CONF-770843-1
THERMAL EXPANSION OF MOLTEN MATERIALS BY THE
GAMMA ATTENUATION TECHNIQUE*

William D. Drotning
Sandia Laboratories, Albuquerque, New Mexico 87115

ABSTRACT

An apparatus was constructed for measurement of the density and volumetric thermal expansion of high temperature molten materials using the gamma attenuation technique. It was found that significant improvements in overall experimental precision could be realized by employing an automatic gain control in the linear section of the gamma counting system. This device reduced errors due to system gain shifts and thereby increased the precision of the gamma counting. Corrections were also made for the dead time of the electronics system. A preliminary experimental investigation of the precision of the method was made by measuring small dimensional steps of a tool steel block at a single temperature. A fractional length increment $\Delta l/l$ of 1% was determined to 1%, equivalent to a length change precision of 10^{-4} cm/cm. In addition, the precision of the experimental technique was analytically examined for both absolute and relative density determinations. Three analytical expressions used to reduce data for liquid density determinations were evaluated for their precision. Each allows use of a different set of input data parameters, which can be chosen based on experimental considerations. Using experimentally reasonable values for the precision of the parameters yields a similar resultant density precision from the three methods, on the order of 0.2%.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

* This work supported by the U.S. Energy Research and Development Administration.

6b

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

The density and volumetric thermal expansion of high temperature molten materials are necessary for technological needs as well as of basic scientific interest. An example is the need for data on molten structural and fuel materials for use in nuclear reactor safety studies. The gamma radiation attenuation technique for density determinations of molten materials offers several advantages over other methods at high temperatures. First, the gamma beam offers a probe which is not in thermal or physical contact with the liquid. In addition, since a free liquid surface is not involved in the measurement, a number of problems of other methods are eliminated, including sample volatilization, formation of oxide surface films, and corrections for surface tension and liquid/solid interactions.

Though the technique itself is not new, it has not achieved widespread use as a high temperature technique. Dillon, et al. [1] and LeVert, et al. [2] have reported its use for density measurements of liquid alkali metals, and Döge [3] has used the technique for density measurements in the Pb-Sn system to 1200 K. The densities of liquid lead, cesium, and gallium were examined with the gamma method to 1400 K by Basin and Solov'ev [4]. More recently, the technique has been extended to studies of iron and copper to 1900 K by Yavoyskiy, et al. [5]. The technique has also been used extensively for determining the bulk density and water content of soils [6,7], and for other technological uses at ambient temperature [8].

In this paper, an experimental apparatus using the gamma attenuation method to 1200 K is described, including the details of the electronic counting system. Sample size and gamma source choice considerations are also presented. Next, the basic equation of the method is presented in forms useful for data analysis, including both relative and absolute density determinations. Finally, an analysis of the precision of the method is given. Several experimental considerations are identified which may cause systematic or random errors in the measurement.

EXPERIMENTAL APPARATUS

With this technique, the density of a material is determined from the attenuation which is produced by the passage of a collimated beam of mono-energetic gamma radiation through the material, whose length and absorption coefficient are independently determined. A schematic of the experimental arrangement is shown in Fig. 1. A ^{137}Cs 0.662 MeV gamma source (activity 4 Ci) is housed in a lead vault, which provides both radiological shielding and the initial collimation for the gamma beam. Collimators of stainless steel, inside diameter 6.4 mm, direct the beam into the high temperature tubular furnace. The molten material is contained in a precision-fabricated crucible, with faces machined parallel to each other and perpendicular to the beam direction. The crucible is supported by a ceramic pedestal, both of which are contained in an evacuated ceramic chamber. The alignment of the crucible and pedestal is achieved using a He-Ne laser beam passing through the collimators, prior to lowering of the furnace over the chamber. Emerging from the furnace, the beam is further collimated (aperture 6.4 mm) before striking the NaI(Tl) scintillation detector, which is shielded in lead. Steel filters of various thicknesses are inserted into the beam to establish an appropriate gamma flux for the detection system.

The gamma detection system is outlined in Fig. 2; except for the scintillation detector (Bicron 3M3P), the apparatus was manufactured by Canberra Industries, Inc., Meriden, Conn. The detector consists of a NaI(Tl) crystal (76.2 mm diam. x 76.2 mm length), hermetically attached to a photomultiplier tube window. To achieve count rate stability over extended time periods, the ambient temperature of the detector is thermostatically-controlled. The output pulses are amplified and shaped by the preamplifier (Model 802-9) and amplifier (Model 2010). The amplified pulses pass through a digital stabilizer (Model 1720), which offers automatic gain control of the linear electronics. This device was found necessary to provide system counting stability over long time periods. The stabilizer compensates for gain shifts in the system due to line voltage variations, high voltage power supply variations, count rate changes, and ambient temperature variations. The single channel analyzer (Model 2030) passes the pulses in the ^{137}Cs photopeak to the counter (Model 1790C). The digital format of the output allows for interface to a computer-based data acquisition system for continuous monitoring of sample temperature and count rate, as well as subsequent data analysis.

The precision to which the beam intensity is measured is limited by the statistics which govern the random nuclear emission process. The measurement uncertainty decreases as $1/\sqrt{N}$ for a total number of accumulated counts N . A count rate limit of about 40,000 counts per second (cps) is imposed to accommodate the detection apparatus. At this rate, data accumulation for ten minutes yields a count rate precision of about 0.02%. Using both the automatic gain stabilizer and the thermostated detector, a stabilized detection system has been achieved whose count rate precision over indefinite time periods is determined solely by nuclear counting statistics. For count rates above 1000 cps, a correction is required for the "dead time" of the electronics system, which originates from the probability of a second pulse occurring while the detection system analyzes a first pulse [9]. This dead time can be measured for each detection system by the two-source method [10], or a variation, the two-absorber method [6].

The current apparatus utilizes a resistance-type tubular furnace and graphite crucibles, as shown in Fig. 1, to achieve temperatures to 1200 K. The furnace was modified by drilling collimator clearance holes into the furnace jacket and insulation. The furnace resistance wires were also drilled out and subsequently bypassed in the beam region. Work is in progress to replace the tubular furnace with a high temperature/high vacuum tungsten mesh furnace capable of 3200 K. In this facility, the gamma beam will be directed through ceramic or refractory metal crucibles and through the electrode gaps in the tungsten mesh heating element.

The basic equation which describes the gamma beam intensity and thus defines the analytical method is [9]

$$I = I_0 \exp [-\mu \rho \ell] , \quad (1)$$

for mono-energetic gammas and a narrow beam (well-collimated) geometry. In Eq. (1), I_0 and I are the gamma intensities before and after passage through the sample material, ρ is the material density, ℓ the material length along the beam direction, and μ the mass attenuation coefficient of the material. As the product $(\mu \rho \ell)$ increases, the attenuation increases, and the uncertainty in ρ due to imprecision in I decreases. On the other hand, as $(\mu \rho \ell)$ increases, the count rate diminishes, so that longer times are required to yield a given precision; thus, there exists an optimum $(\mu \rho \ell)$. Considering only uncertainties due to measurement of I and I_0 , one can show that, for a fixed total

counting time, the fractional standard deviation for ρ is a minimum at $(u\rho l) = 2$. (This value also minimizes the counting time necessary to achieve a given precision [7].)

The criterion $(u\rho l) = 2$ can be used for selection of a sample length l and the gamma source, since u varies with gamma energy as well as with atomic number Z . To minimize thermal gradients, sample size should not exceed ~ 4 cm in the current furnace. For $l = 3$ cm and densities which range from 5-15 g/cm³, the above criterion gives $u \sim .13-.04$ cm²/g. A source is desired which has a long isotope half-life; a relatively simple energy spectrum, giving a strong, monochromatic beam with no higher energy peaks contributing Compton scattered photons; and a high specific activity. As a practical matter, source cost, availability, and shielding requirements eliminate many choices. With these considerations, ¹³⁷Cs emerges as the best source for most applications. At the ¹³⁷Cs energy of 0.662 MeV, u is ~ 0.07 cm²/g, and relatively independent of material Z .

DATA ANALYSIS

There are some hidden features to Eq. (1) which have not been universally recognized in some of the previous density/thermal expansion literature. First, the refinement of Eq. (1) to include the dead time of the counting system has been ignored in some earlier works. The actual (corrected) count rate I differs from the measured (uncorrected) count rate R by the equation [9]

$$I = \frac{R}{1-R\tau} \quad , \quad (2)$$

where τ is the dead time of the counting system. For a given apparatus (fixed τ), the difference between I and R depends on the rate R , and will become negligible for small R .

Secondly, one should recognize that I_0 , the (corrected) count rate in the absence of the sample material, can itself be represented by an equation of the form Eq. (1), where $(u\rho l)$ is replaced by $\sum_i u_i \rho_i l_i$, and the subscripts denote the materials in the path of the gamma beam (furnace walls, vacuum chamber walls, crucible walls, etc.). It is then clear that I_0 will be a function of temperature, since $\rho_i l_i$ will vary as the temperature of each material changes. In addition, temperature can be expected to vary the size of collimation apertures as well, causing an additional dependence of

I_0 on T . These effects are taken into account by measurement of $R_0(T)$ as a function of temperature.

Finally, one recognizes that the sample dimension l along the beam direction depends on temperature through the expansion of the containment crucible. These refinements lead to a modified form of Eq. (1) given by,

$$I(T) = \frac{R(T)}{1-R(T)\tau} = \frac{R_0(T)}{1-R_0(T)\tau} \exp \left\{ -u \rho(T) l_1 [1 + \alpha(T-T_1)] \right\} . \quad (3)$$

Here, $R(T)$ and $R_0(T)$ denote measured (uncorrected) count rates at a sample temperature T , l_1 is the sample length at T_1 , and α is the mean linear expansion coefficient of the crucible over the range T_1 to T .

The mass attenuation coefficient is independent of the physical state of the material, and therefore is independent of temperature. However, since u results from both absorption and scattering processes, its value may be slightly dependent on the measurement geometry. Because accurate values of u may be lacking for a given material, it is advisable to measure u experimentally for each material investigated. This can usually be done at room temperature by measuring I through a length L of the material; then u is calculated from

$$u = \frac{1}{\rho L} \ln (I_0/I) . \quad (4)$$

The uncertainty in u results from the uncertainty in ρ and L for the material, since, in principle, one can count indefinitely at room temperature and thereby determine I_0 and I to any precision.

An experimental determination of the counting system dead time τ is necessary, since τ depends on the instruments and their particular settings. The two-source method was used to determine τ . Count rates were measured for irradiation by each of two sources separately, R_1 and R_2 , and for both sources simultaneously, R_{12} . Using Eq. (2) and the restriction $I_1 + I_2 = I_{12}$ yields,

$$\tau = R_{12}^{-1} \left\{ 1 - \left[1 - \frac{R_{12}}{R_1 R_2} (R_1 + R_2 - R_{12}) \right]^{\frac{1}{2}} \right\} . \quad (5)$$

The apparatus described here has $\tau \sim 3 \mu\text{sec}$; thus, for $R \sim 40,000$ cps, I is approximately 12% larger than R .

The gamma attenuation technique can be used to give both absolute and relative liquid density measurements. First, a form is presented for an absolute density determination. Solving Eq. (3) for $\rho(T)$ yields

$$\rho(T) = \frac{\ln [I_0(T)/I(T)]}{u \ell_1 [1 + \alpha(T-T_1)]} \quad (6)$$

where it is understood that I and I_0 are determined from measured rates R and R_0 using Eq. (2). To employ Eq. (6), u is first determined from Eq. (4) by measurements of I_0 , and L and I of the sample material at a temperature (solid) where ρ is determined independently. The length ℓ_1 and expansion α of the crucible are also required. Next, $I_0(T)$ is measured, and finally, $I(T)$ is measured with the molten sample in the crucible to give $\rho(T)$ by Eq. (6). A number of independent measurements are thus required for this method of analysis.

Another approach, which may offer some advantages, is found by solving Eq. (6) for $(u \ell_1)$ at T_1 and equating this expression to the one for another temperature T_2 . This leads to

$$\rho(T_2) = \frac{\rho(T_1)}{[1 + \alpha(T_2-T_1)]} \frac{\ln [I(T_2)/I_0(T_2)]}{\ln [I(T_1)/I_0(T_1)]} \quad (7)$$

In Eq. (7), u and the absolute crucible dimension ℓ_1 do not enter the data analysis; instead, this approach requires independent knowledge of $\rho(T_1)$ in the melt from another method, and is therefore a relative density method.

A third analytical approach is found by writing Eq. (3) at a temperature T_1 and dividing throughout by Eq. (3) at T_2 . One then has

$$\rho(T_2) \ell(T_2) - \rho(T_1) \ell(T_1) = \frac{\ln [I(T_1) I_0(T_2)/I(T_2) I_0(T_1)]}{u} \quad (8)$$

Unlike the previous two equations, this has a term $I_o(T_2)/I_o(T_1)$; if an experimentally-determined expression relating I_o at T_1 and T_2 can be found, some cancellation of terms may result. For I_o weakly-dependent on T , one can expect a functional dependence of the form $I_o(T_2)/I_o(T_1) = f(T_2-T_1)$. Eq. (8) can then be rewritten as

$$\rho(T_2) = \frac{\rho(T_1)}{1 + \alpha(T_2-T_1)} + \frac{\ln [I(T_1)f / I(T_2)]}{u \ell(T_1) [1 + \alpha(T_2-T_1)]} \quad (9)$$

While this form requires knowledge of $\rho(T_1)$, u , and ℓ , it does not explicitly contain I_o . This may be particularly advantageous if f , the temperature dependence of I_o , is known, but I_o is not. This can readily occur for experimental arrangements where the furnace, controlled atmosphere chamber, and collimators are disturbed during sample loading. In addition, the elimination of I_o in Eq. (9) makes the determination of $\rho(T_2)$ much less sensitive to uncertainties in τ , since $I(T_1)$ and $I(T_2)$ will usually be less disparate than $I(T)$ and $I_o(T)$.

Each of these methods requires some independently-determined parameter for the material, either ρ at a reference temperature or u . The accuracy to which $\rho(T_2)$ is determined may thus be limited by the error in $\rho(T_1)$ or u . It can be seen, therefore, that the gamma technique may be more useful in determining changes in density rather than the absolute densities themselves. Either Eqs. (6) or (7) above yields a fractional density change

$$\frac{\rho(T_2) - \rho(T_1)}{\rho(T_1)} = \frac{\ln [I(T_2)/I_o(T_2)]}{[1 + \alpha(T_2-T_1)] \ln [I(T_1)/I_o(T_1)]} - 1 \quad (10)$$

Of course, this expression is independent of $\ell(T_1)$, u , and an explicit knowledge of $\rho(T)$. Dividing Eq. (10) by (T_2-T_1) gives the mean volumetric thermal expansion coefficient α_v over the range T_1 to T_2 . The precision of this value will depend on the count rate precision and a precise knowledge of (T_2-T_1) .

PRECISION OF THE TECHNIQUE

Analysis

By way of introduction to this section, the results of a preliminary experimental investigation of the precision of the method are briefly mentioned. Small dimensional steps in a precision-machined tool steel block were measured at ambient temperature using the technique. Since the gamma attenuation is a function of (ρl) , the precision of measurement of length changes at constant ρ can be used to estimate the precision of measurement of small density changes. The step sizes in the steel block as determined by the gamma method agreed with metrology measurements to within the combined experimental error of both measurements. From this test, the sensitivity of the gamma method was confirmed to be $\Delta l/l \sim 10^{-4}$ cm/cm.

Analytical expressions for the precision of various parameters have been obtained by writing the rms deviation due to the propagation of random errors through the data analysis expressions. If $\sigma(X_i)$ denotes the standard deviation in the parameter X_i , then one has the variance

$$\sigma^2(G) = \sum_i \left(\frac{\partial G}{\partial X_i} \right)^2 \sigma^2(X_i) \quad (11)$$

for the case where G is a function of the independent parameters X_i .

The precision analysis (using Eq. (11)) for τ is illustrated with a numerical example. For $R_1 = 4000$ cps, $R_2 = 40,000$ cps, $R_{12} = 43,100$ cps, and a total count time of 18,000 sec (5 hr), $\tau = 3.00 \mu\text{sec} \pm 0.37\%$. Typically, then, one can achieve τ to better than 0.5%.

The determination of the mass attenuation coefficient u was also analyzed in terms of precision, using Eq. (11). As an example, $\rho = 7.2 \text{ g/cm}^3 \pm .05\%$, $l = 2 \text{ cm} \pm .05\%$, R and $R_0 \pm .05\%$, and $\tau \pm 1\%$ together give $u = 0.79 \text{ cm}^2/\text{g} \pm .11\%$. The uncertainty in calculated parameters is usually less sensitive to τ than to other parameters.

For typical values of $R \sim 5000$ - $40,000$ cps, one can readily achieve a count rate precision of 0.02% by counting for 5000-625 sec. Greater precision requires exceedingly long counting times, so that .02% will be used as an experimentally reasonable count rate precision. The various analytical methods described above are now analyzed in terms of their precision.

The absolute density determination defined by Eq. (6) yields a fractional variance of $\rho(T)$ given by

$$\begin{aligned} \left(\frac{\sigma(\rho)}{\rho} \right)^2 = [u \rho \ell(T)]^{-2} & \left\{ \left(\frac{\sigma(R_o)}{R_o} \right)^2 \frac{1}{(1-R_o \tau)^2} + \left(\frac{\sigma(R)}{R} \right)^2 \frac{1}{(1-R \tau)^2} \right. \\ & + \left(\frac{\sigma(\tau)}{\tau} \right)^2 \left[\frac{R_o \tau}{1-R_o \tau} - \frac{R \tau}{1-R \tau} \right]^2 \left. \right\} + \left(\frac{\sigma(u)}{u} \right)^2 + \left(\frac{\sigma(\ell_1)}{\ell_1} \right)^2 \\ & + (1 + \alpha \Delta T)^{-2} \left[(\Delta T)^2 \sigma^2(\alpha) + \alpha^2 \sigma^2(T) + \alpha^2 \sigma^2(T_1) \right], \quad (12) \end{aligned}$$

where $\ell(T) = \ell_1 (1 + \alpha \Delta T)$, $\Delta T = T - T_1$, and $\ell_1 = \ell(T_1)$.

For comparison of the methods, a standard numerical example is chosen:

$$R = 16000 \text{ cps} \pm 0.02\%$$

$$R_o = 40000 \text{ cps} \pm 0.02\%$$

$$\tau = 3 \text{ } \mu\text{sec} \pm 1\%$$

$$u = 0.07 \text{ cm}^2/\text{g} \pm 0.1\%$$

$$\ell_1 = 2 \text{ cm} \pm 0.05\%$$

$$T_1 = 300 \text{ K} \pm 1\%$$

$$T = 700 \text{ K} \pm 1\%$$

$$\alpha = 7 \times 10^{-6}/\text{K} \pm 10\%$$

These values in Eqs. (6) and (12) yield $\rho(700 \text{ K}) = 7.087 \text{ g/cm}^3 \pm 0.15\%$, where it is noted that u , τ , and ℓ_1 contribute most significantly to $\sigma(\rho)$. The variance contribution from the parameters is summarized in Table I, along with effects of changing some parameters.

The second method described for calculating the density is Eq. (7). While not including the analytical expression for $\sigma(\rho)$ which corresponds to Eq. (12), it should be noted that the sensitivity to R , R_o , τ , α , and T will be similar, and that $\sigma(\rho_1)/\rho_1$ (at T_1) will contribute directly to $\sigma(\rho_2)/\rho_2$ (at T_2), as do u and ℓ_1 in Eq. (12). To employ Eq. (7), an independently-measured value of ρ in the melt is needed. Crawley [11] has reviewed several methods for liquid metal density measurements; it appears that 0.2% may be a typical error for other methods. Using the above numerical example

and $\rho(300 \text{ K}) = 7.30 \text{ g/cm}^3 \pm 0.2\%$ in Eq. (7) gives $\rho(700 \text{ K}) = 7.018 \text{ g/cm}^3 \pm 0.21\%$. The same result obtains for an uncertainty in τ of $\pm 10\%$; indeed, this method is extremely insensitive to the imprecision of τ . It is, as expected, very sensitive to the uncertainty in $\rho(T_1)$. The accuracy of a value for $\rho(T_1)$ is the limiting factor in the resultant error of $\rho(T_2)$. Table II summarizes these results.

The third calculational method for determining ρ at a temperature T_2 was given by Eq. (9). Again, the fractional standard deviation $\sigma(\rho_2)/\rho_2$ was calculated from the contributions to the variance $\sigma^2(X_i)$ from each parameter. Inserting the standard set of values leads to $\rho(700 \text{ K})$ with an uncertainty 0.23%. The relation

$$f = 1 + (10^{-5}) (T_2 - T_1) \quad (13)$$

was used in Eq. (9) for this calculation, so that $I_0(T)$ increases 0.1% per 100 K. The primary contributions to the uncertainty in $\rho(T_2)$ using Eq. (9) are from $\rho(T_1)$ ($\pm 0.2\%$) and f ($\pm 0.1\%$). (This uncertainty in f allows that the value 10^{-5} in Eq. (13) may be in error as much as 25%.) As expected, the sensitivity to τ is small; in fact, an error in τ of as much as 50% had little effect on $\rho(T_2)$. It was found that $\rho(T_2)$, using Eq. (9), is particularly insensitive to u and ℓ_1 . This is because u and ℓ_1 enter into the second term in Eq. (9), which is basically the correction added to $\rho(T_1)$ due to the change in temperature to T_2 . For the above result, errors in ℓ_1 and u of 2% had little effect on the result. Table III summarizes these findings.

In each of the three methods described, resultant error due to uncertainties in T and α was very small. Similarly, the values of count rate intensities $\pm 0.02\%$ were sufficiently precise to cause negligible error in the calculated density. Increasing the rate uncertainties to 0.2%, which represents a 100X reduction in counting time, approximately doubles the resultant uncertainty in the density, for the examples given.

In calculating the mean volumetric expansion (using Eq. (10)) and its uncertainty, R_0 and R were chosen as above ($\pm 0.02\%$), with values such that $\alpha_v \sim 10^{-4}/\text{K}$. Values for τ and α were unchanged. Using a precision for T of $\pm 0.2\%$, the resultant uncertainty in α_v was $\pm 2.3\%$, $\pm 4.5\%$, and $\pm 8.6\%$ for $\Delta T = (T_2 - T_1)$ of 200 K, 100 K, and 50 K, respectively. Systematic errors in temperature contribute significantly less to the analysis.

Experimental Considerations

To conclude, an identification and discussion of several experimental conditions which contribute to both systematic and random errors in the gamma attenuation method is presented. For discussion, the experimental system is separated into 1) gamma beam and that apparatus which the beam traverses (except crucible and sample), 2) electronics, 3) crucible, and 4) sample material.

1) Gamma Beam and Apparatus. The gamma source decays with time, leading to a time-varying count rate. For ^{137}Cs , with a half-life of 30 years, the correction is ~ 2.5 cps (.006%) change per day for a rate of 40,000 cps. In most instances, this can be ignored. The length of beam collimators should be considered, since the analysis requires a narrow-beam geometry. If the collimators are too short, beam divergence at the sample can systematically influence the results, since gammas scattered through large angles will be detected (the so-called "build-up factor" [9]). The effective sample length will then be larger than its physical length. For this reason, it is desirable to measure μ of the sample with the same collimation as that used throughout, thus insuring an unchanging beam geometry. For a well-collimated beam, and $(\mu \rho t) \sim 1-2$ (so that the gamma mean free path in the sample is ~ 1), the build-up factor in the sample may be neglected.

For a source (unlike ^{137}Cs) for which there exist gammas of energies above those observed by the electronics, Compton events in the detector can also bias the measured results. One must also consider those detected counts caused by background radiation; proper shielding can minimize this effect.

In spite of efforts to achieve precision in alignment and positioning of the furnace, collimators, and vacuum chamber, it has been found difficult to repetitively reproduce the gamma flux through the bare apparatus (I_0) to better than 0.1%. This problem results from a design where the furnace and collimators are disturbed for sample loading, and will be avoided in the higher temperature apparatus. Where the flux I_0 cannot be reproducibly obtained, a data analysis using Eq. (9) may be employed. This problem is also reduced by minimizing the attenuation due to the apparatus as much as possible.

2) Electronics. Drift of the electronics system with voltage and ambient temperature fluctuations can seriously affect count rate reproducibility. The system described above employs a thermostated detector housing and an automatic gain control to eliminate such fluctuations. The gain control also compensates for system gain shift due to count rate dependence, a typical problem with nuclear counting systems. An alternative solution is to collect the complete gamma spectrum with a pulse height analyzer and to computer-analyze the counts in the desired peak, regardless of its location. This approach should not be used if the detected gamma peak shifts during the measurement, however.

Detector fatigue or hysteresis may affect the system gain, and thus the measured count rates, if high gamma fluxes are incident [12]. With the above apparatus, no effects were seen by establishing the procedure of waiting ~ 30 minutes after drastic rate changes are made before resumption of counting.

The correction for electronics system dead time has already been discussed. Using Eq. (6) and the parameters in Table I, but neglecting the dead time correction, yields $\rho = 6.527 \text{ g/cm}^3$, approximately 8% in error (systematic). If Eq. (7) is used, the systematic error which results is reduced to 0.15%.

3) Crucible. Depending on the data analysis method, the inside dimension of the crucible along the beam direction may need to be known precisely at some temperature; in addition, a correction should be made for its expansion with temperature. Accurate knowledge of the crucible length should also include a determination of the porosity and roughness of the crucible wall surface. For containment of corrosive liquids at high temperatures for long periods, the possibility of a changing crucible dimension, due to surface attack, should also be considered.

Cylindrically-shaped crucibles have also been used, with a correction made for the crucible curvature [5]; in light of the difficulties in knowing the cross-sectional gamma intensity profile at the sample in order to calculate an effective crucible length, this method is not advised. For analysis methods which do not depend on a knowledge of l , the error due to use of a cylindrical crucible would be much smaller.

4) Sample. A density measurement using the gamma method requires either the solid sample density and dimension with which to compute ρ , or an independent measure of the sample density at a temperature in the melt. It has been shown that lack of accurate values for these parameters may limit the successful determination of ρ at other melt temperatures.

Sample-crucible compatibility should also be considered; if the crucible is attacked, the composition of the sample may change along with the crucible dimension. Compositional uniformity in complex materials may also be of concern. Depending on the sample and atmosphere, vapor deposition onto internal chamber walls may be an additional source of a temperature (and time) dependent I_0 .

Temperature uniformity must be matched with sample size to avoid thermal density gradients in the sample. Of course, a precise knowledge of the temperature of the sample is necessary for precise volumetric thermal expansion coefficients.

SUMMARY

An apparatus for the measurement of liquid densities at high temperatures using the gamma attenuation method was described, along with an electronic detection system with long-term stability against drift and fluctuations. Experimental and theoretical considerations for choice of sample size and gamma source were also presented.

Three data analysis methods for determining the liquid density were presented, along with a precision analysis for each. Depending on the experimental conditions, the methods offer the ability to use different sets of input data, which can be advantageous where experimental determination of some of the parameters is irreproducible or imprecise. In each of the data analysis methods, the necessary corrections for counting system dead time and crucible expansion have been included.

Method 1 allows determination of the liquid density $\rho(T)$ through Eq. (6), and requires an independent determination of the mass attenuation coefficient for the material. Imprecision in measurement of this coefficient, the system dead time τ , and the crucible dimension l_1 are the most significant contributors to the resultant imprecision in $\rho(T)$.

The second method to calculate $\rho(T)$ uses Eq. (7), and requires independent knowledge of $\rho(T_1)$, the liquid density at some fiducial temperature. However, it does not require precise knowledge of the crucible dimension. Using this method, the resultant imprecision of $\rho(T)$ is primarily due to the error in $\rho(T_1)$, and relatively insensitive to measurement of the dead time τ .

Method 3 (Eq. (9)) is advantageous for data analysis when specific values for I_0 , the gamma intensity through the experimental system in the absence of the sample, are not known. As in method 2, a value is needed for the liquid density at a single reference temperature; the error in this value is the primary contributor to the resultant imprecision. Uncertainties in the crucible dimension, dead time, and mass attenuation coefficient are relatively unimportant in this data analysis method.

Use of experimentally reasonable values for the input parameters and their precisions yields a similar resultant density precision from the three methods, on the order of 0.2%.

REFERENCES

1. I. G. Dillon, F. E. LeVert, P. A. Loretan, G. U. Menon, F. M. Siddiqi, and H. J. Tarng, Nucl. Tech. 12, 307-313 (1971).
2. F. E. LeVert, I. G. Dillon, and H. J. Tarng, Rev. Sci. Instrum. 44, 313-315 (1973).
3. G. Döge, Z. Naturforschg. 21a, 266-269 (1966).
4. A. S. Basin and A. N. Solov'ev, Zhur. Priklad. Mekh. Tekhn. Fiziki 6, 83-87 (1967).
5. V. I. Yavoyskiy, et al., Russ. Metall. No. 4, 44-47 (1974).
6. W. H. Gardner, G. S. Campbell, and C. Calissendorff, Soil Sci. Soc. Amer. Proc. 36, 393-398 (1972).
7. K. Preiss, Soil Sci. 110, 151-156 (1970).
8. E. Elias, Y. Segal and A. Notea, Nucl. Tech. 21, 57-66 (1974).
9. R. D. Evans, The Atomic Nucleus, McGraw-Hill, New York, 1955.
10. A. Picot, Rev. Sci. Instrum. 47, 385-386 (1976).
11. A. F. Crawley, Inter. Metall. Rev. 19, 32-48 (1974).
12. R. J. Reginato, Soil Sci. Soc. Amer. Proc. 38, 156-157 (1974).

TABLE I

Method 1. $\rho(T)$ calculated from Eq. (6). Resultant % error in ρ shown for each of four sets of uncertainties in the input data parameters. Sets B, C, and D show the result of changing the % standard deviation from the values in set A. The % standard deviation for a parameter X_1 is defined by $100 \times (\sigma(X_1)/X_1)$, where $\sigma(X_1)$ is the standard deviation of the parameter X_1 .

Parameter		Set A		% Standard Deviation		
		% Standard Deviation	Variance Contrib. (10^{-6})	Set B	Set C	Set D
R(T)	16000 cps	0.02	.045	10.0	0.2	0.4
R ₀ (T)	40000 cps	0.02	.052		0.2	
τ	3 μ sec	1.0	.75			
u	0.07 cm ² /g	0.1	1.00			
$l(T_1)$	2.0 cm	0.05	.25			
T ₁	300 K	1.0	.0004			
T	700 K	1.0	.002			
α	$7 \times 10^{-6}/K$	10.0	.079			
$\rho(T)$	7.127 g/cm ³	$\pm 0.15\%$		$\pm 0.87\%$	$\pm 0.34\%$	$\pm 0.41\% *$

* Same results using $l(T_1) \pm 0.4\%$.

TABLE II

Method 2. $\rho(T_2)$ Calculated from Eq. (7). See Table I caption for additional notes.

Parameter		Set A		% Standard Deviation		
		% Standard Deviation	Variance Contrib. (10^{-6})	Set B	Set C	Set D
$\rho(T_1)$	7.30 g/cm ³	0.2	4.0	0.5		
$R(T_1)$	15400 cps	0.02	.041			0.2
$R_o(T_1)$	40000 cps	0.02	.048			0.2
$R(T_2)$	16000 cps	0.02	.044			0.2
$R_o(T_2)$	40100 cps	0.02	.052			0.2
τ	3 μ sec	1.0	.0002		10.0	
T_1	300 K	1.0	.00002			
T_2	700 K	1.0	.0001			
α	$7 \times 10^{-6}/K$	10.0	.078			
$\rho(T_2)$	7.018 g/cm ³	$\pm 0.21\%$		$\pm 0.50\%$	$\pm 0.21\%$	$\pm 0.48\%$

TABLE III

Method 3. $\rho(T_2)$ Calculated from Eq. (9). See Table I caption for additional notes.

Parameter		Set A		% Standard Deviation		
		% Standard Deviation	Variance Contrib. (10^{-6})	Set B	Set C	Set D
$\rho(T_1)$	7.30 g/cm ³	0.2	4.3		0.5	
$R(T_1)$	15400 cps	0.02	.045			
$R(T_2)$	16000 cps	0.02	.045			
τ	3 μ sec	1.0	.0004	50.0		
u	0.07 cm ² /g	0.1	.001	2.0		
$l(T_1)$	2.0 cm	0.05	.0003	2.0		
f	1.004	0.1	1.0			0.4
T_1	300 K	1.0	.0004			
T_2	700 K	1.0	.002			
α	$7 \times 10^{-6}/K$	10.0	.078			
$\rho(T_2)$	7.022 g/cm ³	$\pm 0.23\%$		$\pm 0.28\%$	$\pm 0.53\%$	$\pm 0.46\%$

Figure 1. Schematic diagram of gamma attenuation experimental apparatus.

Figure 2. Block diagram of gamma detection electronics.