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Measurement of Mercury Mass in the Deep Space Atomic Clock's (DSAC's) rf-Discharge Lamp

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Abstract

Using Differential Scanning Calorimetry (DSC), we demonstrate an ability to measure mercury mass in Hg rf-discharge lamps used in space-qualified Hg^+ atomic clocks. In particular, for a DSAC Hg lamp provided by JPL, we measure a mass of 205 ± 15 μgms. We believe the mass uncertainty is low enough to allow us to perform Hg consumption studies on these lamps, and through those studies define minimum Hg fills for the lamps to ensure specified space-mission lifetimes. Additionally, we show that photographic images of Hg droplets can provide a means for roughly estimating Hg mass in rf-discharge lamps.

I. Introduction

The Deep Space Atomic Clock (DSAC) shown in Figure 1 was designed and built by researchers at the Jet Propulsion Laboratory (JPL) [1], and it was launched into low Earth orbit for a year-long mission to test its utility for autonomous, one-way, deep space radio navigation on June 25, 2019 [2]. The DSAC is a compact, extremely precise mercury-ion (Hg^+) atomic clock that provides frequency stability several times better than that of the rubidium (Rb) atomic clocks now flying on GPS satellites [3]. Like the GPS clocks, the Hg^+ clock takes advantage of "optical pumping" [4,5] to create its atomic signal, and for that purpose employs a Hg rf-discharge lamp in its physics package.

Figure 1: The DSAC Hg^+ atomic clock [6].

Arguably, the most critical element in Rb atomic clocks (and the one whose physics is least well understood) is the rf-discharge lamp [7,8]. A complete failure of the Rb discharge lamp is tantamount to failure of the frequency standard, and a partial failure (*e.g.*, significantly altered or fluctuating lamplight intensity) can cause degradation of the atomic frequency standard's performance [9]. One should therefore expect the DSAC's rf-discharge lamp to also be a critical, potentially life-limiting component of the clock. Consequently, for future space-system applications it is crucial to determine the reliability/longevity of the Hg discharge lamps used in these devices by investigating the physical and chemical mechanisms that could lead to the lamp's total or partial failure.

At present, we are primarily concerned with one potential (but significant) failure mechanism: diffusion and chemical reaction(s) that can consume free metallic mercury [10] or the noble-gas buffer in the lamp [11]. In particular, our immediate goal is to demonstrate a capability to non-destructively measure Hg mass in the discharge lamp's glass bulb using the well-established method of Differential Scanning Calorimetry (DSC) [12]. As a result, we evidence an ability to assess Hg consumption in rf-discharge lamps by measuring Hg mass in lamps as a function of lamp operating time. Similar DSC investigations performed at The Aerospace Corporation [13] and Air Force contractors have been successfully used to predict lamp (and hence Rb atomic clock) lifetimes. The present results imply that the same could be done for Hg^+ clocks.

II. Metal Mass Measurement in a Discharge Lamp via Differential Scanning Calorimetry

Differential Scanning Calorimetry is a constant-pressure calorimetric technique that can be used to study chemical phase changes. During the phase change, heat is absorbed or released as the temperature of the sample is scanned through the phase-transition region. The quantity of heat absorbed or released is proportional to the mass of the sample, with the proportionality constant equal to the product of the sample's latent heat of condensation (for example) and a calorimeter constant. The calorimeter constant is derived from a similar measurement with a known mass calibration standard.

Rather than directly measuring the change in heat flow of a sample confined in a single sample oven, the DSC utilizes a differential technique in which a sample's heat-flow change is measured relative to a second empty container located in a separate reference oven [12]. This differential method allows one to measure minute sample-induced changes in heat flow that would ordinarily be masked by large sloping baselines, which are predominantly a consequence of the temperature dependence of the difference in heat capacity between the sample and reference containers. The use of the differential method coupled with additional electronic baseline correction techniques yields extremely high detection sensitivity – in rubidium lamps we have demonstrated sensitivity at the microgram level in lamp envelopes possessing several millionfold greater mass [13].

Prior to performing a DSC Hg mass measurement, the Hg in the lamp should be condensed onto the (generally) concave interior surface of the lamp bulb's base by cooling the base while simultaneously heating its walls and dome. This drives the lamp's Hg to a single spherical droplet at the base of the lamp. The lamp should then be carefully placed in the sample oven of the DSC, and a similarly dimensioned empty lamp (ideally having the same mass and composition as the Hg lamp bulb but without Hg) should be placed in the DSC's reference oven (taking precaution not to disturb and possibly fragment the Hg droplet during the lamp's physical transfer from the "drive-down" apparatus to the DSC).

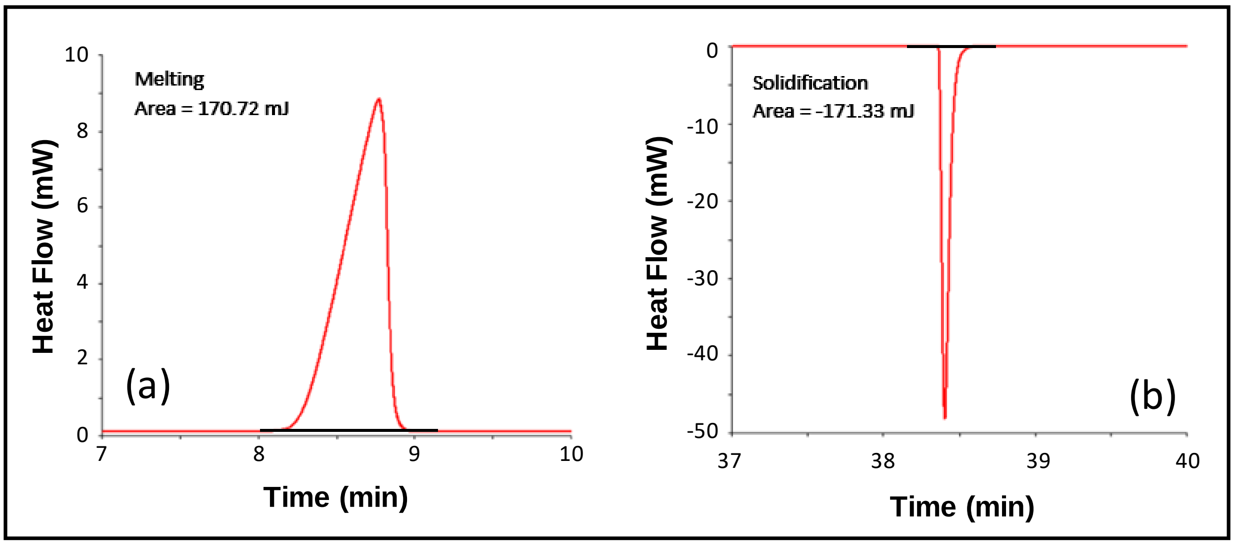

Figure 2: Heating (a) and cooling (b) scans of a 6 mg sample of indium encapsulated in an aluminum pan obtained with Aerospace's Perkin Elmer Diamond DSC. The temperature of the sample and reference ovens is ramped across the solid-to-liquid phase-transition temperature in (a), and back through the liquid-to-solid transition in (b). The rise in heat flow (endothermic is up) is due to the increased heat that is required for indium melting; the reduction in heat flow is due to the reduced heat demand generated by the evolved heat during indium solidification. The areas on the traces were generated by integrating the curves over the regions shown in black using the calorimeter's PYRIS software. When combined with the sample's latent heat of condensation, these areas yield the mass.

A DSC scan can be performed by either cooling the sample and reference ovens from above to below the melting point (MP) of Hg (–39.8 °C), or by heating them across the phase-transition temperature. The DSC scanning operation simultaneously raises or lowers the temperature of the sample and reference ovens, controlling the flow of heat to both ovens to maintain the equality of their temperatures. During a solid-to-liquid phase transition, excess heat must be supplied to the sample oven to melt the sample; during a liquid-to-solid transition excess heat must be supplied to the reference oven to compensate for the heat evolved during sample solidification. One measures this differential heat flow as the temperature of the ovens are scanned across the thermal region of interest. The differential heat flow signal obtained with the Perkin-Elmer Power-Compensated DSC that we use for this measurement is the difference in the electrical power supplied to the sample and reference ovens, and it is a true representation of the differential heat flow generated by the phase transition. Other DSC-like instruments (Differential Thermal Analyzers, and Heat-

Flux DSCs) do not directly measure this heat flow, but infer it from either temperature measurements in the sample or heat flux measurements between a sample and a reference that are both contained within a single oven. Examples of DSC endothermic melting and exothermic solidification scans produced by a 6 mg indium calibration standard encapsulated in an aluminum calorimeter pan are shown in Figure 1.

Initially, the DSC must be calibrated using a known mass of indium or other suitable calibration standard, obtaining the results shown in Figure 1 for the absorbed/evolved heat. The integrated areas per unit weighed mass of standard are then input to the calorimeter software to calibrate the heat flow of the calorimeter prior to measuring an unknown sample.

III. Experimental Methods and Results

A photograph of the smaller of two Hg lamps provided to Aerospace by JPL is shown in Figure 3; this was the lamp used for our calorimetric measurements. The lamp is slightly less than ¼ inch in diameter and approximately one inch in length with 1 mm thick walls; it was manufactured from UV transparent quartz (Heraeus Type 00090065 Suprasil 310 [14]) to permit transmission of the 194 nm optical-pumping light. Mercury metal was condensed into a single droplet of liquid located at the bottom of the lamp by heating the walls of the lamp to 50 °C overnight, while maintaining its rounded base in contact with a conically shaped metal pedestal that was cooled by recirculating refrigerant maintained at −40 °C. The Hg lamp, and a similarly shaped and dimensioned Rb containing ampoule that was used as a reference, were transferred into the sample and reference calorimeter ovens held at 10° C in the presence of a high flow rate N_2 gas.*

The temperature of the calorimeter head was then reduced to −70 °C to solidify the Hg after external insulating enclosures were placed over the puck to prevent condensation, and further isolate the calorimeter ovens from the environment. The oven temperatures were maintained at this temperature for at least 30 minutes to ensure that thermal equilibrium was achieved, and that the Hg droplet had sufficient time to solidify.

Figure 3: Hg lamp from a Hg^+ clock supplied to Aerospace by JPL.

IV. Assessing the Lamp's Hg Mass from the Calorimetric Measurements

Calorimetric measurements were performed by scanning the sample and reference oven temperatures over the range −70 °C to −30 °C at a scan rate of 20 °C/minute. A typical DSC scan over the region of the Hg melting phase transition is shown in Figure 4. The mass of Hg in the lamp was computed from the integrated area of this endothermic peak, a quantity that yields the amount of energy required to melt the solid Hg. The Hg mass was obtained by dividing this energy by mercury's heat of fusion (*i.e.*, 11.47 J/g [15]). The mass data displayed in Figure 4 corresponds to the average and standard deviation of ten separate integrations of this trace with each integration possessing slightly different integration limits to set the baseline. DSC scans were repeated six times to obtain

* The Rb in the reference ampoule was driven to the dome of the ampoule prior to using it as a reference. To mechanically stabilize the lamp and ampoule in their ovens, and prevent motion during the measurements, the calorimeter head assembly was covered with a circular aluminum retaining disk. The disk had holes slightly larger than the cylindrical diameters of the sample and reference, and these were concentric with the circular sample and reference ovens of the calorimeter. The Hg lamp and its reference were inserted through these openings and pressed down onto 20 mg of thermally conductive compound in standard aluminum DSC sample pans that had been previously placed in the two ovens of the calorimeter head assembly. The retaining disc satisfactorily held the ampoule and lamp in place, and inhibited their motion in the plane of the disk during the measurements. Electrical tape was used to secure the lamp and reference to the disk, and ensure that the rounded bases remained immersed in the thermal compound during the measurement. The calorimeter head assembly was then covered and sealed from the atmosphere with a solid polymer puck having holes milled from below at the location of the ovens in order to accommodate the protruding length of the lamp and ampoule. The puck was then tightly sealed to the calorimeter head via a center bolt that fastened the puck and circular disk to the calorimeter head assembly.

the results in Table 1, with a separate Hg condensation and calorimetric loading step performed for each of these trials. The average of these measurements yields a Hg mass in this lamp of 186 ± 14 μgms.

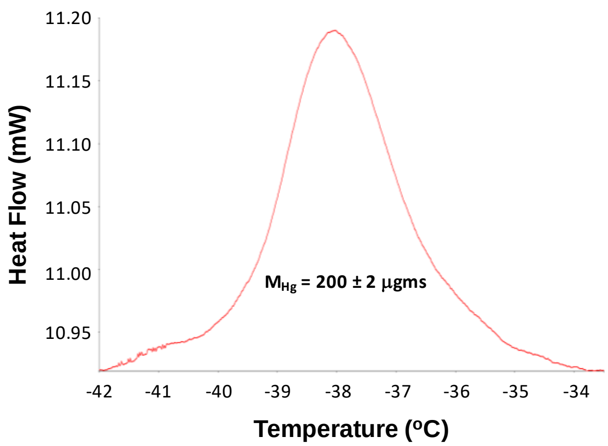

Figure 4: DSC scan over the Hg melting temperature range: A melting curve.

Table 1: DSC Mass Determinations in the Test Lamp for Several Distinct Trials.

Trial	Hg Mass (μgms)
1	165
2	191
3	205
4	200
5	169
6	173
Average	**186 ± 14**
Corrected Average*	**205 ± 15**

* See Section V: Lamp-envelope correction factor for an explanation.

V. Lamp-Envelope Correction Factor

An additional calorimetric measurement was performed to ascertain the effect of the long quartz lamp envelope (shown in Figure 3) on the Hg mass determination. In past work on Rb rf-discharge lamps, we observed thatt the calorimetrically determined masses were 5% to 7% *lower* than the Rb mass determined from Neutron Activation Analysis (NAA) [16]. Taking the NAA assessments of Rb mass as truth, we consequently applied a lamp-envelope correction factor to the DSC mass measurements in all of our subsequent work. To be clear, this correction factor is not indicative of a systematic error in the DSC technique, but rather a systematic error arising from our need to measure metal masses in "odd geometry," glass-encapsulated containers. In the present investigation, we suspected that the oblong shape of the Hg lamp might also reduce the DSC-measured mass of metal in the lamp. To determine an envelope correction factor, we therefore placed a weighed amount of indium in an open quartz ampoule having approximately the same dimensions and weight as the Hg lamp, and measured the indium mass with the DSC. We obtained a DSC-derived mass 10% lower than the known, weighed indium mass. Consequently, (for the present lamp's geometry) we have a lamp-envelope correction factor of 1.1. Using this correction factor, our best estimate of the lamp's Hg mass via DSC measurements is 205 ± 15 μgms.

VI. Assessing the Lamp's Hg Mass from a Photographic Image of the Hg Droplet

In part, to verify the DSC mass measurement discussed above, but more importantly to provide researchers with a *non*-DSC means of coarsely estimating Hg fills in lamps, we attempted to determine the Hg mass in the lamp from a photographic image of the Hg droplet. The volume of a sessile drop small enough to be considered a spherical segment is given by [17]

$$V = \frac{\pi h}{6}\left(3a^2 + h^2\right), \qquad (1)$$

where h is the height of the drop and 2a is its base diameter. This equation is valid only for small drops, whose dimensions are much less than the capillary length $\lambda = (\gamma/\Delta\rho g)^{1/2}$, where γ is the surface tension of the liquid (0.425 N/m for Hg), $\Delta\rho$ is the mass density difference between Hg and the buffer gas in the lamp (1353 kg/m^3),† and g the acceleration due to gravity. The computed capillary length for Hg drops in lamps is 5.7 mm, so that drops larger than this would begin to be flattened by gravity. A hemisphere having this base diameter would have a mass of 0.64 gms, nearly 3500 times larger than the mass of the droplet in the discharge lamp estimated from DSC measurements. Thus, we believe Eq. (1) to be valid for present purposes.

A visible focal plane array camera fitted with a 13.5 cm focal length lens was used to determine the dimensions of the droplet, and the lens was extended an additional 20.0 cm away from the focal plane to obtain greater magnification of the droplet. Side-on

† At several torr of a noble-gas buffer, we assumed that the mass density of the buffer-gas was negligible relative to Hg.

images of the droplet are shown in Figure 5, and Figure 6 shows an image viewing through the bottom of the lamp's base (*i.e.*, end-on). Calibration of the dimensions in these images was obtained by comparison to similar images of a reticle that contained a finely divided rule placed at the approximate location of the droplet after removing the lamp.

The base diameter of the droplet obtained from the side-on image was about 78% of the diameter of the circular droplet boundary shown in the end-on image. Presumably, the cylindrical shape of the lamp bulb, coupled with the extension tube magnification, has an anamorphic focusing effect that reduces the estimated diameter in the side-on image. For this reason, we opted to use only the droplet diameter from the end-on image for the Hg volume calculation, since it is less susceptible to this kind of distortion.

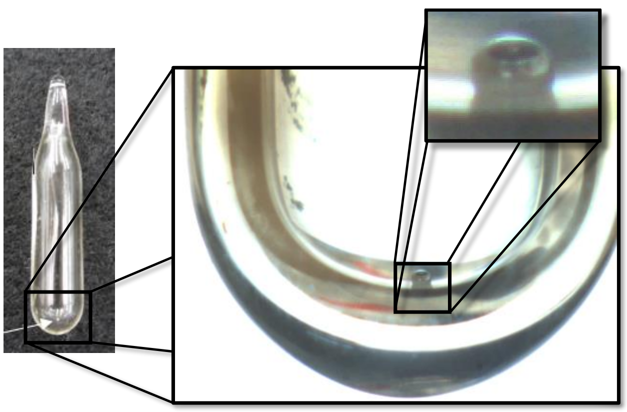

Figure 5: Side-on image of the Hg droplet in the discharge lamp bulb.

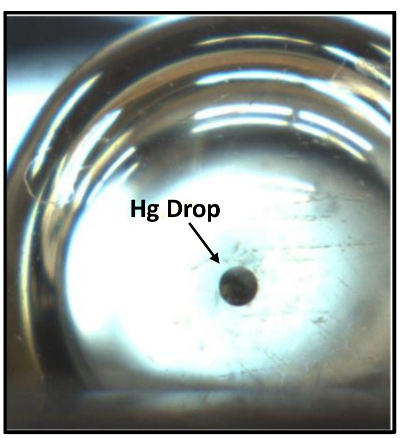

Figure 6: End-on image of the Hg droplet in the discharge lamp bulb.

The height of the droplet could only be obtained from a side-on image, however. If the lamp is (close to) perfectly cylindrical with parallel walls, then there will be no reduction or magnification of the observed side-on image height: the measurement provides an accurate estimation of the droplet's true height. Using the end-on droplet base diameter and the side-on droplet height, we determined the Hg droplet's volume as 14.3 ± 2.2 nL, which results in a Hg droplet mass of 193 ± 30 μgms. This value is in good agreement with the calorimetrically assessed mass of 205 ± 15 μgms. Thus,

a. We have evidence that the DSC measurement of the Hg mass in the lamp is correct.

b. We have justification for employing droplet images to coarsely estimate mercury mass in Hg^+ clock discharge lamps.

VII. Summary

In this report we have discussed The Aerospace Corporation's ability to measure Hg mass in mercury rf-discharge lamps employed in Hg^+ atomic clocks. The present uncertainty in mass measurements is ±15 μgms, which we believe is good enough to initiate Hg consumption studies. Results from those studies would be useful in defining minimum mass mercury fills for the lamps used in space-qualified Hg^+ atomic clocks, and thereby guarantee specified multi-year mission lifetimes for those clocks.

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