates.

To determine the liquidus-point temperature from the experimental data for freezing curves, we recommend the maximum as the best approximation. For melting curves, an extrapolation to the liquidus point should be performed considering the individual properties of the fixed-point materials and the uncertainty in measuring the temperature of the liquid-solid interface. The uncertainty in determining the liquidus-point temperature must be included in the uncertainty budget for the fixed-point realization in addition to the uncertainty attributable to chemical impurities.

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Appendix 1. Example of an elemental analysis required by the SIE method.

National Research Council Canada
Conseil national de recherches Canada

Institute for National Measurement Standards

Chemical Metrology

Standards Council of Canada
Accredited Laboratory
Scope of Accreditation 474
Conseil canadien des normes
Laboratoire accrédité
Portée d'accréditation 474
TM

ISO/IEC 17025

October 6, 2003

NO. 27871

To: Ken Hill, INMS

Analyst: A. Mykytiuk/B. Methven

Glow Discharge Mass Spectrometric Report - ppb (weight)

	Sn 2003/09/26		Sn 2003/09/26
Li	<0.5	Br	<14
Be	<0.2	Rb	<0.4
B	<0.5	Sr	<0.3
C	5000	Y	<0.3
N	340	Zr	<0.5
O	3900	Nb	<0.5
F	<0.7	Mo	<1
Na	<0.8	Pd	
Mg	5	Ag	<2
Al	4	Cd	<28
Si	12	In	<220
P	2	Sn	Matrix
S	210	Sb	1000
Cl	3	Te	<26
K	<17	I	<4
Ca	<5	Cs	<7
Sc	<0.3	Ba	<7
Ti	0.3	La	<1
V	<0.2	Ce	<5
Cr	0.9	Hf	<1
Mn	<0.4	Ta	
Fe	48	W	<0.7
Co	<7	Pt	<3
Ni	<11	Au	<10
Cu	<2	Hg	<15
Zn	<2	Tl	<2
Ga	<1	Pb	66
Ge	30	Bi	<0.7
As	3	Th	<0.9
Se	<10	U	<4

Note: Uncertainties associated with the results given in this report should typically be considered to be ± a factor of two (±5-fold for C, N, and O)