Evaluation of a Thallium Atomic Beam Frequency Standard at the National Bureau of Standards

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Abstract—**The original NBS cesium standard (NBS I) has been converted to a thallium standard and was operated for one and one-half years with a typical precision of 2×10^{-12} and an accuracy of 1×10^{-11}. Experiments are described which were performed to establish these precision and accuracy estimates. These results, which are comparable to those obtained with longer cesium standards, are considered sufficiently encouraging to justify the conversion of a longer cesium standard to thallium for a more thorough evaluation.**

I. Introduction

In 1957, P. Kusch pointed out the possible advantages that thallium should have over cesium in atomic beam frequency standards [1]. The small quadratic dependence of the frequency on the uniform magnetic field in which the transition occurs is given by

$$\nu(\mathrm{Cs}^{133}) = \nu_0(\mathrm{Cs}) + 427H^2(\text{in Hz}), \tag{1}$$

$$\nu(\mathrm{Tl}^{205}) = \nu_0(\mathrm{Tl}) + 20.4H^2\,(\text{in Hz}). \tag{2}$$

The fractional uncertainties in frequencies resulting from uncertainties in H are given by

$$\left(\frac{\Delta\nu}{\nu_0}\right) = 9.1\times10^{-8}H\Delta H, \qquad \text{for cesium, and} \tag{3}$$

$$\left(\frac{\Delta\nu}{\nu_0}\right) = 1.9\times10^{-9}H\Delta H, \qquad \text{for thallium.} \tag{4}$$

Thus, the $(1, 0)\leftrightarrow(0, 0)$ transition in thallium is 1/50th as sensitive to the field as is cesium. This is no longer as great an advantage as it was originally, since the C fields have been so drastically improved in the cesium beams [2].

A further advantage for thallium arises from its simpler atomic spectrum, since there are only two microwave transitions neighboring the $(1, 0)\leftrightarrow(0, 0)$ σ transition already mentioned. These two π transitions are the $(F=1,\ m_F=1)\leftrightarrow(F=0,\ m_F=0)$ transition and the $(F=1,\ m_F=-1)\leftrightarrow(F=0,\ m_F=0)$ transition. Thus, with different C-field orientations necessary to excite these two sets of transitions, proper parallelism of the σ-oriented C field with the two oscillating field regions in the resonant cavity end sections should insure freedom from overlap of π transitions. Also, the simpler thallium spectrum should allow a greater signal intensity for the $(1, 0)\leftrightarrow(0, 0)$ thallium transition than for the corresponding $(4, 0)\leftrightarrow(3, 0)$ transition in cesium, since a greater percentage of the thallium atoms have energies in the desired states. Finally, the thallium transition frequency is more than double that of cesium, so that, for the same absolute uncertainty in the frequency, a higher relative precision of measurement is obtained for the thallium standard than for the cesium standard.

II. The NBS Thallium Beam Standard

These possible advantages led to the conversion of NBS I, the original NBS cesium standard with an interaction length of 55 cm, to a thallium standard in September, 1962. The thallium standard is shown in Fig. 1.

A considerable amount of time was spent in developing and improving a suitable detection system. Wire

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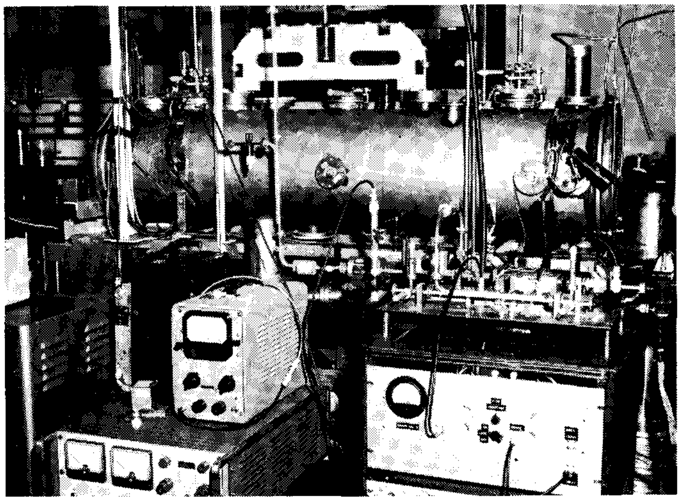

Fig. 1. Thallium atomic beam frequency standard.

0.013 cm in diameter drawn from a pure, single crystal of tungsten has given the most noise-free performance as a surface ionization detector for the thallium beam. Since thallium has an ionization potential of about 6.1 volts, the tungsten wire must be oxidized to provide a work function high enough to allow efficient ionization of the thallium atoms. The oxidation and operating procedures that have been developed are as follows:

1) Before the oven temperature is raised to its operating value of 610°C, pure oxygen is admitted to the vacuum system by opening a variable leak rate valve mounted on the detector cover plate of NBS I. The detector wire temperature is near 900°C as measured by an optical pyrometer.

2) Enough oxygen is admitted to raise the system pressure to one torr or higher.

3) The detector temperature drops below 700°C under these conditions. The temperature is, however, next increased to about 900°C. After approximately one minute, the variable leak rate valve is closed.

4) As the oxygen is being evacuated from the system, the detector current is decreased as necessary in order to maintain the temperature near 900°C.

5) Frequency measurements can be made when the system pressure falls below 3×10^{-6} torr, usually within 10 minutes, if the oven is up to temperature.

Although repeated oxidation of the detector with the oven hot no longer causes clogging of the oven slit, this procedure is detrimental to the molybdenum heater coils and is therefore used no more than is absolutely necessary.

The detector is normally operated at a relatively high temperature in order to decrease the "sitting" time of the atoms on the wire so that a servo technique of measurement involving 37.5 Hz modulation of the microwave excitation can be utilized. At 900°C–1000°C the oxide is stable for as long as 13 hours—this is the longest continuous operating time to date on the thallium system. During this and similar long-term runs, the oxide showed no tendency to deteriorate. Ionization efficiency for this system has been estimated to be at least 50 percent. Signal-to-noise ratios for the central peak of the Ramsey resonance curve are generally in the vicinity of 300–400.

The interaction length of 55 cm for the NBS I thallium standard results in a spectral line width of about 280 Hz as compared to 330 Hz for the same machine operated with cesium. The loaded Q of the resonant cavity is 2800. The frequency shift observed upon rotation of the cavity by 180° about a vertical axis, presumably resulting from a phase difference between the two oscillating field regions, is less than 2×10^{-12}. Two such rotations were performed.

During the course of the thallium investigations, this cavity was found to have become detuned by about 6 MHz. This detuning of the cavity from the thallium transition frequency was accompanied by a shift in this frequency of 4×10^{-11}. This detuning was attributed to a temperature-stress-tuning correlation even though this cavity had been provided with considerable mechanical bracing. Further, the measured thallium transition frequency depends significantly on the cavity tuning plunger position, with a frequency minimum occurring when the cavity is tuned to the thallium line frequency. This effect is not believed to be a result of frequency pulling by the resonant cavity, which is calculated to be only 0.0093 Hz or about 4.4×10^{-13} for a detuning of 6 MHz, but rather a result of a changing phase difference between the two oscillating field regions of the cavity due to possible asymmetry of the tuning mechanism.

This cavity, which is the second one constructed for the thallium system, has been provided with electroformed copper end sections, smaller beam coupling holes, and electroformed extensions out from the beam holes to minimize field fringing effects at these holes. As a result, the dependence of the measured thallium transition frequency on microwave power level that had been observed with the first cavity is eliminated, at least for power levels below 50 mW.

Considerations of accuracy are, for the present, necessarily confined to internal estimates. A second thallium standard is nearly ready for operation and should provide a better indication of accuracy.

In order to obtain an estimate for ΔH, the uncertainty in the magnitude of the uniform magnetic field, two independent calibrations of the field using the (4, 1) $\leftrightarrow$(3, 1) transition in cesium and the (1, 1)$\leftrightarrow$(0, 0) π transition in thallium were compared. At the relatively high field of 0.140 Oe used in most of the early measurements, the calibrations agreed to within 0.002 Oe. Considering ΔH to be ± 0.001 Oe, we find $\Delta\nu/\nu$ to be $\pm 3\times10^{-13}$. These data were taken with a power supply not as stable or well regulated as the one used for NBS II and NBS III, the NBS cesium standards.

To operate at 0.070 Oe reasonable evidence must exist that no overlap effects occur due to the π transitions. This evidence is obtained from two sources. First, careful searches were made for π transitions with the C-field direction oriented for σ transitions. The signal-to-noise ratio of the σ transition was always as good as 200. No evidence of π transitions has ever been detected. Second, further evidence of the absence of overlap shifts is provided by the plot of the frequency of the normal $(1, 0)\leftrightarrow(0, 0)$ transition vs. the square of the C-field current shown in Fig. 2. The half length of the vertical bar at each plotted point represents the precision of measurement (standard error of the mean). Any overlap shifts should be most pronounced at low values of the C field. No significant deviation from linearity appears even at the lowest field used of 0.015 Oe, which corresponds to a C-field correction of only 2×10^{-13}. The rms deviation of the points from the least squares line is only 4×10^{-12}.

Reversal of the C-field polarity produced no frequency shift within the measurement precision of 2.5×10^{-12}. Such a shift had been observed with the earlier thallium cavity where significant leakage of the microwave radiation field from the beam holes was present.

Magnetic shielding of the C-field region is accomplished by an outer soft iron cylinder and an inner mu-metal cylinder. The measured nonuniformity of field along the length of the C-field region is within ±0.001 Oe at a field of 0.050 Oe. This and the residual field of ±0.001 Oe produce negligible uncertainties in the frequency measurements and are not considered limitations at present.

A block diagram of the servo measurement system appears in Fig. 3. The same two independent servo systems, employing 37.5 Hz modulation, that are used regularly with the NBS cesium standards are also usable in the thallium case. The only modification required is to increase the peak frequency deviation due to the modulation because of the greater relative line width for NBS I. Comparisons of recent manual measurements with servo measurements show agreement to within 2×10^{-12} The precision of measurement for the manual data was 2.4×10^{-12}, and that for the servo data was 1.5×10^{-12}. Interchange of the vacuum tube servo system with the transistorized servo system resulted in a frequency shift of less than 2.5×10^{-12}, which was the precision of measurement. A detailed evaluation of the vacuum tube servo system has been reported previously [3].

The power spectrum of the frequency multiplier chain used in the measurement system has been improved by the addition of more adequately filtered power supplies. The brightest sidebands of 60 Hz and 120 Hz are now down about 35 dB at the thallium transition frequency. Previous power supplies contributed time dependent, asymmetric sidebands which caused many nonreproducible frequency shifts in the thallium transition frequency.

The average precision of measurement for the thallium standard over one hour averaging times, as determined from more than one year's data, is 2×10^{-12} when

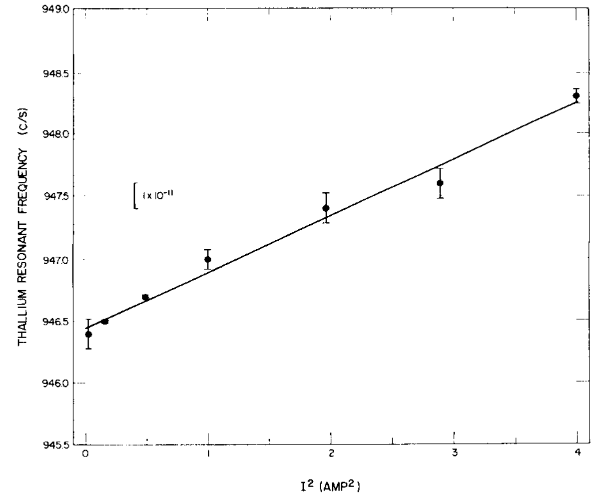

Fig. 2. Thallium resonant frequency vs. square of C-field current.

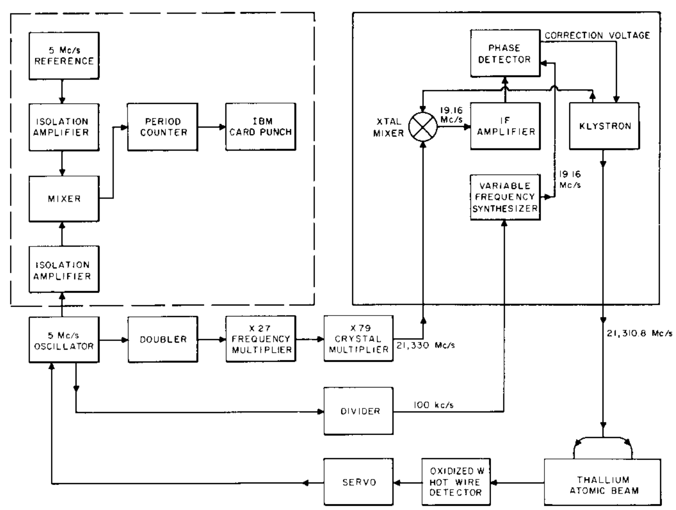

Fig. 3. Block diagram of the thallium servo measurement system.

compared with a high quality quartz oscillator or either of the NBS cesium standards. Occasionally, measurement precisions of 4×10^{-13} have been observed with one of the cesium standards as reference. When the average standard error of the mean of 2×10^{-12} for a one-hour measurement is compared to the standard deviation of 1×10^{-11} for daily measurements made over a period of months, a discrepancy is apparent, suggesting a lack of statistical control in the measurement process. For intermediate-length measurement periods of several hours within a given day, however, such as the thirteen-hour-frequency comparison of the thallium standard with NBS III, shown in Fig. 4, much better control is indicated. Here, the average precision of the one-hour measurements is 1×10^{-12}, while the standard error of the mean for the group of 13 one-hour points is about 6×10^{-13}, this being an indication of the precision expected for a measurement averaged over a thirteen-hour period. The one-hour precision for NBS III is typically 5×10^{-13} which is only about 4 times better than the corresponding figure for the much shorter thallium

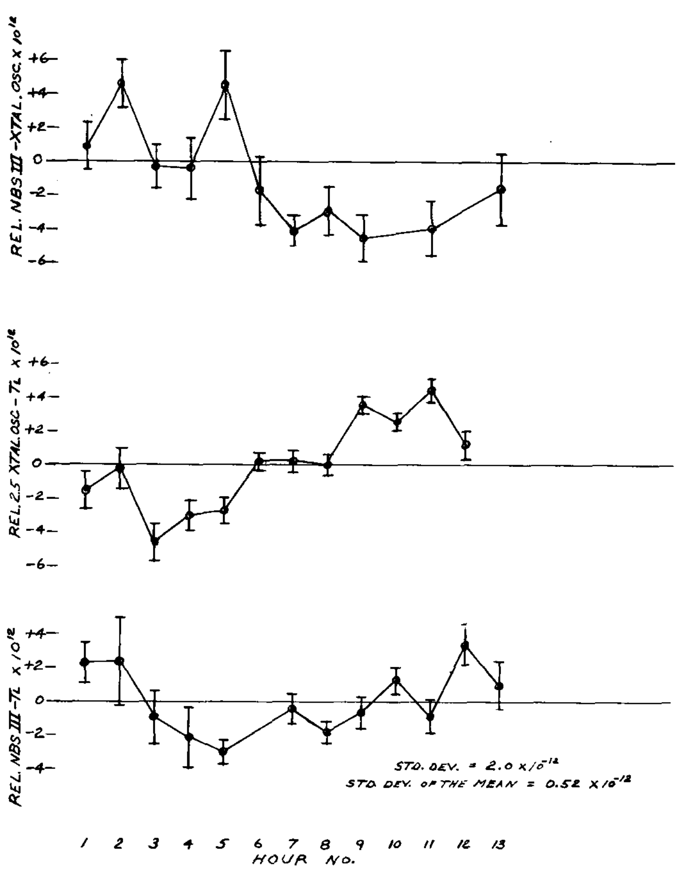

Fig. 4. 13-hour stability comparison of thallium standard, NBS III, and a crystal oscillator (April 16–17, 1964).

standard. In view of the ratio of the interaction lengths of about 7, this precision comparison is encouraging.

The precision associated with the thallium standard does depend on the oxide coating on the detector wire. As the detector wire ages and is oxidized away, the detection efficiency for the 0.013-cm wide beam drops, along with the intensity of the Ramsey pattern. As long as this intensity is a reasonable value (2–5×10^{-12} amperes of detected beam current), the precision is quite satisfactory.

The best value for the measured frequency of the $(F=1,\ m_F=0)\leftrightarrow(F=0,\ m_F=0)$ transition in thallium in zero magnetic field [with respect to an assigned frequency of 9192631770 Hz to the $(F=4,\ m_F=0)\leftrightarrow(F=3,\ m_F=0)$ transition in cesium] is

$$\nu_0(\text{Tl}) = 21,\,310,\,833,\,945.9 \pm 0.2 \text{ Hz}.$$

The quoted accuracy figure of ±0.2 Hz or $\pm1\times10^{-11}$ is a tentative but best estimate from the accumulated data. This frequency determination agrees with that obtained by the Swiss group at Neuchatel Observatory (ν_0 21,310,833,945.1$\pm$1.0 Hz) to within the quoted limits [4].

Future intentions for thallium standards include installation of permanent magnets of higher field intensity than those presently used in NBS I, and evaluation of NBS II as a thallium standard. The use of NBS II will allow direct comparison of two thallium standards with the added benefit of the narrower spectral line width of NBS II.

Conclusion

The results obtained from the short thallium standard have been sufficiently encouraging to justify an evaluation of a longer and more refined thallium system. Comparison of two independent thallium standards should provide a more reliable accuracy figure for comparison with cesium and hydrogen.

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