QUICK AND ACCURATE DENSITY DETERMINATION OF LABORATORY WEIGHTS

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1. Introduction

In the past two decades the United States National
Bureau of Standards (NBS) has undertaken programs to
improve classical hydrostatic weighing [1] and to
develop a density scale based on the density of a
solid object [2]. The methods reported here are a
continuation of that effort and, in many instances,
will eliminate the need for classical hydrostatic
weighing and most of its inherent difficulties in
determining the density of a solid. Additionally,
the solid-object density standard is used to its
full advantage.

2. Historical

In 1886 Thiesen noted the benefits to be gained by
completely immersing a balance [3] for the measure-
ment of an object's density. Until recently this
idea lay forgotten as there was no practical way of
pursuing the concept. With the recent development
of the high-precision so-called "top loading elec-
tronic balance" a form of Thiesen's idea has been
successfully implemented. The results of measure-
ments presented here indicate the density of standard
kilograms could be assigned with a precision as
good as 7 ppm (parts per million).

The work of Bowman and Schoonover [1] was primarily
directed toward surmounting the difficulties encoun-
tered when a modern, single-pan analytical balance
is used to weigh an object immersed in water in
order to determine the object's density to a very
high accuracy. The most notable difficulties are
cleanliness of the water, fabrication of the immersed
portion of the balance suspension, degassing of the
sample and the awkwardness of weighing under the
balance with a remote sample-loading device.

The uncertainty of 5 ppm or more that is usually
assigned to the density of water was overcome with
the development of the solid-object density scale
[2] based on single-crystal silicon. The assigned
uncertainty to to silicon crystals is about 2 ppm.
From this work also came the experience with fluoro-
carbon liquid and its remarkable properties that
are essential to this work.

In the earlier work [1] it was speculated that a
null-operated, linear force balance, when immersed,
would eliminate nearly all of the problems encounter-
ed in the density measurement. The success of this
work has shown that opinion to be correct.

The following describes a modification of a commerci-
ally available, servo-controlled, top-loading
balance which permits its operation, without loss
of precision, while submerged in a fluid of special
properties. Next, we present data obtained by
using the device to determine the volumes of various
objects to an accuracy of better than 30 ppm in a
fraction of the time which would have been required
using conventional techniques. Finally, we discuss
industrial and scientific applications of the
submerged balance.

3. Apparatus

The balance modified for this work is a Mettler
PL1200,[1] the important specifications of which are:

weighing range	0 - 1200 g
reproducibility	±0.005 g
linearity	±0.01 g

Significant mechanical and electronic modifications
were introduced to the balance and its enclosure.
These are described below along with descriptions
of the thermostated bath and fluorocarbon liquid
used in our measurements.

3.1 Mechanical Modifications to the Balance.

The balance was supplied by the manufacturer in a
modified form. That is, the measuring cell (electro-
magnetic force transducer) and the error-detecting
electronics of the servo system were removed from
the original chassis and remounted in a separate,
identical chassis. Thus the factory-modification
provided a measuring cell remote from the indicator
unit. The latter contains most of the electronic
circuitry and provides protection from hostile
environments. However, the remote measuring cell
package in this configuration was excessively bulky
for immersion in liquid and further modification
was required to reduce its size.

The weighing cell was removed from the chassis and
remounted on an aluminum base plate of approxi-
mately 17 cm diameter. Three leveling screws were
provided such that the center of gravity of the
assembly is within the triangle which they define.
Surrounding the measuring cell is an aluminum tube
of the same diameter as the base plate and 12 cm in
height with provision for passage of the electronic
cable. Resting on the upper end of the tube is a
cover plate of the same material with an opening
for mounting the weighing pan on the measuring
cell.

Buoyant forces on the immersed balance pan cause a
zero-shift that cannot be compensated by the elec-
tronic circuitry of the balance so additional tare
weight is required. However, to facilitate reliable
sample handling and to minimize corner load errors
the entire pan assembly was rebuilt. The original
weighing pan was disassembled. The spring element
was then remounted beneath a rectangular pan (5 cm
x 5 cm) of sufficient mass to allow the instrument
both to zero and to indicate full scale.

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[1]Certain trade names and company products are
identified in order to adequately specify 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 are necessarily the best
available for the purpose.

The upper pan surface was divided in quarters by two shallow vee grooves at right angles to each other. This pan design easily accommodates samples in the shape of cylinders (on their side), spheres, and any object with a flat surface. A completely flat upper pan surface was avoided in order to minimize cohesion of a flat-bottomed weight to the pan.

Lastly, the cable connector at the weighing cell was removed and placed on the end of a 1 meter length of 12-conductor ribbon cable; three unused conductors were removed from the ribbon cable to reduce its bulk. This modification provides a flexible cable for immersion in the fluid bath and keeps to a minimum the path for heat leakage.

3.2 Electronic Modifications.

The electronic elements submersed with the measuring cell are the magnetic force coil, the permanent magnet and the error-sensing circuit of the servo-controller. In addition, there is circuitry to maintain the magnetic flux of the stationary magnet constant as ambient temperature changes. The temperature signal for this circuitry is provided by a transistor embedded in the stationary magnet. The heat-sinking compound surrounding this transistor was removed prior to immersion of the balance. The fluorocarbon fluid provides the needed thermal contact without running the risk of heat-sinking compound floating about in the interior of the measuring cell.

When the measuring cell was submersed in the fluoro-carbon and the balance was turned on, the pan began to oscillate and no reading could be obtained. In order to make the balance behave as desired, it was necessary to modify the analog servo electronics. Specifically, the 2.2 µF capacitor (C14) in the feedback loop of the analog amplifier was increased to 3.2 µF. (The input to this amplifier is proportional to the instantaneous position error of the balance. The output signal is a linear combination of the input, its derivative, and its integral.) After making this simple change, the balance performed as well in the fluid as it had previously performed in air.

3.3 Liquid Bath.

A suitable liquid bath was designed for complete immersion of the measuring cell and a large number of samples in the fluid. A double-walled vessel was blown from borosilicate glass as shown in fig. 1.

Several notable features of the fluid bath are summarized as follows:

a) continuous inner bath surface for easy cleaning.

b) Transparent structure for visual detection of air bubbles and dust particles on samples.

c) Provision for adjustable air head to dampen pump pulsations produced by the thermostatic controller.

Between the inner and outer walls of the bath, thermostated water is circulated at 7 liters per minute. A commercially available thermostated bath controller with a 200 W thermal capacity at 0°C seems to be adequate for this work. Experience with this controller indicates a thermal stability of its internal reservoir of about 0.005°C per hour. The temperature of the bath was set at room temperature (22°C).

Adequate sample manipulation is achievable by for-ceps, left in the bath at all times for thermal soaking. The forcep jaws are covered with a soft plastic tube to protect the samples.

3.4 Fluorocarbon Liquid.

Clearly, the fluid in which an electronic measuring cell is submerged must have many special properties: it must be electrically insulating, it must be chemically inert, it must be optically transparent (in order for the servo optics to function properly), and it should not evaporate quickly. These characteristics may be found, for example, in FC-75, a fluorinated fluid manufactured by the 3M Company. A comparison of some of the properties of FC-75 with those of water is given in Table 1. An additionally noteworthy property of FC-75 is its immense appetite for gases. For example, the fluid is able to dissolve about 0.3 g of air per kilogram of fluid. This ability to dissolve atmospheric gases, combined with the fluid's low surface tension, greatly inhibits bubble formation on immersed objects - one of the most serious problems in conventional high-precision hydrostatic weighing. Finally, the fluid is 77 percent more dense than water at room temperature thereby increasing the signal to noise in comparison to a normal hydro-static weighing. The major disadvantages of this fluid as compared to water are its large coefficient of thermal expansion and its cost. However, use of FC-75 instead of water for conventional "hydrostatic" weighing has many advantages. [2] The density of FC-75 is usually not known accurately enough for the liquid to serve as a density standard. Instead, the fluid density is calibrated at the time of use by including a solid object of known mass and volume in the weighing scheme. [2]

Table 1. Comparison of Properties
of FC-75 and Water.

Property (at 25°C)	FC-75[a]	Water
Density (g/cm^3)	1.8	1.0
Coefficient of expansion (°C^{-1})	1.6×10^{-3}	2.5×10^{-4}
Kinematic viscosity (cm^2/s)	0.82×10^{-2}	0.89×10^{-2}
Vapor pressure (mm Hg)	30	24
Surface tension (dynes/cm)	15	72
Heat capacity (J/g-°C)	1.0	4.2
Thermal conductivity (W/cm-°C)	1.4×10^{-3}	6.1×10^{-3}

[a]Values for FC-75 supplied by the manufacturer.

4. Principles of Use

We illustrate the use of the submersible balance by finding the volume, V_A, of an object, A, when its mass, M_A, is known. Placing the object on the balance produces a reading, O_A, which is related to the other parameters through the equation

$$O_A = K \left[M_A - \rho(t) V_A(t) \right] \qquad (1)$$

where O_A is the difference in reading of the loaded and unloaded balance.

Here ρ is the density of the fluorocarbon and K is a constant scale-factor which may be adjusted by turning a potentiometer controlling the calibration of the balance. Both ρ and V_A are functions of the ambient temperature, t. In succeeding equations the functional dependence on temperature is not shown explicitly.

Normally K is adjusted by the balance manufacturer or user so that the balance will read directly the mass of an object of density 8.0g/cm^3 in air of density $1.2 \times 10^{-3} \text{g/cm}^3$, i.e. $K = 1.000150$. We found it convenient (though, of course, not essential) to readjust K to exact unity. Thus we can ignore K in the succeeding equations. Hence,

$$V_A = \frac{M_A - O_A}{\rho} \qquad (2)$$

The problem with using eq. 2 is that the precision with which V_A can be measured far exceeds the accuracy with which ρ is known. Thus, for best results, one should also measure an object whose mass and volume are known. Placing such an object on the balance essentially calibrates the density of the fluorocarbon at the time of weighing. Let the known object be called S1. Then

$$\rho = \frac{M_{S1} - O_{S1}}{V_{S1}}$$

and

$$V_A = \frac{M_A - O_A}{M_{S1} - O_{S1}} V_{S1} \qquad (3)$$

Further improvement in the results are realized by use of two known objects, S1 and S2, whose masses are near M_A and whose volumes bracket V_A, whence

$$V_A = V_{S1} + (V_{S2} - V_{S1}) \frac{(O_{S1} - O_A) - (M_{S1} - M_A)}{(O_{S1} - O_{S2}) - (M_{S1} - M_{S2})} \qquad (4)$$

Note from the form of eq. 4 that only differences in balance readings are required and, therefore, it is not necessary that the reading for the unloaded balance be on scale.

There are also applications, for instance in quality control, which only require the ratio of the volume of an object A to a working standard S1. In this case the actual value of V_{S1} in S.I. units is of no consequence. Using the submersible balance one can obtain the desired quantity

$$\frac{V_A}{V_{S1}} = \frac{M_A - O_A}{M_{S1} - O_{S1}} \qquad (5)$$

5. Measurements

The simplest measurement one can make using the submersed balance is to use eq. 5 to determine the ratio of the volumes of two similar objects. We chose two hermetically sealed, hollow, stainless steel weights each of which has a mass of one kilogram and a volume of about 337 cm^3. Each weight was placed on the balance twice in a symmetric series, the sequence of measurements requiring less than 10 minutes for completion. The computed ratio of volumes, 0.999156, is identical with that which was derived from a precise hydrostatic weighing. The agreement is somewhat fortuitous because round-off errors in reading the submerged balance would themselves limit the theoretical precision of the ratio measurement to 12 ppm. One might expect to approach the theoretical limit, however, because the measurement consists merely of interchanging nearly identical objects and is insensitive to many of the limitations of a balance (e.g. non-linearity).

The next test which we made of the submerged balance was to use eq. 3 to find the volume of a one-kilogram germanium crystal. Our choice of a standard, S1, for use in eq. 3 was designed to illustrate how a laboratory which lacks the means for precise hydrostatic weighing can obtain a suitable volume standard. The chosen standard was a commercially available, precision ball bearing having a

diameter of 6.35 cm. The mass of such a steel ball is approximately 1043 g. The bearing manufacturer is able to certify the sphericity and diameter of the ball to an accuracy which determines its volume at 20°C to better than 15 ppm.

A symmetric series of weighings was performed in which the steel ball was measured four times and the germanium crystal three. The series of measurements required approximately 20 minutes to complete. Using eq. 3, the volume of the germanium was computed to be 187.7193 g/cm^3, which is 24 ppm lower than that found by hydrostatic weighing. Round-off errors in the balance contribute an uncertainty of 25 ppm for this example.

The measurements we had made thus far suggested that the submerged balance was operating well. An additional experiment, consisting of the measurement on the submerged balance of a set of calibrated, stainless steel weights of nearly equal density, showed the linearity of the balance to be unchanged by its modifications and immersion.

We therefore proceeded to a more careful test of the balance, by making use of eq. (4). The standards, S1 and S2, were a kilogram of tantalum (volume ᵙ 60 cm^3) and one of the two hollow weights described above. The "unknowns" measured were all about one kilogram in mass: a brass weight (volume ᵙ 128 cm^3), the germanium crystal described above, and a titanium bar (volume ᵙ 226 cm^3). All the objects were included in a symmetric series which required about 30 minutes to complete. The six weights could all be kept below the surface of the fluorocarbon, on the storage tray provided (see fig. 1). The series was run five times over a period of several days. The results are summarized in table 2.

It is noteworthy that measurements of the weights with large volume exhibit a lower standard deviation than do those of the higher-density weights. This is to be expected if the experimental scatter is due primarily to round-off errors in the balance. The remarkable feature is that the scatter is as low as is observed. The systematic errors may be due either to combined errors in the hydrostatic measurements of the standards and "unknowns" or to some, as yet unexplainable, source of systematic error introduced by the experimental procedure.

6. Summary

Our experience with the immersed balance warrants the following observations:

1. The linearity and reproducibility of the balance are unaffected by immersion in the fluorocarbon liquid.

2. The calibration factor, K, is also unchanged. (In the liquid, K may be determined by measuring two known objects of dissimilar volume and density and obtaining from the two balance equations (eq. 1) simultaneous solutions for ρ and K. A contamination of the fluorocarbon liquid by magnetic impurities may affect K).

3. The balance reading is stable even when the fluorocarbon liquid is gently agitated. Moving the forceps used in changing weights slowly through the liquid has no affect on the balance reading. When weights are exchanged, the balance attains a steady reading within seconds of reloading the pan, although the liquid surface may still be in motion. Circulation of thermostated water through the outer chamber of the bath does not affect balance stability.

Table 2. Summary of Results.

$$(\frac{\text{measured volume}}{\text{accepted volume}} - 1)\text{ppm}$$

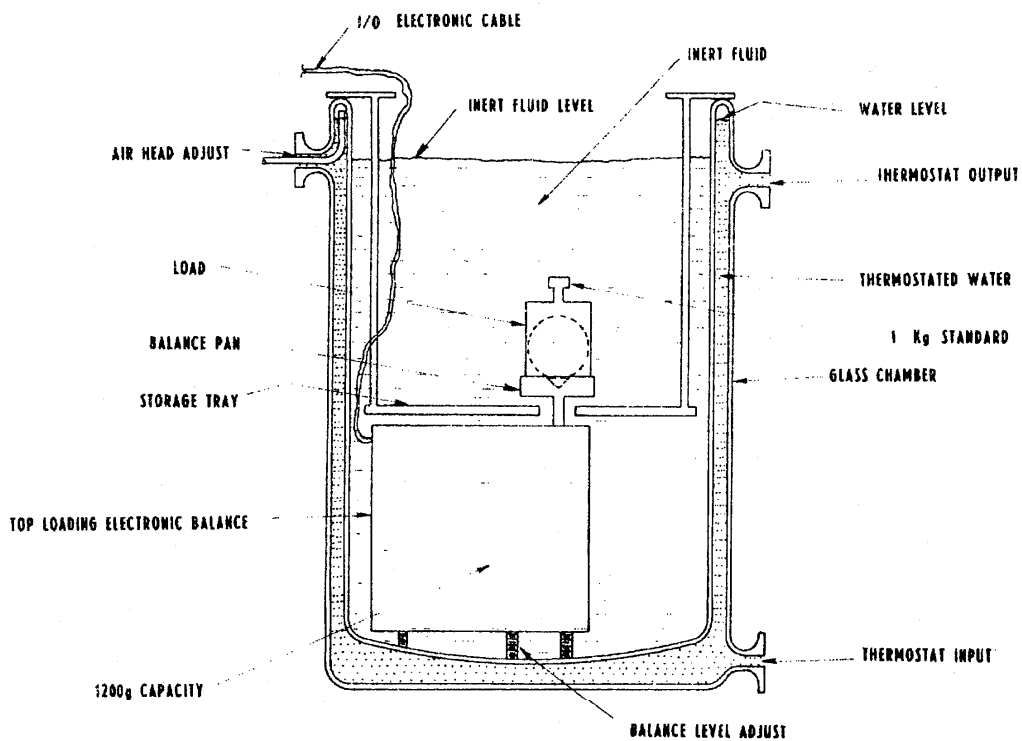| Run number	Brass	Stainless steel	Germanium	Titanium
1	-5	-37	-25	-20
2	-28	-45	-22	-27
3	+7	-1	-15	-27
4	+17	-3	-18	-11
5	+18	-12	-1	-17
Ave Error	+2	-20	-16	-20
Std. Dev.	19	20	9	7

Fig. 1 Cross-sectional view of the balance immersed in its thermostated
bath. A conventionally-shaped standard weight is shown on the
pan. Unconventional loads may also be accommodated by the pan
as suggested by the sphere (drawn with dashed lines).

Finally, we are not certain why the electronic modification was necessary in order for the balance to operate acceptably when submerged. Our hypothesis is that the initial motion of the weighing cell through the liquid generates turbulence which, in turn, couples to the cell. The servo electronics then responds to the changed force in such a way that instability results. Our solution to the problem is, essentially, to increase the time constant of the integration response of the servo regulator. The fact that this strategy achieved the desired results does not, however, prove the hypothesis. It is also worth noting that the electronic modification does not degrade the normal performance of the balance in air.

7. Discussion

Our experience has shown us the immersed balance has two remarkable features which we believe can be used with outstanding advantage. First, although one might expect the immersed balance to be in a hostile environment, we found the opposite to be true. Secondly, the interchange of objects on the balance pan and the recovery of equilibrium are extremely fast compared to a classical hydrostatic weighing. These advantages can be utilized in two distinct and what we believe are important applications.

First, there is scientific interest in density measurements, at the part per million level of accuracy, of solid samples having a mass in the range of 100 g to a few grams or less. Recently commercially available balances of the type used here have appeared with precision estimates of 1 or 2 ppm and ranges between 30 g to 30000 g. A similar treatment of these balances will conceivably result

in density determinations having precision errors about the same as the uncertainty in the silicon density standard.

We intend to pursue the scientific application as part of the NBS Standard Reference Materials program to produce density standards of silicon.

Perhaps a more interesting and important application of these instruments is in the realm of industrial metrology. Because the instrument is protected in a thermostated bath, it can perform well in areas that would ordinarily seem unsuitable. This feature, coupled with the extremely fast measurement cycle, makes possible measurements that were once considered to be too labor-intensive or, in the case of mass production, too slow. An example of such a measurement would be a production-line density determination of sintered turbine blades to assure their integrity. The standard for such a measurement could be a turbine of acceptable quality.

REFERENCES

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