

# Comparative Density Measurements for Solid Specimens Weighing a Few Milligrams

A. D. Franklin and J. R. Donaldson

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(September 18, 1973)

A density comparison technique previously described has been used to compare the densities of tungsten wires weighing about 1.3 mg to within a few percent error. For larger, less dense specimens the expected random error of a few parts in  $10^4$  was confirmed by comparing the known densities of Si and  $\text{CaF}_2$ .

Key words:  $\text{CaF}_2$ ; density; measurement technique; Si; tungsten wires.

## 1. Introduction

In this laboratory we have recently been using a new technique [1]<sup>1</sup> for the comparison, to moderately high precision, of the densities of solid specimens weighing less than 100 mg. In reference [1] we showed that the technique compared the densities of pure and lightly-doped  $\text{CaF}_2$  (density,  $3.2 \text{ g/cm}^3$ ) to about 3 parts in  $10^4$ . The densities of all of these specimens differed among themselves by less than 1 percent, and were not too different from the density ( $1.8 \text{ g/cm}^3$ ) of the flotation liquid used in the determinations, so that as an example of the use of the technique this work presented a particularly favorable case. In the present paper we report the application of the technique to two less favorable cases:

- (i) A comparison of the densities of pure  $\text{CaF}_2$  and Si, with results again precise to about 3 parts in  $10^4$ .
- (ii) A comparison of the densities of one group of 1 mg tungsten wires to that of another group as comparison standards. The precision attained was about 2 to 7 parts in  $10^2$ . The degradation in precision arises from the small specimen size and also from the very high density of tungsten ( $19.2 \text{ g/cm}^3$ ) relative to that of the flotation liquid.

## 2. Experimental Details

The experimental technique and the constants of the density apparatus were as described in reference [1], except that a more sophisticated temperature bath

was employed, so that the temperature was held to within  $0.05 \text{ }^\circ\text{C}$  during the course of a run. The upper liquid used was water containing a few tenths percent ethylene glycol. The lower liquid was a proprietary fluorocarbon marketed by the 3M Company under the designation FC75.<sup>2</sup> Its density at  $25 \text{ }^\circ\text{C}$  is  $1.767 \text{ g/cm}^3$ .

The ratio ( $\rho_u/\rho_s$ ) of the density of an unknown to that of a set of comparison standards is found by measuring the differences in float position when the unknown is substituted for each of the comparison standards. These differences are linear in the masses of the comparison standards, and if the intercept and slope of a plot of difference against mass are designated by  $a$  and  $b$ , the density ratio can be computed using eq (4) of reference [1].

$$\rho_u/\rho_s = [Q + (\rho_s/\rho_2)(1 - Q)]^{-1}, \quad (1)$$

where  $\rho_u$ ,  $\rho_s$ , and  $\rho_2$  are the densities of the unknown, the comparison standards, and the (lower) flotation liquid, and  $Q$  is given by

$$Q = (-a/b)/M_u$$

where  $M_u$  is the mass of the unknown.

The mass values for the density measurements were computed from direct comparisons of the unknown object with items of known mass determined by the Mass, Length, and Volume Section of the National Bureau of Standards. The uncertainty of each value involves both a systematic error (the total uncertainty of the mass value of the mass standards used) and a random error (taken here to be one standard deviation of the weighing process).

The uncertainty in the measurement of a density ratio can also be taken as the sum of a random part and a systematic part. If the uncertainty relative to the value itself be designated by the symbol  $\Delta$ , then the random part can be estimated using a generalization of the equation given in reference [1].

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> Certain commercial products are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products identified are necessarily the best available for the purpose.

$$\Delta_r = (\rho_u/\rho_2 - 1) \left\{ \frac{V_{a/b}}{(-a/b)^2} + \left[ \frac{\Delta_R M_u}{M_u} \right]^2 \right\}^{1/2} \quad (2)$$

where  $V_{a/b}$  is the variance in the ratio  $a/b$  determined directly from the float positions and masses of the comparison standard specimens,<sup>3</sup> the  $\Delta_R M_u$  is one standard deviation of the process determining the mass of the unknown. There is no contribution in eq (2) from the random error in the masses of the comparison standard specimens because this is already contained in the observed variance,  $V_{a/b}$ , of the ratio  $a/b$ . Note that because the random error in the masses of the comparison standards is much smaller than the scatter in the float position, a simple least-squares fit to the data assuming no error in the masses was used.

The systematic part of the uncertainty arises from two sources: the systematic errors in the masses of the specimens, and the error in the ratio,  $\rho_s/\rho_2$ , of the density of the comparison standards to that of the flotation liquid. If we assume these make independently additive contributions to the overall uncertainty, these contributions are:

$$\text{Unknown mass: } \Delta_m = \left| (\rho_u/\rho_2 - 1) \left( \frac{\Delta_s M_u}{M_u} \right) \right| \quad (3)$$

$$\text{Density ratio: } \Delta_\rho = \left| (\rho_u/\rho_s - 1) \left( \frac{\Delta(\rho_s/\rho_2)}{(\rho_s/\rho_2 - 1)} \right) \right| \quad (4)$$

where  $\Delta_s M_u$  is the systematic error in  $M_u$  and  $\Delta(\rho_s/\rho_2)$  is the uncertainty in the ratio  $\rho_s/\rho_2$ .

The systematic errors in the masses of the comparison standard specimens may or may not contribute explicitly to the overall uncertainty. If unrelated systematic errors occur for the comparison standards, then these behave like random errors in the computation of  $a/b$ , and are contained in the variance of  $a/b$ , thus making no explicit contribution. If the comparison standards have the same systematic error, there will be a contribution to the overall uncertainty, given by

$$\Delta'_m = \left| (1 - \rho_u/\rho_2) \frac{\Delta_s M_s}{(-a/b)} \right| \quad (5)$$

The uncertainties reported here will be given as the random error [one standard deviation, eq (2)] and the various systematic errors [eqs (3), (4), and (5)].

### 2.1. Comparison of Densities of Si and CaF<sub>2</sub>

Using the same set of CaF<sub>2</sub> comparison standards as used in the work reported in reference [1], with masses near 34 mg, the ratio of the density of a very

pure specimen of Si to that of CaF<sub>2</sub> was determined at 27.4 °C. The mass of the Si specimen, 62.793 mg, was chosen to produce about the same weight in the flotation (lower) liquid as the CaF<sub>2</sub> comparison standards. These masses were determined as described above. The uncertainties in the measurements of mass were:

	CaF <sub>2</sub> comparison standards	Si, unknown
Random $\Delta_R M$	0.7 $\mu\text{g}$	4.0 $\mu\text{g}$
Systematic $\Delta_s M$	1.0 $\mu\text{g}$	0.6 $\mu\text{g}$

The density of the Si was [2]  $2.32900 \pm 0.00001 \text{ g/cm}^3$  at 25 °C, almost in agreement with the measurement of Smakula and Sils [3]. The measured value of  $Q$  was 0.54709. If we adopt also Smakula and Sils's values for the density of CaF<sub>2</sub> at 25.0 °C (3.17934  $\text{g/cm}^3$ ), and use values for the linear thermal expansion coefficients of Si ( $2.61 \times 10^{-6}$ ) and CaF<sub>2</sub> ( $1.9 \times 10^{-5}$ ), then we calculate the density ratio at 27.4 °C to be 0.73263. The measured value was 0.73285, so that the difference between the measured and calculated values amounts to only 3 parts in 10<sup>4</sup>.

In the random error, eq (2), only the variance in  $(-a/b)$  makes an appreciable contribution. Among the systematic errors, only that involving the ratio  $\rho_s/\rho_2$  of the density of the CaF<sub>2</sub> comparison standards to that of the (lower) flotation liquid is nonnegligible. The density of this liquid at the temperature of measurement was  $1.761 \pm 0.001 \text{ g/cm}^3$ . The calculated uncertainties were:

$$\text{Random: } \Delta_r = 1.9 \times 10^{-4}$$

$$\text{Systematic: } \Delta_\rho = 3.4 \times 10^{-4}$$

Thus the measured and calculated density ratios agree within the limits of uncertainty in the measurement. Note that the systematic error above could be reduced by choosing comparison standards of the same density as the unknown.

### 2.2. Comparison of Densities of Tungsten Wires

A group of four short (about 1 cm long) pieces were cut from a tungsten filament wire (diameter approximately 0.003 in) that had been given a severe heat treatment. These pieces, which served as unknowns, are listed as specimens 1 through 4 in table 1. An additional group (A through E) were cut from a filament not given the heat treatment but otherwise presumably identical, and served as comparison standards. One comparison standard, C, was compared as an unknown against the other comparison standards as a check upon the internal consistency.

<sup>3</sup>There is an error in eq (6) of reference [1], which gives an expression for  $V_{a/b}$ . The quantity  $\left[ n \sum_i m_{ii}^2 - \left( \sum_i m_{ii} \right)^2 \right]$  belongs in the denominator and should have been written with  $-1$  as an exponent.

TABLE 1. Density measurements on tungsten wires

Wire	Set	Masses			Density ratios, $\rho_u/\rho_s$				
		Values ( $\mu\text{g}$ )	Uncertainties, $\mu\text{g}$		Values	Uncertainties, percent			
			$\Delta_R M$	$\Delta_s M$		$\Delta_r$	$\Delta_m$	$\Delta_\rho$	$G^*(\text{g/cm})$
1.....	Unknown.....	1301.8	0.4 (0.03%)	1.2 (0.09%)	0.97 <sub>4</sub>	3.3	0.9	0.02	$6.4 \times 10^{-4}$
2.....	Unknown.....	1261.4	0.4 (0.03%)	0.6 (0.05%)	0.99 <sub>0</sub>	2.8	0.5	0.02	$6.7 \times 10^{-4}$
3.....	Unknown.....	1344.9	0.4 (0.03%)	0.6 (0.04%)	0.97 <sub>7</sub>	1.5	0.5	0.02	$6.3 \times 10^{-4}$
4.....	Unknown.....	1382.6	0.4 (0.03%)	1.2 (0.09%)	0.98 <sub>4</sub>	6.5	0.8	0.02	$5.9 \times 10^{-4}$
A.....	Standard.....	1228.8	0.4 (0.03%)	0.7 (0.06%)					
B.....	Standard.....	1173.2	0.4 (0.03%)	0.7 (0.06%)					
C.....	Standard.....	1225.8	0.4 (0.03%)	0.7 (0.06%)	1.008	1.2	0.6	0.02	$6.4 \times 10^{-4}$
D.....	Standard.....	1298.0	0.4 (0.03%)	1.2 (0.09%)					
E.....	Standard.....	1404.5	0.4 (0.03%)	0.9 (0.06%)					

\*G multiplied by the acceleration due to gravity is the buoyant force gradient experienced by the float, as obtained from the density measurement itself. Cf. reference [1].

The masses of the wires are listed in column 3 of table 1, and their uncertainties in columns 4 and 5. They have been measured as described under section 2, Experimental Details. Due to the limited range of the balance used, the wires were not all compared to the same combination of mass standards. This is reflected in the variation of the systematic errors of the wires, from 0.64  $\mu\text{g}$  to 1.18  $\mu\text{g}$ . Because different mass standards were used to compute the masses of the wires, the systematic portion of the uncertainty in the masses of the comparison standards appears as a random scattering of the mass values in conjunction with the density measurements, and is included in  $V_{a/b}$ .

The measured values of the ratios of the densities of the unknown wires to that of the comparison standards are given in column 6, followed by the percentage uncertainties calculated with eqs (2), (3), and (4). The values of  $Q$  were all unity to within 0.3 percent.

In the last column is the buoyant force gradient calculated, as in reference [1], in the course of the density measurements themselves. If the upper liquid were perfectly homogeneous, with no density gradients, then the buoyant force gradient would be the product of the cross-sectional area of the suspension wire ( $8 \times 10^{-4} \text{ cm}^2$ ) and the difference in density of the upper and lower liquids (0.76  $\text{g/cm}^3$ ). This product is  $6.1 \times 10^{-4} \text{ g/cm}$ , very close to the observed values listed in table 1. The agreement between the expected and observed buoyant force gradient is very much better than it was in the work reported in reference [1], and probably reflects the use of water rather than benzene as the upper liquid. The negligible solubility in water of the fluorinated hydrocarbon used as a lower liquid precludes formation of concentration, and therefore density, gradients at the float.

To within the estimated experimental uncertainty, all values of the density ratio of the unknown to known tungsten wires are equal. The values for all four unknown wires, No. 1 through No. 4, lie slightly below unity, which may reflect the special heat treatment given this filament. The difference from unity of the mean value for the unknowns is statistically significant, being 5.2 times the estimated standard deviation of the mean. The measured density of wire C is the same as that of the other comparison standards well within the experimental error.

Most of the relative errors in determining the density ratios of these wires, shown also in columns 6, 7, and 8 of table 1, are larger by as much as two orders of magnitude than they were for the measurements on  $\text{CaF}_2$  (ref [1]) or Si above. This increase arises from two causes, which can be understood on the basis of eqs (2) and (3):

- (i) The square root in eq (2) was about 10 times larger for the tungsten wires than it was for  $\text{CaF}_2$ . Equations (1), (2), and (6) of reference [1] show that  $a/b$  should be about 30 times smaller for the tungsten wires, and that  $V_{a/b}$ , which under the conditions of the experiments reported here is roughly proportional to  $b^{-2}$ , should be about 10 times smaller. These changes result from the smaller masses ( $\times 30$ ) and weights in the lower liquid ( $\times 15$ ) for the tungsten wires.
- (ii) The initial factor in eqs (2) and (3) is about 12 times larger for the tungsten wires than it was for the  $\text{CaF}_2$ , because of the very large tungsten density (19.2  $\text{g/cm}^3$ ) compared to that (3.2  $\text{g/cm}^3$ ) for  $\text{CaF}_2$  and for the lower liquid (1.8  $\text{g/cm}^3$ ).

On the other hand, the uncertainty  $\Delta_\rho$  (eq 4) arising from errors in the ratio  $\rho_s/\rho_2$  of the density of the comparison standards to that of the flotation liquid was much smaller for the tungsten wires than for the

Si/CaF<sub>2</sub> ratio. In the former case the unknown and comparison standard densities were almost the same, making the first factor in eq (4) small, and the density of the comparison standards was much larger than that of the flotation liquid, making the denominator of the second factor larger. These changes were more than enough to offset an increase in the uncertainty in the ratio  $\rho_s/\rho_2$  itself because of the rather large uncertainty ( $\pm 0.1$  g/cm<sup>3</sup>) in the actual density  $\rho_s$  of the tungsten.

### 3. Summary and Conclusions

The density comparison technique described in reference [1] has been used to compare the densities of very small (1.3 mg) tungsten wires (density 19.2 g/cm<sup>3</sup>), with errors in the range 2 to 7 percent. It was shown that both the very small size of these specimens and their very high density contribute to produce this rather high error.

On the other hand, a check upon the method was obtained by comparing the density of very pure (63

mg specimen, density 2.3 g/cm<sup>3</sup>) Si to that of pure CaF<sub>2</sub>. The ratio obtained agreed with measurements in the literature to within 3 parts in 10<sup>4</sup>, confirming the expected precision of the density comparison method.

---

The authors would like to thank Dr. George Comenetz, Westinghouse Research Laboratories, for providing all of the tungsten wires, and Dr. W. Horton for a very careful and helpful reading of the manuscript.

### 4. References

- [1] Franklin, A. D., and Spal, R. D., Rev. Sci. Instr., **42**, 1827 (1971).
- [2] Deslattes, R. D., private communication.
- [3] Smakula, A., and Sils, V., Phys. Rev., **99**, 1744 (1955).

(Paper 78A1-800)