Paper

Quantitative Measurement of the Evaporation and Absorption of Mercury from Zn–Hg Amalgams*

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ABSTRACT

Quantitative measurements have been performed on the evolution and absorption of mercury from Zn–Hg fluorescent lamp amalgams. Thermogravimetric analysis (TGA) under atmospheric pressure and vacuum (1.4–1.6 torr) conditions has been employed to study mercury evolution from Zn–Hg amalgam spheres. Conditions for the accurate determination of total Hg content of single Zn–Hg amalgam spheres under linear temperature ramp and hold conditions have been determined. Isothermal TGA has been used to measure both the short-term and long-term evaporation rate of Hg from single Zn–Hg spheres. In a related experiment, the total weight loss on 1500 individual Zn–Hg spheres was measured and statistically analyzed. Finally, using a special fulcrum apparatus the reversible evolution and re-absorption of mercury from Zn–Hg spheres was studied and characterized under simulated lamp conditions.

1. Introduction

Zinc-mercury (Zn–Hg) amalgam spheres provide an accurate method for dosing small amounts of mercury into fluorescent lamps. Zn–Hg amalgams^{1)–7)} can provide Hg vapor pressure comparable to pure Hg⁸⁾ or can serve as a precise dispenser of Hg for compact lamps employing other vapor pressure regulating metals such as In, Sn or Pb. They may also be of environmental value by reducing the amount of mercury used in fluorescent lamps. The Zn–Hg material is beginning to see significant commercial application in both circular and compact lamps. The available mercury content and the rate of Hg loss are important parameters for lamp and process design. In this study we have employed various forms of thermogravimetric analysis to study the amount and rate of mercury vaporization from Zn–Hg amalgam spheres.

Because weight loss can be continuously monitored by vacuum thermogravimetric analysis (vacuum TGA) we have developed a method for the accurate determination of the total Hg content of single Zn–Hg amalgam spheres. Using an optimized temperature program for the analysis, the mercury released from both freshly prepared and aged Zn–Hg samples was studied. Some features of the evaporation of Hg from Zn–Hg spheres as recorded in the vacuum TGA experiments are also noted. Standard TGA analysis at atmospheric pressure is also investigated.

Isothermal vacuum TGA experiments at temperatures between 65°C and 140°C were performed in order to further quantify the rate of Hg loss in Zn–Hg spheres. The short-

term behavior of these measurements can be related to lamp warm-up time from a cold start as a function of temperature while the long-term evaporation rate is important to assure adequate mercury delivery throughout the life of the lamp. The experimental data is analyzed in terms of these requirements.

Multiple pill weight loss experiments were used to measure sphere-to-sphere variations in Hg content. In these experiments the total weight loss under vacuum of hundreds or thousands of individual spheres can be rapidly determined. The statistical data generated allows one to accurately assess the minimum and maximum Hg doses expected with typical Zn–Hg spheres.

Finally, the release and absorption of Hg vapor by Zn–Hg spheres is studied under simulated lamp conditions using a special fulcrum apparatus. The reversibility of the Hg absorption and re-absorption processes is demonstrated, and the rate of these processes is reported.

2. Experimental

All Zn–Hg materials (50% Zn, 50% Hg by weight, hereafter referred to as Zn–Hg) used in the present study were prepared in the form of free-flowing spheroidal particles by jetting molten Zn–Hg through a small orifice^{9),10)}. Starting materials were 99.99% zinc and triple distilled mercury. Chemical analyses were done by thiocyanate titration of the approximately 0.5 grams of material.

2.1 Continuously recorded weight loss

A Perkin Elmer TGA-7 instrument was used in both linear temperature programmed and isothermal modes. A schematic of the TGA balance pan, furnace and sample location is illustrated in Fig. 1.

Fig. 1 Schematic view of the TGA furnace and sample location.

The instrument was operated at two different pressures:

- (1) Atmospheric pressure under 30 cm³/min of Ar purge gas through the top balance inlet only. This is the standard mode of operation.
- (2) Vacuum of 1.4 to 1.6 Torr of Ar.

Initial sample weights were recorded at ambient temperature and pressure using the standard mode above. The upper purge gas was reduced to approximately 20 cm³/min of Ar and the lower purge vent of the TGA sample compartment was attached to a small mechanical vacuum pump (with Ar refill valve) and vacuum applied. The pumping speed of the vacuum pump was adjusted to match the flow of purge gas in order to maintain a constant pressure of about 1.4–1.6 Torr of argon. After each experiment was completed the chamber was refilled with 1 atm of Ar and the 30 cm³/min purge through the top balance inlet was restored. Final sample weights were then recorded at atmospheric pressure.

The 20 cm³/min purge during vacuum operation was used to protect the sensitive components of the balance chamber from exposure to mercury vapor. An unfortunate side effect of the high velocity gas flow was an apparent increase in the sample weight of about 7% for the nominal 8 mg samples used. This effect was constant and stable throughout the experiments. An uncorrected vacuum TGA curve, shown in Fig. 4, has an offset of about 7% in the positive direction. In the graphical presentation of the TGA results the constant offset has been subtracted so that all curves start from 100%. The accuracy of the initial and

final weights was not affected by the offset since they were both recorded to ± 0.001 mg under the standard 1 atm conditions.

The accuracy of the TGA balance was confirmed by weighing eight initial and final samples on an independent Mettler microbalance with readout to ± 0.001 mg. Agreement was always to within ± 0.007 mg, and typically to within ± 0.002 mg. Mass and temperature scales on the TGA-7 were calibrated according to standard procedures for the instrument using a 100 mg class A weight and Ni and Perkalloy[®] Curie point standards.

Individual spheres from a batch of freshly prepared 8 mg Zn–Hg spheres were randomly selected for initial TGA experiments. Six months later a second set of TGA measurements from the same batch was performed. The amalgam spheres were stored at room temperature under air in tightly closed sample bottles – these spheres are referred to as ‘aged’ spheres.

Isothermal TGA measurements were performed at temperatures between 65°C to 140°C under vacuum conditions on single spheres from a different batch of fresh 9 mg Zn–Hg spheres. Single spheres were held at 30°C for 1 minute, ramped to the final temperature in 2 minutes and held at the final temperature for 150 minutes.

2.2 Multiple sphere weight loss experiments

Total weight loss of individual Zn–Hg spheres was performed in groups of 100–200 spheres. The spheres were placed in labeled, shallow holes in graphite blocks. The graphite blocks were then placed in a large glass tube and heated under a 20 cm³/min flow of Ar gas at a pressure of 1.5–1.6 Torr. The optimum temperature program was a ramp from 30°C to 300°C at 10°C/min followed by a hold at 300°C for 90 minutes. The pellets were then cooled under argon at atmospheric pressure for about 2 hours until they reached room temperature. Individual sphere weights were recorded to a precision of ± 0.001 mg before and after the heat/vacuum treatment. Measurements were performed on the same batch of 8 mg aged spheres used in section 2.1, except the spheres had a thin coating of fumed silica applied as an anti-sticking agent (“HTS” coated). It was assumed that the weight loss was due entirely to mercury and that all of the mercury in the pellet is released. An earlier test in this apparatus showed that a slight amount of zinc is also lost if the furnace temperature is too high. Zinc vaporized at 350°C and condensed at the outlet end of the furnace tube but at 300°C no vaporized zinc was seen.

2.3 Re-absorption and re-release of Hg

A tubular balance vessel, shown schematically in Fig. 2, was constructed of borosilicate glass. The vessel, constructed of 15 mm diameter tubing, was 40 cm long and had arms extending 12 cm downward. The vessel was attached at its center of mass to a stainless steel support and was then loaded with 5 grams of 8 mg Zn–Hg spheres on one side and sealed off under a pressure of 1.3 Torr argon.

Fig. 2 Schematic of the mercury re-absorption apparatus. Constant temperature baths and heating tapes are not shown.

The release and re-absorption experiment was then conducted in two stages: an unequal and an equal temperature mode. The unequal temperature mode was used to release the mercury contained in the Zn-Hg spheres and to drive the mercury to the opposite end of the tube. The end of the tube containing the pellets was kept at 70°C by submerging it into a heated bath. The opposite end of the tube was kept at room temperature, nominally 23°C. The center section of the tubing was maintained between 100°C to 150°C with heating tapes. The system was kept in the unequal mode for 11 days to drive a measurable amount of mercury, typically 700 mg, to the opposite end of the vessel.

Mercury movement was recorded by using the entire apparatus as a balance. First the apparatus was removed from the heated bath(s) and one of the two heating tapes was removed. The heat-exchange fluid was cleaned from the ends of the apparatus with deionized water and dried. The apparatus was then balanced on the fulcrum and adjusted to a null position by an external weight. A laser beam reflected from the polished top surface of the stainless steel support indicated a null position. The position of the weight on the vessel that achieved a null position indicated the amount of mercury transported.

The system was then switched to equal temperature mode to determine if the free mercury would re-amalgamate with the Zn-Hg pellets. Both ends of the apparatus were submerged into heated baths maintained at 70°C and the center section was maintained between 100°C to 150°C with heating tapes. The weight of the re-absorbed mercury was determined by the same method.

Finally, re-release of the Hg already re-absorbed was verified by establishing the initial temperature gradient (Zn-Hg end at 70°C, empty end at 23°C) and monitoring the weight change.

3. Results and Discussion

3.1 Continuously recorded weight loss

3.1.1 Atmospheric pressure conditions

The behavior of single sphere samples of freshly prepared 8 mg Zn-Hg at 1 atm of Ar pressure was initially explored by a linear temperature program from 30°C to 400°C at 20°C/min. No weight loss was observed under these conditions. Apparently the dense mercury vapor blankets the sample and prevents further volatilization of Hg. A higher temperature with a 50°C/min temperature program was then tested to explore when Hg would be released. At about 460°C the sphere exploded into fragments. Another similar atmospheric pressure test was performed, except the temperature was ramped rapidly to 400°C and then programmed slowly at 5°C/min from 400°C to 550°C. The sphere exploded at about 460°C as shown in Fig. 3. This behavior is consistent with the normal boiling point of about 470°C reported in the gas-liquid phase diagram¹¹⁾ for a 50% Zn-50% Hg composition. Quantitative measurement of Hg loss and Hg content clearly requires different conditions.

Fig. 3 TGA behavior of a single Zn-Hg sphere at one atmosphere Ar pressure. Temperature was programmed at the maximum rate to 400°C and then at 5°C/min from 400°C to 550°C.

3.1.2 Vacuum conditions – freshly prepared spheres

An initial vacuum TGA experiment was thus performed at 1.5 Torr Ar with a linear temperature program from 30°C to 400°C at 10°C/min. The Hg evolution rate slowly decreased until 400°C was reached. Since the evolution rate was small but nonzero at 400°C it indicated that a higher temperature or longer time is required for quantitative removal of Hg.

A final temperature of 450°C was thus investigated. Fig. 4 shows that above 400°C the weight loss begins to accelerate and that the final weight percentage was 45.9%. At 450°C dark blue coatings formed on the glass tube and

the furnace support tube and small dendritic crystals grew on the balance hang-down wire above the furnace. Zinc metal is apparently evaporating at this temperature and pressure. These results are consistent with the known vapor pressure of Zn⁸⁾ of about 0.3 Torr at 440°C and clearly show the temperature must be maintained below 400°C to avoid errors in Hg content determination due to Zn evaporation.

Fig. 4 TGA behavior of a single Zn-Hg sphere under 1.5 Torr argon pressure. The temperature was programmed at 10°C/min from 30°C to 450°C. A constant 7% positive offset due to the Ar gas flow through the TGA balance has been subtracted in the corrected curve as described in Sec. 2.1.

The temperature program shown in Fig. 5 was thus evaluated. It consists of holding at 30°C for 1 minute, ramping to 350°C at 10°C/min, and holding at 350°C for 30 minutes. As can be seen from the typical vacuum TGA curve illustrated in Fig. 5, the weight loss over the last 20 to 25 minutes at 350°C is quite small and consisted of less than 0.02% over the last 15 minutes of the run. These conditions appear to be well suited for Hg determination in the Zn-Hg material with the TGA-7 thermogravimetric analyzer.

Two interesting features are noted in Fig. 5. First, a rapid loss in weight of about 4–5% is observed 7 minutes into the experiment at about 90–100°C. This may correspond to the decomposition of γ phase^{12)–16)} and the rapid formation of more Hg-rich liquid which allows a higher rate of Hg evaporation^{1),12)}. Second, the rate of weight loss then continues to increase slowly until a rapid increase occurs between about 240–290°C.

The results from six additional tests performed under the same conditions as those illustrated in Fig. 5 are plotted in Fig. 6. The general features of the seven curves are similar. All Zn-Hg spheres show a rapid loss in weight of about 4–5% after 7 to 8 minutes at about 90–100°C. The second large weight decrease is more variable and occurs as early as about 13 minutes and as late as about 23 minutes.

Fig. 5 Typical TGA curve for a single Zn-Hg sphere at 1.5 Torr Ar pressure using the optimized ramp and hold temperature program.

One explanation for the variability in mercury release is a non-uniform material transport rate within the sphere. Mercury-rich liquid in the center of the sphere may actually be bubbling towards the surface. Examination of spheres after the experiments show spherical bumps or buds of various sizes on the surface of the residual Zn network. These results are consistent with variation in liquid transport to the surface. Since all curves show a constant weight from 40 to 60 minutes this is a good indication that the Hg has been quantitatively removed and that Zn evaporation is not significant.

Fig. 6 TGA curves at 1.5 Torr Ar pressure for freshly prepared Zn-Hg spheres.

3.1.3 Vacuum conditions – aged spheres

Fig. 7 shows the results from 9 additional vacuum TGA experiments on Zn-Hg spheres aged for 6 months. These data also show two phases of weight loss generally similar to the results on freshly prepared spheres. Comparing Figs. 6 and 7, the freshly prepared spheres typically show an initial rapid loss in weight of about 4–5% at about 7 minutes, while the aged spheres typically show an initial rapid weight loss after 8–13 minutes at temperatures of 100–140°C. The second large weight decrease occurred in

fresh spheres between about 13 minutes and 23 minutes and in aged spheres between about 23 and 27 minutes. Aged spheres also show spherical bumps of varying size on the surface of the remaining Zn network after the experiment is completed.

The aged spheres thus show a shift in weight loss behavior to longer time and higher temperatures when compared to fresh spheres. One possible explanation for this shift is the further slow equilibration of liquid Hg and Zn to form an intermediate phase^{1),12),13)}. A greater amount of β or γ phase will result in less free Hg in the aged spheres, and higher temperatures may be required to decompose the additional intermediate phase and release mercury vapor.

Fig. 7 TGA curves at 1.5 Torr Ar pressure for aged Zn-Hg spheres.

Similar to previous results, the weight loss over the last 20 to 25 minutes at 350°C is quite small. These results are a good indication that the Hg has been quantitatively removed and that Zn evaporation is not significant.

Two aged Zn-Hg spheres exhibited anomalously low overall Hg loss, with percentages of only 67% and 64% of the original weight at the end of the 63 minute temperature program. Data for these two spheres are not shown in Fig. 7. While the initial weight loss and curve shape in the first 10–15 minutes is similar to the other nine aged Zn-Hg spheres, the weight loss at longer times and higher temperatures is more sluggish and incomplete. Although additional vacuum heating of one of these spheres resulted in a normal weight loss of about 50% there is no clear explanation for the delayed mercury release.

3.1.4 Summary of fresh and aged sphere vacuum ramp and hold results

Table I summarizes the Hg content measured in the vacuum TGA tests. The average values of 50.44% Hg for fresh spheres and 50.19% Hg for aged spheres are in good agreement with each other and with the results of chemical analysis (49.92% Hg and a relative standard deviation of 0.21% for three analyses). We conclude that the vacuum TGA method is suitable for accurate determination of Hg content in Zn-Hg.

In fluorescent lamps the total amount of Hg in the dose is an important parameter. The TGA tests already described have only examined the variation of the Hg content of individual spheres. Since the total initial sphere mass may also vary on either side of the specification, here 8 mg, it is useful to compare the variation in Hg content as measured by vacuum TGA with the variation in initial sphere mass.

Table 1 Vacuum TGA Weight Loss Results for Fresh and Aged Zn-Hg Spheres Using Optimum Temperature Program of Fig. 5.

Sample ID (fresh spheres)	% Hg (fresh spheres)	Sample ID (aged spheres)	% Hg (aged spheres)	All tests combined
1	49.77	1	50.19	
2	50.69	2	50.47	
3	50.38	3	50.75	
4	50.56	4	49.54	
5	50.45	5	50.31	
6	50.61	6	50.04	
7	50.60	7	50.21	
		8	50.45	
		9	50.61	
Average	50.44		50.19	50.32
Standard Deviation	0.31		0.37	0.35
Relative Standard Deviation	0.62%		0.74%	0.70%

An analysis of the initial sphere mass of a large sample of the batch used in this study shows a mean initial mass of 7.78 mg with a standard deviation of 0.285 mg (relative standard deviation of 3.66%). These data are typical for 8 mg Zn-Hg material. The 3.66% relative standard deviation in initial mass is much larger than the relative standard deviation for Hg content of 0.70% reported for all samples in Table 1. Therefore, the variation in the amount of Hg available for vaporization in a fluorescent lamp will be primarily determined by the variation in *initial sphere mass* and not by variation in Hg content on individual spheres.

3.1.5 Isothermal vacuum TGA measurements

Isothermal weight loss experiments were conducted at 65°C, 70°C, 80°C, 90°C, 120°C and 140°C by vacuum thermogravimetric analysis. Typical results of an isothermal weight loss experiment are shown in Fig. 8. At each temperature, two distinct regions are usually observed: a short-time release of 5–10% mercury and a long-time gradual release of mercury.

Fig. 8 Typical TGA curve under isothermal conditions at 140°C and 1.5 Torr argon pressure for a single 9 mg Zn-Hg sphere.

3.1.5.1 Short-term Hg Loss

Analysis of the short-term behavior of the isothermal vacuum TGA experiments was performed to evaluate the initial mercury evaporation rate and the length of time required to fill a typical fluorescent lamp tube to the optimum working pressure of 6×10^{-3} Torr Hg. As an illustration we have performed the calculations for a lamp volume of 1.39 liters (typical 4 foot T12 lamp) with a dose of 2×9 mg Zn-Hg spheres. The amount of Hg required to fill the lamp to 6×10^{-3} Torr Hg was calculated from the ideal gas law ($n = pV/RT$) for each measured temperature. For example, at 65°C, $n = 0.40 \mu\text{mol}$ Hg or $80 \mu\text{g}$ Hg. The average time required to release the

required quantity of Hg at each temperature was determined from each isothermal vacuum TGA curve by inspection. The results are reported in Table 2.

Table 2 Time Needed for Release of Mercury to Fill a 4-foot T12 Fluorescent Lamp Tube to 6×10^{-3} Torr Using 2×9 mg Zn-Hg Spheres

T / °C	Avg. Release Time / min *	Fill Rate / (l/min/sphere)
65	4.2	0.33
70	1.1	0.63
80	2.3	0.30
90	1.5	0.46
120	0.7	0.99
140	0.8	0.87

* for lamp volume of 1.39 liters

The results show considerable variation because of such a small sample size, however, a trend toward slower mercury release rates at lower temperatures is clearly evident. Table 2 also reports the effective lamp fill rate in liters/minute/sphere. The fill rate data can be used to calculate release times for different lamp volumes or for different numbers of Zn-Hg spheres. For instance, a small lamp with a volume of 0.15 liters dosed with a single 9 mg sphere at 120°C would be predicted to have a release time of 9 seconds.

In actual lamp tests¹⁾, delays of about 30 seconds in lumens output after initial start-up were observed in compact fluorescent lamps. This is somewhat longer than the 9 seconds calculated for a 0.15 liter lamp, but since the lamp is a sealed system, as opposed to a flowing system in the vacuum TGA these results might be expected. Upon restarting, the amalgam-filled lamp behaved like a liquid mercury dosed lamp with no delay in measured lumens output.

3.1.5.2 Long-term Hg Loss

The typical isothermal TGA weight loss curve of Fig. 8 shows an initial rapid drop followed by a more gradual loss rate of approximately exponential character. Since no detailed physical model has yet been developed for the kinetics of decomposition of γ phase, nor for the transport or diffusion of Hg from the condensed phase to the surface, we have analyzed the long-term Hg loss data in terms of an empirical exponential function of the form:

$$w(t) = w_{t=\infty} + [w_{t=0} - w_{t=\infty}] \exp[-k(T)t] \quad (1)$$

where $w(t)$ is the TGA weight percent value as a function of time, t , and $k(T)$ is an exponential rate constant which is a function of absolute temperature, T .

If Equation (1) is being obeyed a plot of $\ln[w(t) - w_{t=\infty}]$ versus time should be linear with slope = $-k$ and y-intercept = $[w_{t=0} - w_{t=\infty}]$. Linear regression of

the data shown in Fig. 8 is plotted in Fig. 9 over the time interval of 40 to 150 minutes. The time interval was selected by visual inspection of the data. As can be seen, the fit is reasonably good with slope = $-5.1 \times 10^{-4} \text{ min}^{-1}$, y-intercept of 3.78 and square of the correlation coefficient $r^2 = 0.9945$. Similar regressions were performed for the other isothermal TGA data. Results for the derived rate constant $k(T)$ are shown in Table 3.

Fig. 9 Logarithmic plot of the 140°C isothermal data of Fig. 8 showing the linear fit to the data points between times of 40 and 150 minutes.

Table 3 Long-term Exponential Rate Constant for Mercury Loss from Single Zn–Hg Spheres from 65°C to 140°C.

T / °C	Number of Tests	Rate constant $k(T) / \text{min}^{-1}$
65	1	3.5×10^{-4}
70	2	3.7×10^{-4}
80	2	4.3×10^{-4}
90	1	5.1×10^{-4}
120	3	6.1×10^{-4}
140	3	7.0×10^{-4}

It is useful to examine the temperature dependence of the rate constant, $k(T)$. Fig. 10 shows a plot of $k(T)$ versus temperature along with the linear least squares fit with slope equal to $4.7 \times 10^{-6} \text{ min}^{-1}$, y-intercept of 5.2×10^{-5} and $r^2 = 0.9818$. This simple regression provides a good fit to the data. It is tempting to consider a rate and temperature dependence of the form:

$$k(T) = A \exp(-E_A / RT) \quad (2)$$

where E_A is an activation energy barrier to diffusion or transport of Hg. However, in the absence of a definite transport or diffusional model, and given the limited temperature range of the data of Table III, it would be difficult to draw any sound conclusions from such an analysis. We have thus limited our analysis to the linear plot of Fig. 10.

Fig. 10 Rate constants $k(T)$ as a function of temperature showing a linear fit to the data points.

The good linear fit of Fig. 10 allows the possibility of an extrapolation of the mercury loss rate constant, $k(T)$ to lower temperatures where the long-term rate of Hg loss is very difficult to quantify experimentally. Extrapolation of the data at 45°C gives a value of $k = 2.6 \times 10^{-4} \text{ min}^{-1}$. Extrapolation to temperatures lower than 45°C, (i.e., to temperatures below the peritectic reaction in the binary Zn–Hg system) may not be valid since the evaporation characteristics would be expected to be different below 45°C if the liquid is fully transformed into γ phase¹¹.

It is useful to compare the total Hg required by mercury consumption reactions in a typical fluorescent lamp to the lowest likely rate of Hg evaporation already determined (i.e., $k = 2.6 \times 10^{-4}$ at 45°C). A reasonable worst case assumption would be that the Hg consumption reactions (i.e., removal of Hg by chemical reaction with phosphors, walls, electrodes, etc.) are linear with time and completely consume all available Hg over a 20,000 hour lifetime. Using the mercury evolution rate constant at 45°C, $k = 2.6 \times 10^{-4} \text{ min}^{-1}$, inspection of Equation (1) shows that over 99% of the mercury would be released within the first 300 hours, and that a linear consumption mechanism would not exceed an exponential release with $k = 2.6 \times 10^{-4}$. Indeed, it would require an exponential rate constant over 65 times smaller, $k = 3.8 \times 10^{-6} \text{ min}^{-1}$, to increase the time for release of 99% of the Hg to 20,000 hours. Only then would the exponential release be exceeded by a linear consumption of Hg at long times of 20,000 hours.

Assuming that the rate constants and the exponential behavior observed on the 50 to 150 minute time scale will still apply at times of 10,000 or 20,000 hours would, of course, be very dangerous. The present analysis shows that a release rate 65 times slower would still be adequate over lamp life. Actual life testing and the successful commercial application of the Zn–Hg material in numerous

types of fluorescent lamps over the last few years indicates that these are good assumptions.

3.2 Total Weight Loss for Multiple Spheres

The multiple pill weight loss procedure described in Section 2.2 was implemented since continuously recorded vacuum TGA measurements on individual spheres are time consuming. Although multiple pill weight loss permits total weight loss measurement on hundreds or thousands of individual spheres it does not allow the continuous recording of individual sphere weight. Weight loss measurements were performed on 500 spheres aged for 8 months. The results for the initial 500 spheres are shown in Fig. 11. The mean weight loss percent was 50.2% with a standard deviation of 0.55% and a relative standard deviation of 1.1%. The few results outside the $\pm 3\sigma$ range are most likely attributed to measurement error rather than to variation in the Hg content of the spheres. The mean weight loss of 50.20% closely matches the 50.32% result of the combined vacuum TGA measurements in Table I and also closely matches the chemical analysis result of 49.92% Hg on a bulk sample of the pellets.

One thousand additional spheres from the same batch were measured after 11 months total aging. These results are not illustrated, however, the mean weight loss percent was 50.05% with a standard deviation of 0.57% and a relative standard deviation of 1.1%. These data are statistically indistinguishable from the first set of 500 measurements.

Fig. 11 Total mercury weight loss for 500 individual Zn-Hg spheres using the multiple pill weight loss method.

The multiple pill weight loss technique thus provides rapid, accurate determination of Hg content and indicates a consistent Hg content from sphere to sphere. And as concluded above from vacuum TGA measurements, variation in the amount of Hg available for vaporization in a fluorescent lamp will thus be primarily determined by the variation in *initial sphere mass* and not by variation in Hg concentration.

3.3 Release and Re-absorption of Hg

The release and re-absorption of Hg from Zn-Hg spheres was conducted on a 5 gram sample of 8 mg Zn-Hg spheres. In the initial unequal temperature mode, 699 mg of mercury was driven from the Zn-Hg pellets to the empty arm of the apparatus in 11 days – an average release rate of 64 mg/day. The system was then changed to the equal temperature mode at 70°C and the re-amalgamation of the Hg with the depleted Zn-Hg sample was monitored for 21 days. Fig. 12 shows the measurements recorded at 1, 8, 17 and 21 days. In 21 days a total of 278 mg of Hg was re-absorbed by the depleted spheres. The precision of the measurements was ± 6.5 mg. A linear least squares fit to the data gives an average mercury re-amalgamation rate of 13 mg/day or, on a per sphere basis, 20 $\mu\text{g/day/sphere}$. The re-release of the absorbed Hg was then monitored in the unequal temperature mode using the initial temperature gradient (Zn-Hg end at 70°C, empty end at 23°C). A total of 427 mg of Hg was re-released by the spheres over a 17 day time period, giving a re-release rate of 25 mg/day.

Fig. 12 Weight of Hg re-absorbed as a function of time using the fulcrum apparatus. Equal temperatures of 70°C were maintained on both ends of the apparatus.

The ability of the Zn-Hg material to reversibly re-absorb Hg and re-release it has been demonstrated. The observed slow re-absorption of Hg by the Zn-Hg spheres at equal temperatures is consistent with the slightly lower thermodynamic Hg activity predicted for the Zn-Hg liquid phase^{5)-7),16)}. These data support the assumption that re-absorption of Hg does not affect the mercury vapor pressure or mercury-releasing capacity of the Zn-Hg material.

4. Conclusions

The vacuum TGA method is suitable for accurate determination of Hg content of single Zn-Hg spheres.

Mercury is quantitatively removed from Zn–Hg spheres under the temperature programming conditions of Fig. 5 at 1.4 to 1.6 Torr of argon. Mercury is not readily released from Zn–Hg spheres in TGA measurements at atmospheric pressure.

Variation in Hg content from sphere to sphere is quite small. A relative standard deviation of 0.70% was observed in the 16 samples measured with an optimized temperature program. This is much smaller than the typical relative standard deviation in total mass of the spheres.

Vacuum TGA curve shape and Hg evolution temperatures for aged Zn–Hg spheres differ somewhat from freshly prepared material. This is probably due to slow equilibration of the Zn–Hg material to form γ phase or other intermediate phases. The available Hg content and releasing ability is basically unaffected by aging and equilibration.

Isothermal vacuum TGA measurements indicate that at short times the required Hg operating pressure can be attained within a reasonable time from a cold start at temperatures from 65°C to 140°C. Analysis using an exponential model indicates the long-term release rates are over 65 times greater than required for 20,000 hour lamp life.

Multiple pill weight loss measurements provide a rapid and accurate determination of the mercury content from sphere to sphere. Total weight loss measurements on 1500 individual spheres show relative standard deviations in mercury content on the order of 1%.

The reversibility of release and re-absorption of Hg under simulated lamp conditions has been demonstrated. Continuous absorption and release of Hg are thus not expected to affect the Hg vapor pressure or Hg-releasing capacity of Zn–Hg materials.

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