Accurate wavelengths for the thorium–neodymium stellar chronometer

R. C. M. Learner, J. Davies and A. P. Thorne
Blackett Laboratory, Imperial College, London SW7 2BZ

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SUMMARY
The wavelengths of the thorium and neodymium lines used in the Butcher stellar chronometer have been remeasured, together with those of weak blended lines of iron and nickel. The results are presented here; the absolute accuracy achieved ranges from 0.21 mÅ for the thorium line to 1.52 mÅ for the weak iron line. The uncertainty of the wavelengths presented in the literature or deduced from published energy levels is discussed in detail. The database used for astrophysics proves to be much older and much less accurate than is often assumed. New instruments, especially Fourier transform spectrometers, offer the possibility of remeasurement to the higher standards needed to interpret current astrophysical observations.

1 INTRODUCTION
It was recently claimed by Butcher (1987) that a stellar chronometer can be made by measuring, in stars of different ages, the intensity of a line in the spectrum of thorium, which has one very long-lived isotope, relative to a nearby line of some stable element of similar excitation characteristics. The two lines he suggested as fulfilling these criteria are Th II 4019.13 Å and Nd II 4018.82 Å. The thorium line, however, lies on the wing of a blend of two lines, one of Fe I and the other of Ni I, which together have an equivalent width much greater than that of the Th line — see Fig. 1, which shows the relevant part of the solar spectrum from Delbouille, Roland & Neven (1973). The relative wavelengths of the components of the 4019-Å blend must be known very accurately in order to model the stellar spectra for extraction of the Th line strength and hence the required intensity ratio.

In this paper we discuss first the uncertainties in the existing database, which led us to remeasure the lines. The following section reports these measurements, which were made in the laboratory by Fourier transform spectrometry (FTS), using hollow cathode lamps as the light sources. In the final section of the paper we present the lessons learned about the reliability and accuracy of published (and re-published) data and describe the limits attainable using modern spectrometers of high resolution and high luminosity.

2 THE DATABASE
Since direct observations of the lines or of the levels from which the wavelengths can be deduced are available in the standard literature, why should re-measurement be necessary? Only a very small fraction of the line and level data used in astronomy is accompanied by a clear estimate of its uncertainty, and consultation of the references cited in the standard literature reveals that the number of decimal places given in the lists is in many cases a misleading indicator of accuracy. It also reveals other problems: much of the original work was published in sources of considerable obscurity, and there is a tendency for compilations of spectroscopic data to rely on previous compilations. The antiquity of some of the data has thus been heavily disguised by repeated republication.

Two of the spectra considered here (Fe and Th) are exceptional in that they are used to provide wavelength standards, and discussion on the accuracy of these can be found in the recent literature. The other two, Ni and Nd, are more typical of routine data but are sufficiently similar in complexity of spectrum and in excitation to Fe and Th that we can assess their uncertainty with some confidence. As the wavelength, 4000 Å, is one where the ease of measurement and the quality of the data is better than average, the conclusion will be, if anything, a flattering evaluation of the more general data.

We consider the four lines in the order Fe, Ni, Th, Nd and discuss first direct observations and then deduction from published energy levels.

2.1 Fe I 3d⁶ 4s² 5p² F2 – 3d⁶(5pF) 4s4p(5P) x² G3
The most accessible source for the wavelength is as part of multiplet 219 in the Revised Multiplet Tables (RMT) (Moore 1959). The line is not in the MIT tables (Harrison 1939), nor in Striganov & Svendskii (1968). The RMT gives 4019.05 Å, referenced as MIT unpublished material (1947). The value of the wavelength is the same as that in Russell & Moore (1944), in which it is explained that about 70 percent of the entries given to only two decimal places were a private communication from Harrison, while about 25 percent were from Kayser (1912). Harrison’s measurements are of the
very faint lines that were not included in the MIT tables. The 4019-Å line is in fact one of these, but it is worth looking at the antecedents of the other two-decimal-place lines. These are from Vol. VI of Kayser’s 1912 Handbuch in a table whose chief purpose was to correct the measurements of Kayser & Runge (1888) from Rowland’s scale to the new International Angstrom. Some of the 1888 data has appeared in every one of the references cited, though it is common practice to reference only its most recent refurbishment. Thus the 1968 Stigranov & Svendetskii data refers only to its immediate antecedent (RMT 1959).

A similar trap affects the words as well as the dates: ‘Revised’ in the Revised Multiplet Tables refers to the 1945 revision of the 1933 original, and the 1959 date for the RMT records only a more accessible republication of the 1945 tables, not a further revision.

What, then, of the accuracy of the wavelength? The internal consistency (i.e. the relative precision) can be assessed by considering how well lines of the same class in Russell & Moore (two decimal places, from Harrison’s unpublished measurements) fit the analysis. Fifty-seven lines in this class in a wavelength range centred on 4019 Å have an rms error of $\pm 0.08$ cm$^{-1}$ (80 mK), or $\pm 13$ mÅ. The internal consistency of the smaller set of lines used to establish $x^5G_3$ is $\pm 90$ mK. Source shifts resulting from the use of an arc in air are less than 30 mK (Edlén 1959), and the errors of the absolute scale are negligible. A final error of $\pm 100$ mK, or $\pm 15$ mÅ, is a reasonable estimate.

The energy levels are reported in Spectroscopic Data for Iron (Wiese 1985) and in identical form in Atomic Energy Levels for the Iron-period Elements (Sugar & Corliss 1985). The $b^3F_2 - x^5G_3$ difference is 24874.503 cm$^{-1}$ (4019.045 Å), but one level in $x^5G$ is marked as questionable, another is given to only two decimal places, and the term is not regarded as sufficiently well-established to contribute to the set of Ritz standards given in Kaufmann & Edlén (1974), where precision is estimated to be 1 mÅ (6 mK at 4000 Å). We have therefore examined the source of the AEL data; the energy levels for the 4019-Å line are from Crosswhite (1975), who remeasured some 4700 lines in the iron–neon hollow cathode (a low-pressure source) and derived a best-fit set of energy levels. His published wavelengths are not the original measurements, but values deduced from these levels. The lower level, $b^3F_2$, is based on 22 lines, of which 13 have intensity 25 or less on a scale running from 0 to 25,000, and the only strong line (intensity 300) is to the very high-state $x^5G_3$. The laws of natural perversity are in full operation, for this line is given a wavelength that is not consistent with the energy levels (the discrepancy being 54 mK), and its upper level is given to only two decimal places and questioned. The upper level for our 4019-Å line is in somewhat better shape: although two of the five transitions to it have intensity 0, two of the other three are reasonably strong (250 and 300) and connect with well-determined levels. A detailed analysis, based on reasonable estimates of line width and signal-to-noise ratio, suggests that both the levels are determined to about $\pm 15$ mK, giving $\pm 20$ mK (3 mÅ) for the 4019-Å line. The systematic error of 3 mK (Learner & Thorne 1988) can be neglected.

2.2 NiI $3d^8\ 4s^2\ a^3P_2 - 3d^8(3P)\ 4s4p(3P)\ 5P_2$

This is another weak spin-forbidden line, though it is a little more accessible than the Fe line with which it is blended in the solar spectrum. The MIT tables give 4019.046, intensity 5 (on a scale on which the resonance lines have intensity 1000 R); RMT gives 4019.055, with intensity 3, for the whole of multiplet 72 – the identification of the upper level with the $5P$ term came later. The RMT wavelength comes from Hamm (1913), even though MIT tables are used for other lines. (Three of the NiI references used in the RMT for other lines are taken from Kayser’s 1912 compilation and originate in 1909, 1904 and 1896.) A more recent set of measurements teeters on the brink of ‘unpublished’: the papers of Burns & Sullivan (1947) are in a journal of such modesty that no copies appear to be held in the UK.

The error of the 1913 measurements on nickel can be estimated most simply by comparison of contemporary work on the titanium arc (Exner & Hascheck 1911) with the recent remeasurement of the Ti spectrum by Forsberg (1987) – which, incidentally, resulted in the discarding of 50 of the levels assigned to Ti I and listed in Sugar & Corliss (1985). In the region of 4000 Å, the old Ti work shows a systematic shift of 9 mÅ (60 mK), after correcting for the error of the Rowland scale, and an rms scatter (after allowing for the shift) of $\pm 30$ mÅ (200 mK). These errors include the source shifts between arc and hollow cathode, which are, at this level, negligible.

If we assume that the interferometric work of Burns & Sullivan (1947) did not include the weak 4019-Å line, the most recent published value for the wavelength is the one in the MIT tables. The precision of the tables is most easily estimated by comparing Fe standards from Kaufmann & Edlén (1974) with Fe lines in the MIT tables that were not, at that time, established as standards. A sample of 50 such lines centred around 4019 Å shows an rms error of $\pm 11.3$ mÅ.

Figure 1. The solar spectrum at 4019 Å from the Liege Photometric Atlas (Delbouille et al. 1973).
The figures confirm the widely held view that the third decimal place in the MIT tables is not significant. Shifts between atmospheric- and low-pressure sources are likely to be similar in iron and nickel — say 15 and 30 mK for moderately and highly excited levels, respectively.

The energy levels in Sugar & Corliss (1985) predict the transition to be at 24.874.421 cm⁻¹ (4019.046 Å). The levels are deduced from measurements with a low-pressure are by Burns & Sullivan (1947), and their uncertainty is estimated by Sugar & Corliss to be ±10 mK. As spin is a bad quantum number for several states in Ni, it is reasonable to assume that the triplet and quintet manifolds are well linked. The probable error in the 4019-Å line is thus around ±15 mK (2.5 mÅ).

2.3  Th $6d^2(4F) 7s^2 F_{9/2} - 6d^7s(4D) 7p^4 F_{5/2}$

The MIT tables give 4019.137 Å. Comparison of the MIT values with more recent work on Th standards show an rms error for 50 Th lines around 4000 Å of ±12.5 mÅ (80 mK) — much the same as for iron. More recent interferometric measurements by several workers are summarized by Giachetti, Stanley & Zalubas (1970). This last reference gives a weighted mean wavelength of 4019.1287 Å. The error is hard to assess. The difference between two independent measurements used is 0.9 mÅ (6 mK), and pressure shifts of magnitude 1–4 mK are found. It should be remembered that the pressure in one of the ‘low-pressure’ sources used, the electrodeless lamp, can approach (and occasionally exceed) an atmosphere. As (i) Giachetti et al. (1970) found a significant number of measurements discordant by more than 10 mK; (ii) the two sources for the 4019-Å line in their compilation are those given lowest weight; and (iii) the line did not survive to be recommended as a wavelength standard by Kaufmann & Edlén (1974), it seems reasonable to set the error at ±10 mK (1.5 mÅ).

Deduction of the wavelength from the published energy levels (Zalubas & Corliss 1974) yields 24.873.981 cm⁻¹ (4019.1292 Å), 3 mK less than direct measurement. The mutual consistency of the lines indicates a random error of ±2.5 mK, rather less than the uncertainty of 6 mK (1 mÅ) associated with residual pressure shifts and the establishment of an absolute wavelength scale.

2.4  Nd $4f^4(4I) 6s^2 F_{9/2} - 25389_{9/2}$

The accessible value of the wavelength is that in the MIT tables: 4018.826 Å. More recent measurements are less easily found; both Hoekstra (1969) and Wyart (1968) are PhD theses, and the measurements underlying the re-analysis of Blaise et al. (1984) are unpublished. The error of the MIT wavelength must be comparable with that for Th in the same list, ±12.5 mÅ (80 mK). As with Th, this includes any shifts between atmospheric- and low-pressure sources.

There are two contrasting sets of published Nd energy levels: that in the compilation of Martin, Zalubas & Hagan (1978), which is based on modern grating observations, and that of Blaise et al. (1984), for which an infrared/visible FTS was used. The levels in Martin et al. give 24.875.895 cm⁻¹ for the line of interest. The error can be assessed by comparing work on Th using the same spectograph (Zalubas 1960) with the later interferometric standards in Kaufmann & Edlén (1974). The rms difference for 58 lines around 4019 Å is ±4.3 mÅ (27 mK), with a 2-mÅ systematic shift. Random errors in Nd will be similar, and will be reduced by the level-fitting process, but systemic errors will be greater because the spectrum lacks internal standards. A final uncertainty of ±5 mÅ (30 mK) is a minimum figure. The levels reported by Blaise et al. yield 24.875.875 cm⁻¹ (4018.8231 Å) for the 144Nd isotope, with negligible isotope shift. Although they measured hyperfine component separations to 1 mK over the range 3800 Å to 3.8 μm (exploiting the high resolution and good signal-to-noise ratio of the FTS), high absolute wavenumber accuracy was not a priority, and the derived level values were reported only to the nearest 5 mK. Since the FTS wavenumber scale requires calibration if an absolute accuracy of better than about 1:10⁶ is required (see next section), the run-to-run discrepancies of the order of 5 mK in the middle of the spectral range suggest a probable error at the high-frequency end of order ±10 mK (1.6 mÅ).

The status of the four lines is summarized in Table 1. The figures are based on firm ground for Fe and Th, but the error of the absolute scale associated with the other two spectra, which do not generate internal standards, is difficult to quantify.

3 EXPERIMENTAL

Fourier transform spectrometry has three outstanding advantages when precision of measurement of a wavelength or wavenumber is of high priority. The first is its high spectral resolution. The optimum instrumental width for wavenumber precision is about half the source line width, which is 0.06–0.08 cm⁻¹ (about 10 mÅ) in a low-pressure, low-current source such as a hollow cathode lamp. An instrumental resolving power of about 800000 is therefore desirable. Secondly, since measurements with this type of lamp are normally photon noise limited, the high light throughput of the instrument can be exploited to give a good signal-to-noise ratio (Learner & Thorne 1988). The third advantage, crucial to the present problem, is that the wavenumber precision and reproducibility of an FTS relate directly to that of the stabilized He–Ne laser used to control the instrument, and the wavenumber scale is accurately linear. Although this scale does require calibration if an absolute accuracy of better than about 1:10⁶ is required (in principle from a single reference wavelength), the error in measuring relative wavelengths of lines from the same source a few Angstroms apart without this calibration is only a few micro-Angstroms. Any shifts introduced by different illumination of the instrument, whether from lines excited in differ-

<table>
<thead>
<tr>
<th>Table 1. Literature values and estimated errors.</th>
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<tbody>
<tr>
<td><strong>Element</strong></td>
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<tr>
<td></td>
</tr>
<tr>
<td><strong>Th</strong></td>
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<tr>
<td><strong>Ni</strong></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
</tr>
<tr>
<td><strong>Nd</strong></td>
</tr>
</tbody>
</table>

MIT Tables, not later references.
ent parts of the discharge or from a change of light source, are also of the order of micro-Angstroms. Moreover, this relative accuracy applies to measurements made with different spectrometers, so that a single reference line can be used as a transfer standard between two sets of measurements made on different instruments.

With one exception the measurements were carried out at UKAEA Harwell, using a Chelsea Instruments FT-500 visible/UV FTS. Since both the Fe and Ni lines are very weak, the experiment was designed to maximize the signal-to-noise ratio. A characteristic of FTS is that the noise from all lines seen by the detector contributes to the noise at all points in the spectrum, so a narrow-band interference filter (490 cm⁻¹ bandwidth) was used to isolate the spectral region of interest. The effective integration time of the observations was increased to about an hour by co-adding several interferograms.

We attempted initially to measure the Th, Fe and Ni lines simultaneously in a Grimm glow discharge lamp with a cathode containing all three elements, but it proved impossible to detect the Fe and Ni lines in this way. We therefore adopted the alternative strategy of making several relative measurements with different sources, exploiting the wavelength reproducibility of the FTS. This also allowed us to use (except for the Fe line) a set of very similar commercial neon hollow-cathode lamps running at currents between 10 and 20 mA (see Table 2).

The procedure adopted for Nd, Th and Ni was to measure in each case the position of the weak line of interest relative to a stronger line in the same spectrum, using the narrow-band interference filter. A second set of observations, using a wider optical filter, linked each strong line to a single line of similar strength in the neon spectrum at 28937 cm⁻¹ (3456 Å). Because of the similarity of geometry and running conditions between the three lamps, we are confident that this neon line is a suitable transfer standard. Since all lines have similar widths and the noise is 'white', the dominant error in each case arises from the measurement of the weak line.

It was not possible to deal with the weak Fe line in the same way because it was undetectable in the spectrum of a commercial Fe–Ne hollow cathode lamp. It was finally excited at a signal-to-noise ratio of 30 in a demountable iron hollow cathode running in neon at a similar pressure but at a current of 750 mA, and its position was measured relative to a Fe line, some 4000 times stronger, at 24 709.9345 cm⁻¹ (4047 Å) using the FTS at Imperial College, a similar instrument to the FT-500 at Harwell (Thorne et al. 1987). The strong Fe line was then linked to the Ne transfer standard by a measurement with a commercial Fe–Ne hollow cathode, thus completing the chain of relative measurements. In fact, all the lines can be put on an absolute scale by the strong 4047 Å Fe line, which is included in the list of wavelength standards that we recently published (Learner & Thorne 1988).

### 4 RESULTS AND CONCLUSIONS

Table 3 gives the data for the four measurements, obtained from a least-squares fit to a Voigt profile which turns out to be very close to a Gaussian in all cases. Columns 3 and 4 give the errors of the relative wavelengths (standard deviations), and columns 5 and 6 give the errors of the absolute wavelengths. 'Relative' means relative to Fe 24709, while 'absolute' includes the uncertainty of 0.001 cm⁻¹ in the wavenumber of that line. The error analysis includes all uncertainties in line-to-line transfers, based on the well-tested rule derived by Brault (1988)

\[
\text{error} = \frac{\text{full-width-half-maximum}}{2 \times \text{signal-to-noise ratio}}
\]

The precision in the steps involving the strong lines is typically a few micro-Angstroms, and accrued errors are summed in the usual way.

The first conclusion is that we have achieved a considerable gain in the precision of the relative wavelengths of the four lines. The improvements are about an order of magnitude for nickel and neodymium and a smaller factor for the iron and thorium spectra that have been intensively studied as the sources of secondary wavelengths. The changes are sufficient to change the wavelength order of the lines: the shift in the Ni wavelength is one-fifth of the line width of the Fe + Ni blend. The influence of the line wing on the Th component is thus significantly changed.

Secondly, examination of the final column of Table 3 shows that the difference in wavelength between our measurements and the values deduced from the literature usually exceeds the estimated error of that difference. Our own measurements of the relative wavelengths use a calculated error based on objective measurement of the signal-to-noise ratio in the spectrum and a model of the error that we have tested. Even if the subjectively assessed error involved in setting our wavelengths on an absolute scale were doubled, the conclusion would be unchanged. It follows that the analysis of the literature presented in Section 2 has consistently erred toward optimism: the literature must actually be worse than we have suggested, and the need for re-measurement that much more necessary.

Thirdly, it is clear that, even though the hollow cathode lamp is a particularly well-behaved source, we are approach-

### Table 2. Data for weak lines.

<table>
<thead>
<tr>
<th>Element</th>
<th>Current (mA)</th>
<th>Line width (Å)</th>
<th>S/N (1) (a)</th>
<th>S/N (2) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>18</td>
<td>82</td>
<td>26</td>
<td>190</td>
</tr>
<tr>
<td>Th</td>
<td>14</td>
<td>58</td>
<td>608</td>
<td>1200</td>
</tr>
<tr>
<td>Nd</td>
<td>20</td>
<td>70</td>
<td>90</td>
<td>230</td>
</tr>
<tr>
<td>Fe</td>
<td>10</td>
<td>72</td>
<td>-</td>
<td>580</td>
</tr>
<tr>
<td>Fe</td>
<td>750</td>
<td>151</td>
<td>30</td>
<td>165</td>
</tr>
</tbody>
</table>

(a) Signal-to-noise ratio of weaker line; (b) signal-to-noise ratio of stronger line used as link; (c) used to calibrate Ni, Nd and Th spectra; (d) used for weak Fe line; (e) there is no evidence for hyperfine structure in this line.

### Table 3. Results of new measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Rel. error</th>
<th>Abs. error</th>
<th>Wavelength</th>
<th>Diff. from Table 1 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>24873.9780</td>
<td>± 0.82</td>
<td>± 0.13</td>
<td>4019.1298</td>
<td>0.6 ± 0.54</td>
</tr>
<tr>
<td>Ni</td>
<td>24874.3670</td>
<td>± 2.0</td>
<td>± 0.32</td>
<td>4019.0867</td>
<td>8.6 ± 2.4</td>
</tr>
<tr>
<td>Fe</td>
<td>24874.5135</td>
<td>± 1.52</td>
<td>± 0.41</td>
<td>4019.0432</td>
<td>1.6 ± 3.5</td>
</tr>
<tr>
<td>Nd</td>
<td>24875.8576</td>
<td>± 2.7</td>
<td>± 0.44</td>
<td>4018.8259</td>
<td>2.0 ± 1.7</td>
</tr>
</tbody>
</table>

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ing the practicable limit in the realization of the ‘isolated atom’. An error of 1 mK at 4000 Å is 4 parts in 10^6. To achieve this precision requires not only good signal-to-noise but also, for instance, the measurement of the spectrometer pressure and its control to roughly 100 mTorr (0.13 mBar). Fortunately, for most astronomical observations, relative wavelengths are sufficient. There are also problems with the light source: for low photon noise, one must use bright sources, in which residual shifts of the order of ± 1 mK from pressure effects and applied electric fields are unavoidable.

Fourthly, examination of Table 1 shows that, when a precise wavelength is required, recourse should be had to the tabulated energy levels. Published wavelengths, though more convenient, are very significantly less accurate. As Fe and Th are among the few atoms that are used as standards, the Ni and Nd figures give a better idea of the gains that can be achieved in this way for more typical spectra. It is also worth emphasizing that the sacrifice of accuracy is even greater if one relies on the wavelength tabulations in routine use – the MIT tables and the Revised Multiplet Tables.

Fifthly, the work described above on the quality of the literature, plus further work on Hg, Pt, Mo and Ni, support the following generalizations for the visible and near-ultraviolet. The observation of spectra for analysis – that is, with completeness rather than accuracy as the principal aim – can be assigned to three main chronological periods. The first is the first half of this century, when spectrographs with spectrum gratings and photographic detection were used with arcs in air as sources. During this period, accuracy improved from a few tenths of a wavenumber to about one tenth, mainly because of better wavelength standards. The second phase, using replica gratings and low-pressure sources, still with photographic detection, achieved accuracies of a few hundredths of a wavenumber (and was largely concerned with rare-earth spectra). In these two phases, lines measured interferometrically to serve as standards were typically a factor of 10 better than those measured routinely. A third phase, using Fourier transform spectrometers and photodetector, allows routine measurements to be made with much the same accuracy as for standards. Table 3 shows that this claim can be supported even for weak lines.

The final conclusion, therefore, is that modern FT-based measurement offers the possibility of a new database. Such a database should be free of the problems caused by unsuitable sources, inaccurate standards, eye estimates of intensity, non-existent levels, refurbished measurements that prove to be 50 or 100 years old, and, of particular relevance here, subjective or unstated precision. It would also be computer compatible and therefore free of the problem of inaccessible publication and of the difficulty of revision that now devalues the Revised Multiplet and MIT tables.

The effects of such an improvement on observational astrophysics are not trivial; an example is given by Learner & Harris (1987). Data for the spectral region below 2200 Å, the limit both of routine photographic emulsion and of Fe i wavelength standards, is of very significantly lower quality than that discussed in this paper. The mismatch of the quality of the database and the potential of the Hubble Space Telescope is particularly striking. The papers presented at the Amsterdam Conference on Atomic Spectra and Oscillator Strengths for Astrophysics and Fusion Research (Hansen 1990) and the recent review by Smith (1988) describe a large number of observations in which the quality of the conclusions is limited not only by telescope time or detector noise but by the ageing database, which forms the weakest link in the chain of understanding.

ACKNOWLEDGMENTS

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