PROPAGATION OF UNCERTAINTY FOR AN INTERPOLATED RADIATION THERMOMETRY SCALE

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ABSTRACT

An evaluation is made of the expected uncertainties that may be achieved by approximating ITS-90 in the range from the silver point up to 2500 °C by an interpolated scale based on the recently developed carbon-metal eutectic fixed points. Analytic expressions are derived for the sensitivity coefficients for the uncertainties in the measured signals and the estimated temperatures for a generalised non-linear interpolation equation, for both exact fitting and least-squares determinations of the free parameters. These formulae are applied to interpolation between the carbon-metal eutectic fixed points using a modified form of the Sakuma-Hattori interpolation equation. It is shown that in the interpolation region, the combined uncertainty in this approximation to ITS-90 can be kept below the uncertainty in the individual fixed points, provided that the interpolation equation is of sufficiently high order to ensure that the interpolation error is kept low. With expected improvements in the reproducibility of the carbon-metal eutectics, this uncertainty should be much smaller than the uncertainty in the current realisation of ITS-90. In the future, thermodynamics measurements of the fixed-point temperatures may allow ITS-90 to be redefined between the silver point and 3000 °C in terms of this interpolation approach.

1. INTRODUCTION

The interpolation equation approach for primary radiation thermometry is currently only practicable in approximating ITS-90 in the temperature range below the copper point. The lack of fixed points above the copper points means that in this range the equations must be extrapolated, resulting in uncertainties that propagate as T^2 at best. However, the recent development of metal-carbon eutectic fixed points, e.g. [1], in the range 1100 °C to 2500 °C raises the interesting possibility of redefining the ITS-90 temperature scale above the silver point based on interpolation between defined temperatures of the eutectic points. Interpolation equations for radiation thermometers can be shown in principle [2] to be equivalent to the widespread practice of using a temperature-dependent mean effective wavelength in the integral signal ratio equation to solve the for the unknown temperature. In addition, interpolation equations obviate the need to measure the spectral responsivity of the pyrometer and are not prone to errors caused by unaccounted-for out-of-band transmission.

The narrow bandwidth of primary radiation thermometers allows interpolation equations to be developed that contain a small number of free parameters, typically only three or four. Since there are 12 fixed points, including the pure metal fixed points as well as the carbon-metal eutectic points, between the silver point and 2500 °C, least-squares techniques can be used to take advantage of the increased number of degrees of freedom available over the exact fitting case. This reduces the overall uncertainty using interpolation.

Lagrange (polynomial) interpolation is used in many of the ITS-90 sub-ranges below the silver point. White and Saunders [3] have shown how for these cases propagation of uncertainty formulae can be written down by inspection. However, interpolation equations for radiation thermometers are almost exclusively non-linear (see [4] for a special-case exception) and so cannot be expressed in the Lagrange formalism. In this paper we present analytic propagation of uncertainty formulae for a general non-linear equation for both the exact fitting case and the least-squares problem. These formulae are then applied to a specific example of a commonly used radiation thermometry interpolation equation, and numerical results are given.

2. PROPAGATION OF UNCERTAINTY FOR EXACT FITTING

The general form for a non-linear interpolation equation is

$$S = S(T, a_1, a_2, \ldots, a_N)\,, \tag{1}$$

where S is the signal measured by the pyrometer, and is a function of temperature T and a set of N parameters a_i. In the exact fitting case the parameters a_i are determined by requiring equation (1) to pass through N measured temperature-signal pairs, (T_1, S_1), (T_2, S_2), …, (T_N, S_N). That is, each of the parameters a_i is a function of all the measured pairs. Thus, equation (1) can be rewritten as

$$S = S(T, T_1, T_2, \ldots, T_N, S_1, S_2, \ldots, S_N)\,. \tag{2}$$

Because the interpolation equation is non-linear it is usually not possible to write it down explicitly in the form of equation (2), and the parameters a_i are determined numerically. Nevertheless, application of the propagation of uncertainty formula requires the evaluation of each of the sensitivity coefficients $\partial S/\partial T_i$ and $\partial S/\partial S_i$.

Appendix A gives the derivation of the sensitivity coefficients for the exact fitting case. These can be written in the compact form

$$\frac{\partial S}{\partial T_i} = -\left.\frac{\partial S}{\partial T}\right|_{T=T_i} \sum_{j=1}^{N} \mathbf{M}_{ij}^{-1} \frac{\partial S}{\partial a_j} \tag{3}$$

and

$$\frac{\partial S}{\partial S_i} = \sum_{j=1}^{N} \mathbf{M}_{ij}^{-1} \frac{\partial S}{\partial a_j} \tag{4}$$

where $\mathbf{M}_{ij}^{-1}$ is the i,j^{th} element of the inverse of the $N \times N$ square matrix $\mathbf{M}$ given by

$$\mathbf{M} = \begin{bmatrix} \left.\frac{\partial S}{\partial a_1}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_1}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_1}\right|_{T=T_N} \\ \left.\frac{\partial S}{\partial a_2}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_N} \\ \vdots & \vdots & \vdots & \vdots \\ \left.\frac{\partial S}{\partial a_N}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_N} \end{bmatrix}. \tag{5}$$

All the derivatives on the right-hand sides of equations (3) to (5) are easily evaluated from the form of the interpolation equation given by equation (1). The only difficult step is determining the inverse of the matrix $\mathbf{M}$; however, in practice this is most easily performed numerically, and needs only to be calculated once for a given interpolation equation and set of fixed-point temperatures. Note that unlike Lagrange interpolation, it is necessary to determine the values of the parameters before being able to calculate the sensitivity coefficients.

The propagation of uncertainty formula for the uncertainty in the pyrometer signal, u_S, in the absence of correlations, is [5]

$$u_S^2 = \sum_{i=1}^{N} \left(\frac{\partial S}{\partial T_i}\right)^2 u_{T_i}^2 + \sum_{i=1}^{N} \left(\frac{\partial S}{\partial S_i}\right)^2 u_{S_i}^2\,, \tag{6}$$

where u_{T_i} and u_{S_i} are the uncertainties in the temperatures and measured signals, respectively, that define the interpolation equation. Equation (6) is converted to an uncertainty in T through the equation

$$u_S = \frac{\partial S}{\partial T} u_T \ . \tag{7}$$

3. PROPAGATION OF UNCERTAINTY FOR LEAST-SQUARES FITTING

Least-squares fitting uses redundancy in the number of measured points, which provides assurance that the measurements are consistent and that the radiation thermometer interpolates well, and provides a measure of the interpolation error through the error of fit. The additional number of degrees of freedom allows a reduction in the total uncertainty by a factor of the order of $\sqrt{N/M}$ where M measurements are used to determine N parameters ($M > N$).

For the least-squares problem, the parameters in equation (1) are all functions of the M measurement pairs. Thus equation (2) becomes

$$S = S(T, T_1, T_2, \ldots, T_M, S_1, S_2, \ldots, S_M) \ . \tag{8}$$

For unweighted least squares, the parameters are determined by minimising the chi-squared function

$$c^2 = \sum_{i=1}^{M} \left[S_i - S(T_i) \right]^2 \ , \tag{9}$$

where, for the purpose of clarity, $S(T_i)$ is used to mean the value of S obtained by substituting $T = T_i$ into equation (1) or (8).

In Appendix B the sensitivity coefficients are derived using equation (9) as the starting point. The results, after applying a minor approximation, are

$$\begin{bmatrix} \dfrac{\partial S}{\partial T_1} \\ \dfrac{\partial S}{\partial T_2} \\ \vdots \\ \dfrac{\partial S}{\partial T_M} \end{bmatrix} = \mathbf{B}\,\mathbf{H}^{-1} \begin{bmatrix} \dfrac{\partial S}{\partial a_1} \\ \dfrac{\partial S}{\partial a_2} \\ \vdots \\ \dfrac{\partial S}{\partial a_N} \end{bmatrix} \tag{10}$$

where the matrix elements of the $M \times N$ matrix $\mathbf{B}$ are

$$\mathbf{B}_{ij} = -\left(\frac{\partial S}{\partial T} \frac{\partial S}{\partial a_j} \right)\Bigg|_{T=T_i} + \left[S_i - S(T_i) \right] \frac{\partial^2 S}{\partial T \partial a_j}\Bigg|_{T=T_i} \quad \text{for } i = 1 \text{ to } M, j = 1 \text{ to } N \ , \tag{11}$$

and

$$\begin{bmatrix} \dfrac{\partial S}{\partial S_1} \\ \dfrac{\partial S}{\partial S_2} \\ \vdots \\ \dfrac{\partial S}{\partial S_M} \end{bmatrix} = \begin{bmatrix} \left.\dfrac{\partial S}{\partial a_1}\right|_{T=T_1} & \left.\dfrac{\partial S}{\partial a_2}\right|_{T=T_1} & \cdots & \left.\dfrac{\partial S}{\partial a_N}\right|_{T=T_1} \\ \left.\dfrac{\partial S}{\partial a_1}\right|_{T=T_2} & \left.\dfrac{\partial S}{\partial a_2}\right|_{T=T_2} & \cdots & \left.\dfrac{\partial S}{\partial a_N}\right|_{T=T_2} \\ \vdots & \vdots & \vdots & \vdots \\ \left.\dfrac{\partial S}{\partial a_1}\right|_{T=T_M} & \left.\dfrac{\partial S}{\partial a_2}\right|_{T=T_M} & \cdots & \left.\dfrac{\partial S}{\partial a_N}\right|_{T=T_M} \end{bmatrix} \mathbf{H}^{-1} \begin{bmatrix} \dfrac{\partial S}{\partial a_1} \\ \dfrac{\partial S}{\partial a_2} \\ \vdots \\ \dfrac{\partial S}{\partial a_N} \end{bmatrix}, \tag{12}$$

where **H** is a square symmetric matrix given by

$$\mathbf{H} = \begin{bmatrix} \sum_{i=1}^{M}\left(\left.\dfrac{\partial S}{\partial a_1}\right|_{T=T_i}\right)^2 & \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_1}\dfrac{\partial S}{\partial a_2}\right)_{T=T_i} & \cdots & \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_1}\dfrac{\partial S}{\partial a_N}\right)_{T=T_i} \\ \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_2}\dfrac{\partial S}{\partial a_1}\right)_{T=T_i} & \sum_{i=1}^{M}\left(\left.\dfrac{\partial S}{\partial a_2}\right|_{T=T_i}\right)^2 & \cdots & \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_2}\dfrac{\partial S}{\partial a_N}\right)_{T=T_i} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_N}\dfrac{\partial S}{\partial a_1}\right)_{T=T_i} & \sum_{i=1}^{M}\left(\dfrac{\partial S}{\partial a_N}\dfrac{\partial S}{\partial a_2}\right)_{T=T_i} & \cdots & \sum_{i=1}^{M}\left(\left.\dfrac{\partial S}{\partial a_N}\right|_{T=T_i}\right)^2 \end{bmatrix}. \tag{13}$$

The dimensions of the vectors and matrices in equations (10) and (12) are $[M\times 1] = [M\times N]\times[N\times N]\times[N\times 1]$. Once again, all the derivatives on the right-hand sides of equations (10) to (13) are straightforward to evaluate. The matrix **H** is usually called the curvature matrix in the context of least-squares fitting (and is related to the Hessian). As expected, when $M = N$ equations (10) and (12) are identical to equations (3) and (4), respectively (although this is not immediately obvious!).

4. INTERPOLATION THROUGH METAL-CARBON EUTECTIC FIXED POINTS

In this section we demonstrate the application of the propagation of uncertainty formula (equation (6)), with the sensitivity coefficients given by equations (10) and (12), to simulated measurements made at several of the carbon-metal eutectic fixed points. The interpolation equation was chosen to be the Planck version of the Sakuma-Hattori equation,

$$\text{Signal} = \frac{C}{\exp\left(\dfrac{c_2}{AT+B}\right)-1}, \tag{14}$$

where A, B, and C are the fitted parameters. Because of the exponential nature of this equation, unweighted least-squares fitting tends to skew the residuals. This problem is largely overcome by fitting the logarithm of the signal as a function of temperature. Thus, we use the interpolation equation

$$S = a_1 - \ln\left[\exp\left(\frac{c_2}{a_2 T + a_3}\right)-1\right], \tag{15}$$

where $a_1 = \ln C$, $a_2 = A$, $a_3 = B$, and the values of the measurements S_i are the logarithms of the simulated signals. The derivatives appearing in equations (10) and (12) are all easily calculated from equation (15).

4.1 Propagated Uncertainty

To simulate the measured signals the Planck function was integrated over a spectral responsivity curve with a centre wavelength of 650 nm and a bandwidth of 50 nm with a shape corresponding to that of a true interference filter, including a small secondary peak 200 nm from the main peak. The temperatures used for the carbon-metal eutectic points were rounded to the nearest degree, as given by Yamada et al. [1]. Equation (15) was fitted successively to 3, 4, 5, and 10 fixed points. These points are summarised in Table 1. The first three sets of points are identical to those chosen by Yamada et al. [1] in their calculation of uncertainty using a Monte Carlo technique.

Number of Points	Points Used	Fixed-Point Temperature (°C)
3	Cu	1084.62
	Pt-C	1738
	Re-C	2474
4	Cu	1084.62
	Pd-C	1492
	Ru-C	1953
	Re-C	2474
5	Cu	1084.62
	Pd-C	1492
	Pt-C	1738
	Ir-C	2290
	Re-C	2474
10	Ag	961.78
	Cu	1084.62
	Fe-C	1153
	Ni-C	1329
	Pd-C	1492
	Rh-C	1657
	Pt-C	1738
	Ru-C	1953
	Ir-C	2290
	Re-C	2474

Table 1. Fixed-points and their temperatures for the 3-point, 4-point, 5-point, and 10-point data sets used to illustrate the propagation of uncertainty equation.

Also, to be consistent with Yamada et al., the uncertainty in each fixed-point temperature was chosen to be 0.1 °C. However, here we also assume that there is a 0.05% uncertainty in each of the measured signals at the fixed points. Figure 1 shows the combined uncertainty in the interpolated temperature for each set of points.

Although each curve in Figure 1 was calculated using equation (10) and (12), the 3-point curve could be determined using the simpler equations (3) and (4), since for the case $M = N$ the two sets of equations are identical (for exact fitting the residuals are zero). It is clear that increasing the number of points reduces the uncertainty in the interpolated temperature, and the combined uncertainty can be well below the uncertainty in an individual measurement. However, in the extrapolation region the uncertainty increases quite rapidly. These conclusions are the same as those reached by Yamada et al., and indeed by assuming a zero uncertainty in each of the measured signal, the first three curves in Figure 1 are identical to the corresponding curves of Yamada et al. (notwithstanding slight differences in assumed spectral responsivity).

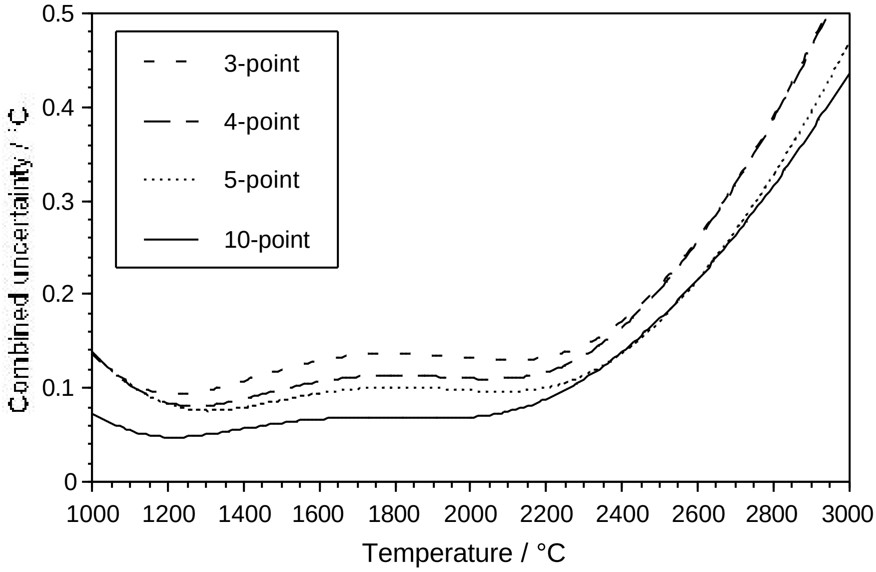

Figure 1. Combined uncertainty calculated using equations (6) and (7), with the sensitivity coefficients given by equations (10) and (12), for the 3-parameter interpolation equation (14). The fixed points used for each curve are listed in Table 1. The uncertainties in the temperature of each fixed point is assumed to be 0.1 °C and the uncertainty in each of the measured signals is assumed to be 0.05%.

4.2 Interpolation Error

An important consideration in the interpretation of Figure 1 is interpolation error. The uncertainty plotted in this figure describes how the interpolation equation varies with the uncertainties in its defining points. It does not account for differences between the interpolation equation and the true behaviour of the pyrometer. Equation (14) is semi-empirical and contains the implicit assumption that the extended effective wavelength [2] is a linear function of inverse temperature. This is a good approximation for narrow bandwidths and short temperature ranges. However, the temperature range here is quite large and this approximation may limit the performance of equation (14).

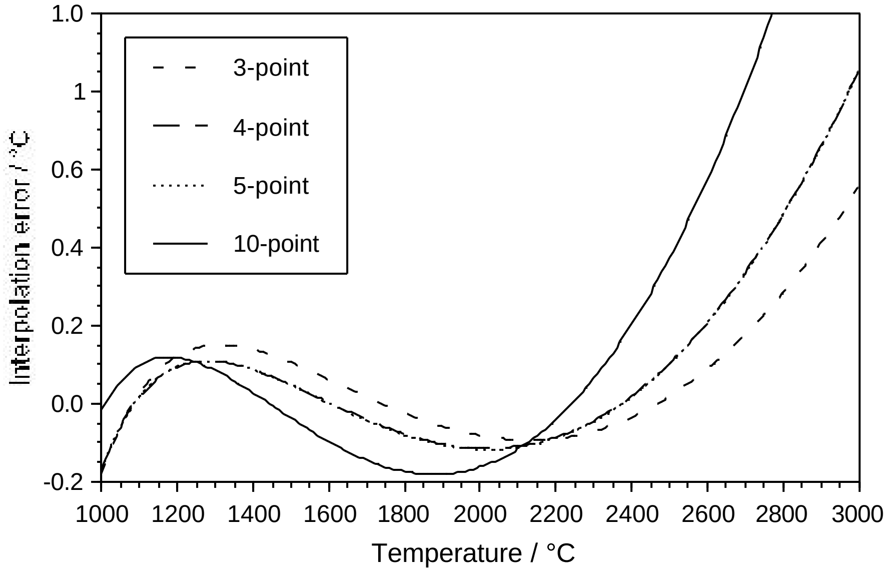

Figure 2. The interpolation error for each of the data sets for the interpolation equation (14). The curves for the 4- and 5-point data sets are almost identical.

The interpolation error is plotted in Figure 2 for each set of points. Note that the interpolation error is given by the temperature calculated from the interpolation equation minus the true temperature. Even within the interpolation region the error is of a similar magnitude to, or larger than, the combined uncertainty shown in Figure 1. The extended effective wavelength is plotted in Figure 3 as a function of inverse temperature, and indeed there is significant curvature in the line, consistent with the interpolation error of Figure 2. Figure 4 shows the residuals for both a linear fit and a quadratic fit to the curve in Figure 3. For the linear fit, implicit in equation (14), the wavelength errors are of the order of several tenths of a nanometre. On the other hand, the quadratic fit performs within about ±0.025 nm over most of the temperature range and would appear to offer significant improvement over the linear approximation.

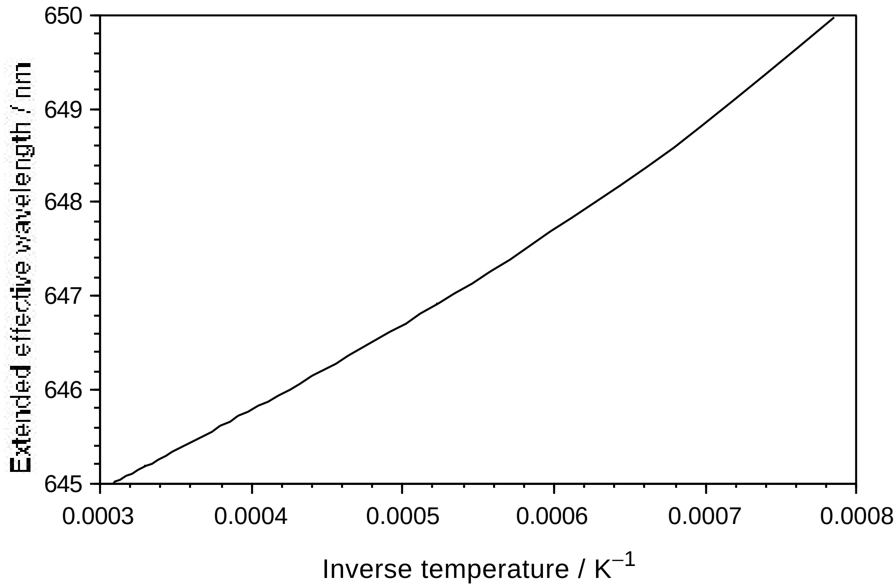

Figure 3. Extended effective wavelength as a function of inverse temperature for the spectral responsivity assumed for the calculations. There is clearly some curvature over the relatively large temperature range used.

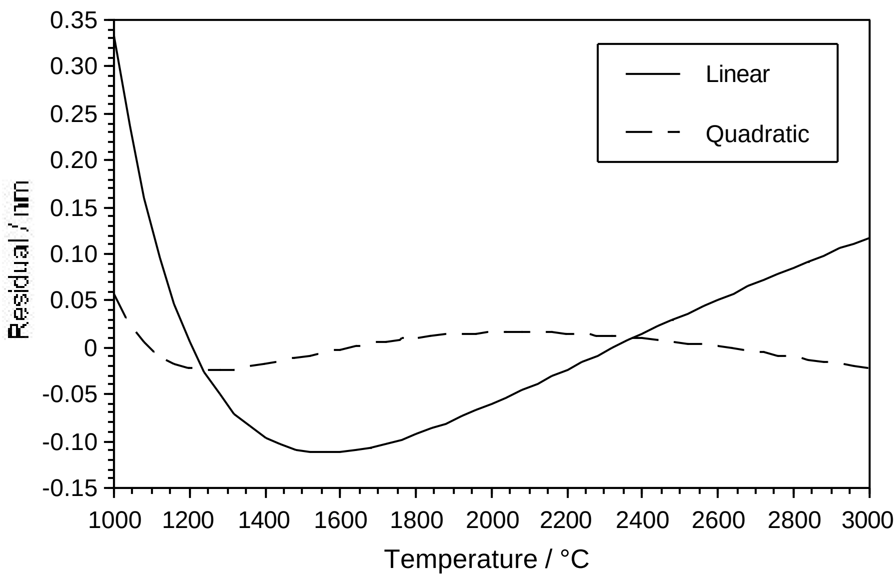

Figure 4. Residuals for a linear and a quadratic fit to the extended effective wavelength plotted in Figure 3.

Extending equation (14) to take account of this curvature yields

$$\text{Signal} = \frac{C}{\exp\left(\dfrac{c_2}{AT + B + D/T}\right) - 1}, \tag{16}$$

where we have introduced the extra parameter D. To solve for the parameters of this interpolation equation we again use its logarithmic form:

$$S = a_1 - \ln\left[\exp\left(\frac{c_2}{a_2T + a_3 + a_4/T}\right) - 1\right]. \tag{17}$$

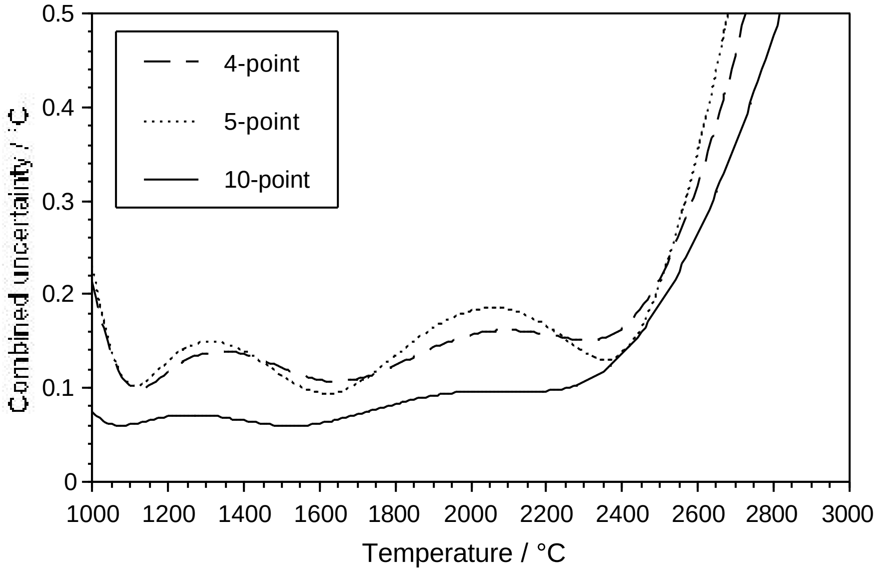

Figure 5. Combined uncertainty as for Figure 1, but for the interpolation equation (16).

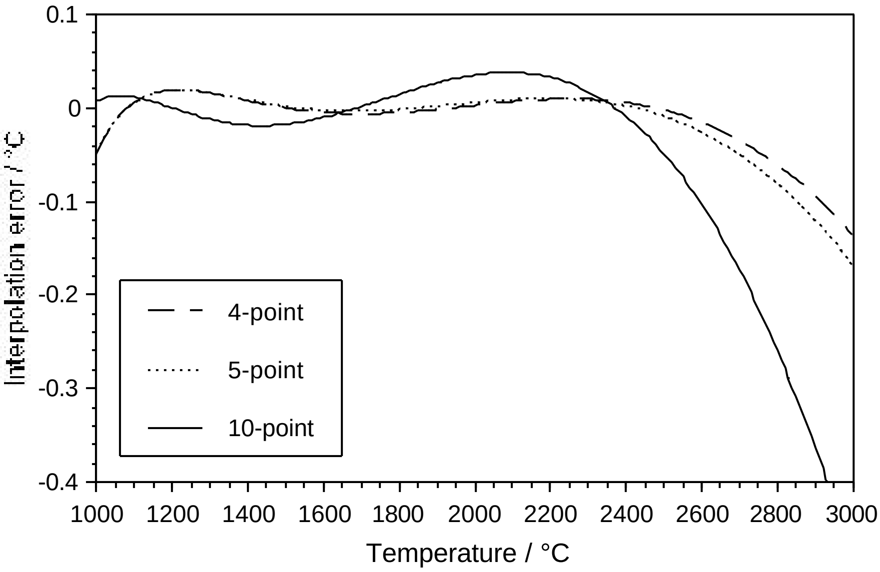

Figure 6. Interpolation error as for Figure 2, but for the interpolation equation (16).

Figures 5 and 6 give the combined uncertainty and interpolation error, respectively, for the 4-point, 5-point, and 10-point data sets. The combined uncertainty for this 4-parameter interpolation equation is slightly higher than for the 3-parameter equation shown in Figure 1, mainly due to the reduced number of degrees of freedom. However, the interpolation error is significantly reduced over that shown in Figure 2, to the extent that it is now below the level of the combined uncertainty.

The interpolation error may be reduced further by finding a more suitable fit, than a simple polynomial, to the extended effective wavelength versus temperature relationship. A possible 3-parameter description of this relationship has been suggested by Schreiber [6]:

$$l_{\mathrm{x}} = A + \frac{B}{T + C}, \tag{18}$$

where A, B, and C are the free parameters. This yields an interpolation equation of the form

$$S = \frac{a_1}{\exp\left(\dfrac{1 + a_4/T}{a_2 T + a_3}\right) - 1}. \tag{19}$$

Indeed, in the case considered here, equation (19) produces a marginally smaller error of fit than equation (16). However, an even better extended effective wavelength versus temperature relationship is

$$l_{\mathrm{x}} = A + \frac{B}{T} + \frac{C}{T^4}. \tag{20}$$

In this case the interpolation equation is

$$S = \frac{a_1}{\exp\left(\dfrac{c_2}{a_2 T + a_3 + a_4/T^3}\right) - 1}. \tag{21}$$

This equation gives almost identical combined uncertainty curves to those plotted in Figure 5, but the interpolation error is approximately 4 times smaller in magnitude than the curves in Figure 6 and has a similar shape.

5. CONCLUSIONS

This paper has provided an algebraic solution to the propagation of uncertainty problem for both exact-fitting and least-squares interpolation using non-linear interpolation equations. This gives a simple means of analysing the utility of an interpolated radiation thermometry scale, since interpolation equations for radiation thermometers are fundamentally non-linear. The recent development of carbon-metal eutectic fixed points between 1100 °C and 2500 °C provides conveniently spaced reference points for interpolation to be practicable over this temperature range.

The propagated uncertainty for an interpolated scale, within the interpolation region, is generally no greater than the uncertainty associated with the measurements at each of the fixed points. For least-squares fitting this combined uncertainty decreases with the number of measurements used. With future improvements in the reproducibility of the carbon-metal fixed points, this combined uncertainty will be easily below the uncertainty in the current ITS-90 realisation, which is generally about 1 °C to 2 °C above 2000 °C [1]. By defining the temperatures of the fixed points, following their thermodynamic measurement, the uncertainty in the interpolated scale will be reduced even further. However, in the extrapolation region the uncertainties increase fairly rapidly, so an interpolated scale is only useful up to the temperature of the highest fixed point, and perhaps a bit higher.

To cover the full temperature from the silver point to 2500 °C requires a 4-parameter interpolation equation in order to ensure that interpolation errors are less than 0.05 °C for the 650 nm, 50 nm bandwidth spectral responsivity used for the calculations presented here. Equation (21) reduces this interpolation error to 0.01 °C and is maintained below 0.02 °C with extrapolation up to 3000 °C. On the other hand, use of a 3-parameter equation results in errors as large as 0.2 °C; this is larger than the expected reproducibility of the fixed points. It should be noted that the pyrometer signals must be corrected for non-linearity and size-of-source effect for the interpolation error to be kept low. It may be that other interpolation equations are more suitable for pyrometers with different operating wavelengths, bandwidths, spectral responsivity shapes, and required to operate over different temperature ranges. This should be investigated in future work. It is likely that determining the best interpolation equation for a given pyrometer requires only a rough estimate of its spectral responsivity, not a detailed determination as required for the ITS-90 approach.

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APPENDIX A — DERIVATION OF SENSITIVITY COEFFICIENTS FOR EXACT FITTING

For the exact fitting case the interpolation equation contains N parameters, which are determined by requiring the equation to pass through N measured temperature-signal pairs. Thus

$$S = S(T, a_1, a_2, \ldots, a_N)\,, \tag{A1}$$

where

$$\begin{aligned} a_1 &= a_1(T_1, T_2, \ldots, T_N, S_1, S_2, \ldots, S_N) \\ a_2 &= a_2(T_1, T_2, \ldots, T_N, S_1, S_2, \ldots, S_N) \\ &\vdots \\ a_N &= a_N(T_1, T_2, \ldots, T_N, S_1, S_2, \ldots, S_N) \end{aligned}\;. \tag{A2}$$

In addition, since we have exact fitting, the following equations hold:

$$\begin{aligned} S_1 &= S(T_1, a_1, a_2, \ldots, a_N) \\ S_2 &= S(T_2, a_1, a_2, \ldots, a_N) \\ &\vdots \\ S_N &= S(T_N, a_1, a_2, \ldots, a_N) \end{aligned}\;. \tag{A3}$$

To determine the sensitivity coefficients $\partial S/\partial T_i$ we differentiate both (A1) and each of the equations in (A3) with respect to each of the T_i, bearing in mind the dependencies given in (A2), and compare the results. Differentiating equation (A1) gives

$$\begin{aligned} \frac{\partial S}{\partial T_1} &= \frac{\partial S}{\partial a_1}\frac{\partial a_1}{T_1} + \frac{\partial S}{\partial a_2}\frac{\partial a_2}{\partial T_1} + \ldots + \frac{\partial S}{\partial a_N}\frac{\partial a_N}{\partial T_1} \\ \frac{\partial S}{\partial T_2} &= \frac{\partial S}{\partial a_1}\frac{\partial a_1}{T_2} + \frac{\partial S}{\partial a_2}\frac{\partial a_2}{\partial T_2} + \ldots + \frac{\partial S}{\partial a_N}\frac{\partial a_N}{\partial T_2} \\ &\vdots \\ \frac{\partial S}{\partial T_N} &= \frac{\partial S}{\partial a_1}\frac{\partial a_1}{T_N} + \frac{\partial S}{\partial a_2}\frac{\partial a_2}{\partial T_N} + \ldots + \frac{\partial S}{\partial a_N}\frac{\partial a_N}{\partial T_N} \end{aligned}\;. \tag{A4}$$

This can be written conveniently in matrix form:

$$\begin{bmatrix} \dfrac{\partial S}{\partial T_1} \\ \dfrac{\partial S}{\partial T_2} \\ \vdots \\ \dfrac{\partial S}{\partial T_N} \end{bmatrix} = \mathbf{A} \begin{bmatrix} \dfrac{\partial S}{\partial a_1} \\ \dfrac{\partial S}{\partial a_2} \\ \vdots \\ \dfrac{\partial S}{\partial a_N} \end{bmatrix}, \tag{A5}$$

where the $N \times N$ square matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \begin{bmatrix} \frac{\partial a_1}{\partial T_1} & \frac{\partial a_2}{\partial T_1} & \cdots & \frac{\partial a_N}{\partial T_1} \\ \frac{\partial a_1}{\partial T_2} & \frac{\partial a_2}{\partial T_2} & \cdots & \frac{\partial a_N}{\partial T_2} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial a_1}{\partial T_N} & \frac{\partial a_2}{\partial T_N} & \cdots & \frac{\partial a_N}{\partial T_N} \end{bmatrix}. \tag{A6}$$

In general we cannot directly evaluate the derivatives in equation (A6) because we cannot explicitly write the parameters a_i in terms of the temperatures T_i. However, we can eliminate **A** from equation (A5) by differentiating each of the equations in (A3). This gives

$$\begin{aligned}
\frac{\partial S_1}{\partial T_1} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_1}\frac{\partial a_1}{\partial T_1} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_1}\frac{\partial a_2}{\partial T_1} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_1}\frac{\partial a_N}{\partial T_1} + \left.\frac{\partial S}{\partial T}\right|_{T=T_1} \\
\frac{\partial S_1}{\partial T_2} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_1}\frac{\partial a_1}{\partial T_2} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_1}\frac{\partial a_2}{\partial T_2} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_1}\frac{\partial a_N}{\partial T_2} \\
&\vdots \\
\frac{\partial S_1}{\partial T_N} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_1}\frac{\partial a_1}{\partial T_N} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_1}\frac{\partial a_2}{\partial T_N} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_1}\frac{\partial a_N}{\partial T_N} \\
\frac{\partial S_2}{\partial T_1} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_2}\frac{\partial a_1}{\partial T_1} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_2}\frac{\partial a_2}{\partial T_1} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_2}\frac{\partial a_N}{\partial T_1} \\
\frac{\partial S_2}{\partial T_2} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_2}\frac{\partial a_1}{\partial T_2} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_2}\frac{\partial a_2}{\partial T_2} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_2}\frac{\partial a_N}{\partial T_2} + \left.\frac{\partial S}{\partial T}\right|_{T=T_2} \\
&\vdots \\
\frac{\partial S_N}{\partial T_1} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_N}\frac{\partial a_1}{\partial T_1} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_N}\frac{\partial a_2}{\partial T_1} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_N}\frac{\partial a_N}{\partial T_1} \\
&\vdots \\
\frac{\partial S_N}{\partial T_N} &= \left.\frac{\partial S}{\partial a_1}\right|_{T=T_N}\frac{\partial a_1}{\partial T_N} + \left.\frac{\partial S}{\partial a_2}\right|_{T=T_N}\frac{\partial a_2}{\partial T_N} + \ldots + \left.\frac{\partial S}{\partial a_N}\right|_{T=T_N}\frac{\partial a_N}{\partial T_N} + \left.\frac{\partial S}{\partial T}\right|_{T=T_N}
\end{aligned} \tag{A7}$$

Since all the S_i values are constant, each of the left-hand sides is equal to zero. These equations can also be rearranged into matrix form:

$$\begin{bmatrix} -\left.\frac{\partial S}{\partial T}\right|_{T=T_1} & 0 & \cdots & 0 \\ 0 & -\left.\frac{\partial S}{\partial T}\right|_{T=T_2} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & -\left.\frac{\partial S}{\partial T}\right|_{T=T_N} \end{bmatrix} = \mathbf{A} \times \mathbf{M} \tag{A8}$$

where the matrix **A** is given by equation (A6) and **M** is an $N \times N$ square matrix given by

$$
\mathbf{M}=\begin{bmatrix}
\left.\frac{\partial S}{\partial a_1}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_1}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_1}\right|_{T=T_N} \\
\left.\frac{\partial S}{\partial a_2}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_N} \\
\vdots & \vdots & \vdots & \vdots \\
\left.\frac{\partial S}{\partial a_N}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_{21}} & \cdots & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_N}
\end{bmatrix}. \qquad \text{(A9)}
$$

A can now be determined by right-multiplying both sides of equation (A8) by $\mathbf{M}^{-1}$. The result is then substituted into equation (A5) to yield the required sensitivity coefficients:

$$
\begin{bmatrix}
\frac{\partial S}{\partial T_1} \\
\frac{\partial S}{\partial T_2} \\
\vdots \\
\frac{\partial S}{\partial T_N}
\end{bmatrix}
=
\begin{bmatrix}
-\left.\frac{\partial S}{\partial T}\right|_{T=T_1} & 0 & \cdots & 0 \\
0 & -\left.\frac{\partial S}{\partial T}\right|_{T=T_2} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & -\left.\frac{\partial S}{\partial T}\right|_{T=T_N}
\end{bmatrix}
\mathbf{M}^{-1}
\begin{bmatrix}
\frac{\partial S}{\partial a_1} \\
\frac{\partial S}{\partial a_2} \\
\vdots \\
\frac{\partial S}{\partial a_N}
\end{bmatrix}. \qquad \text{(A10)}
$$

The other set of sensitivity coefficients, $\partial S/\partial S_i$, are derived in a similar fashion. This time we differentiate equations (A1) and (A3) with respect to each of the S_i. Differentiating (A1) yields equations identical to (A5) and (A6) but with each of the T_i replaced by the corresponding S_i. Differentiating (A3) similarly gives equations (A8) and (A9) with the same replacements, but additionally the matrix on the left-hand side of equation (A8) is in this case the identity matrix. Following the same procedure as above, the equation for the sensitivity coefficients is simply

$$
\begin{bmatrix}
\frac{\partial S}{\partial S_1} \\
\frac{\partial S}{\partial S_2} \\
\vdots \\
\frac{\partial S}{\partial S_N}
\end{bmatrix}
= \mathbf{M}^{-1}
\begin{bmatrix}
\frac{\partial S}{\partial a_1} \\
\frac{\partial S}{\partial a_2} \\
\vdots \\
\frac{\partial S}{\partial a_N}
\end{bmatrix}, \qquad \text{(A11)}
$$

where the square matrix **M** is again given by equation (A9). Note that equations (A10) and (A11) are given in equivalent form as equations (3) and (4) in the main text.

APPENDIX B — DERIVATION OF SENSITIVITY COEFFICIENTS FOR LEAST SQUARES

For the least-squares fitting case the interpolation equation contains N parameters, which are determined by fitting the equation to a set of M measured temperature-signal pairs, where $M > N$. Thus

$$S = S(T, a_1, a_2, ..., a_N)\ , \tag{B1}$$

where

$$\begin{aligned}
&a_1 = a_1(T_1, T_2, ..., T_M,\ S_1, S_2, ..., S_M) \\
&a_2 = a_2(T_1, T_2, ..., T_M,\ S_1, S_2, ..., S_M) \\
&\vdots \\
&a_N = a_N(T_1, T_2, ..., T_M,\ S_1, S_2, ..., S_M)
\end{aligned}\quad . \tag{B2}$$

For least squares, an equation similar to equation (A3) does not hold.

In unweighted least squares the coefficients are solved for by minimising the function

$$c^2 = \sum_{i=1}^{M} [S_i - S(T_i)]^2\ , \tag{B3}$$

which is achieved by setting each of the derivatives $\partial c^2 / \partial a_i$ equal to zero and solving the resulting set of N simultaneous equations:

$$\begin{aligned}
&\frac{\partial c^2}{\partial a_1} = -2\sum_{i=1}^{M} [S_i - S(T_i)] \left.\frac{\partial S}{\partial a_1}\right|_{T=T_i} = 0 \\
&\frac{\partial c^2}{\partial a_2} = -2\sum_{i=1}^{M} [S_i - S(T_i)] \left.\frac{\partial S}{\partial a_2}\right|_{T=T_i} = 0 \\
&\vdots \\
&\frac{\partial c^2}{\partial a_N} = -2\sum_{i=1}^{M} [S_i - S(T_i)] \left.\frac{\partial S}{\partial a_N}\right|_{T=T_i} = 0
\end{aligned}\quad . \tag{B4}$$

To determine the sensitivity coefficients $\partial S / \partial T_i$, each of the equations in (B4) is differentiated with respect to each of the T_i. For example, differentiating the first equation with respect to T_1 yields

$$\begin{aligned}
&\frac{\partial a_1}{\partial T_1}\sum_{i=1}^{M}\left\{\left(\left.\frac{\partial S}{\partial a_1}\right|_{T=T_i}\right)^2 - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_1^2}\right|_{T=T_i}\right\} \\
&\quad + \frac{\partial a_2}{\partial T_1}\sum_{i=1}^{M}\left\{\left.\frac{\partial S}{\partial a_2}\frac{\partial S}{\partial a_1}\right|_{T=T_i} - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_2 a_1}\right|_{T=T_i}\right\} \\
&\quad + \ldots \\
&\quad + \frac{\partial a_N}{\partial T_1}\sum_{i=1}^{M}\left\{\left.\frac{\partial S}{\partial a_N}\frac{\partial S}{\partial a_1}\right|_{T=T_i} - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_N a_1}\right|_{T=T_i}\right\} \\
&\quad = -\left.\left(\frac{\partial S}{\partial T}\frac{\partial S}{\partial a_1}\right)\right|_{T=T_1} + [S_1 - S(T_1)]\left.\frac{\partial^2 S}{\partial T \partial a_1}\right|_{T=T_1}
\end{aligned} \tag{B5}$$

The full set of derivatives can be written in matrix form as

$$\mathbf{D} \times \mathbf{H} = \mathbf{B} \tag{B6}$$

where

$$\mathbf{D} = \begin{bmatrix} \frac{\partial a_1}{\partial T_1} & \frac{\partial a_2}{\partial T_1} & \cdots & \frac{\partial a_N}{\partial T_1} \\ \frac{\partial a_1}{\partial T_2} & \frac{\partial a_2}{\partial T_2} & \cdots & \frac{\partial a_N}{\partial T_2} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial a_1}{\partial T_M} & \frac{\partial a_2}{\partial T_M} & \cdots & \frac{\partial a_N}{\partial T_M} \end{bmatrix}. \tag{B7}$$

The matrix elements of the $N \times N$ matrix $\mathbf{H}$ are

$$\mathbf{H}_{ij} = \sum_{k=1}^{M} \left\{ \left(\frac{\partial S}{\partial a_i} \frac{\partial S}{\partial a_j} \right) \Bigg|_{T=T_k} - \left[S_k - S(T_k) \right] \frac{\partial^2 S}{\partial a_i \partial a_j} \Bigg|_{T=T_k} \right\} \text{ for } i = 1 \text{ to } N, j = 1 \text{ to } N\,, \tag{B8}$$

and the matrix elements of the $M \times N$ matrix $\mathbf{B}$ are

$$\mathbf{B}_{ij} = -\left(\frac{\partial S}{\partial T} \frac{\partial S}{\partial a_j} \right) \Bigg|_{T=T_i} + \left[S_i - S(T_i) \right] \frac{\partial^2 S}{\partial T \partial a_j} \Bigg|_{T=T_i} \text{ for } i = 1 \text{ to } M\,, j = 1 \text{ to } N\,. \tag{B9}$$

If we now differentiate equation (B1) with respect to each of the T_i (as we did in Appendix A for equation (A1)), we obtain

$$\begin{bmatrix} \frac{\partial S}{\partial T_1} \\ \frac{\partial S}{\partial T_2} \\ \vdots \\ \frac{\partial S}{\partial T_M} \end{bmatrix} = \mathbf{D} \begin{bmatrix} \frac{\partial S}{\partial a_1} \\ \frac{\partial S}{\partial a_2} \\ \vdots \\ \frac{\partial S}{\partial a_N} \end{bmatrix}. \tag{B10}$$

From equation (B6), $\mathbf{D} = \mathbf{B} \times \mathbf{H}^{-1}$, so the sensitivity coefficients are given by

$$\begin{bmatrix} \frac{\partial S}{\partial T_1} \\ \frac{\partial S}{\partial T_2} \\ \vdots \\ \frac{\partial S}{\partial T_M} \end{bmatrix} = \mathbf{B}\,\mathbf{H}^{-1} \begin{bmatrix} \frac{\partial S}{\partial a_1} \\ \frac{\partial S}{\partial a_2} \\ \vdots \\ \frac{\partial S}{\partial a_N} \end{bmatrix}. \tag{B11}$$

Note that the matrix **H** contains sums of residuals multiplied by second derivatives. In general, these terms are small in comparison with the other terms, partly because the second derivatives are themselves small and partly because the residuals are small and random in sign. Thus we can approximate **H** by

$$\mathbf{H} \approx \begin{bmatrix} \sum_{i=1}^{M}\left(\left.\frac{\partial S}{\partial a_1}\right|_{T=T_i}\right)^2 & \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_1}\frac{\partial S}{\partial a_2}\right)\Bigg|_{T=T_i} & \cdots & \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_1}\frac{\partial S}{\partial a_N}\right)\Bigg|_{T=T_i} \\ \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_2}\frac{\partial S}{\partial a_1}\right)\Bigg|_{T=T_i} & \sum_{i=1}^{M}\left(\left.\frac{\partial S}{\partial a_2}\right|_{T=T_i}\right)^2 & \cdots & \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_2}\frac{\partial S}{\partial a_N}\right)\Bigg|_{T=T_i} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_N}\frac{\partial S}{\partial a_1}\right)\Bigg|_{T=T_i} & \sum_{i=1}^{M}\left(\frac{\partial S}{\partial a_N}\frac{\partial S}{\partial a_2}\right)\Bigg|_{T=T_i} & \cdots & \sum_{i=1}^{M}\left(\left.\frac{\partial S}{\partial a_N}\right|_{T=T_i}\right)^2 \end{bmatrix}. \tag{B12}$$

Because the matrix **B** contains only individual residuals, these terms cannot be neglected.

The other set of sensitivity coefficients, $\partial S/\partial S_i$, are obtained by differentiating equation (B1) and each of equations (B4) with respect to each S_i. The result of differentiating the first of equations (B4) with respect to S_1, for example, is

$$\begin{aligned} &\frac{\partial a_1}{\partial S_1}\sum_{i=1}^{M}\left\{\left(\left.\frac{\partial S}{\partial a_1}\right|_{T=T_i}\right)^2 - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_1^2}\right|_{T=T_i}\right\} \\ &\quad + \frac{\partial a_2}{\partial S_1}\sum_{i=1}^{M}\left\{\left.\frac{\partial S}{\partial a_2}\frac{\partial S}{\partial a_1}\right|_{T=T_i} - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_2 a_1}\right|_{T=T_i}\right\} \\ &\quad\quad +\ldots \\ &\quad\quad\quad + \frac{\partial a_N}{\partial S_1}\sum_{i=1}^{M}\left\{\left.\frac{\partial S}{\partial a_N}\frac{\partial S}{\partial a_1}\right|_{T=T_i} - [S_i - S(T_i)]\left.\frac{\partial^2 S}{\partial a_N a_1}\right|_{T=T_i}\right\} \\ &\quad\quad\quad\quad = \left(\frac{\partial S}{\partial a_1}\right)\Bigg|_{T=T_1} \end{aligned} \tag{B13}$$

Following the same procedure as above, the sensitivity coefficients are

$$\begin{bmatrix} \frac{\partial S}{\partial S_1} \\ \frac{\partial S}{\partial S_2} \\ \vdots \\ \frac{\partial S}{\partial S_M} \end{bmatrix} = \begin{bmatrix} \left.\frac{\partial S}{\partial a_1}\right|_{T=T_1} & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_1} & \cdots & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_1} \\ \left.\frac{\partial S}{\partial a_1}\right|_{T=T_2} & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_2} & \cdots & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_2} \\ \vdots & \vdots & \vdots & \vdots \\ \left.\frac{\partial S}{\partial a_1}\right|_{T=T_M} & \left.\frac{\partial S}{\partial a_2}\right|_{T=T_M} & \cdots & \left.\frac{\partial S}{\partial a_N}\right|_{T=T_M} \end{bmatrix} \mathbf{H}^{-1} \begin{bmatrix} \frac{\partial S}{\partial a_1} \\ \frac{\partial S}{\partial a_2} \\ \vdots \\ \frac{\partial S}{\partial a_N} \end{bmatrix}, \tag{B14}$$

where **H** is given by equation (B9) and is well approximated by equation (B12).