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Density Measurements of Small Amounts of High-Density Solids by a Floatation Method

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A floatation method for determining the density of small amounts of high-density solids is described. The use of a float combined with an appropriate floatation liquid allows us to measure the density of high-density substances in small amounts.

Using the sample of 0.1 g in weight, the floatation liquid of 3.0 g cm^{-3} in density and the float of 1.5 g cm^{-3} in apparent density, the sample densities of 5, 10 and 20 g cm^{-3} are determined to an accuracy better than ±0.002, ±0.01 and ±0.05 g cm^{-3}, respectively that correspond to about ±1 x 10^{-5} cm^3 in volume.

By means of appropriate degassing treatments, the densities of $(Th,U)O_2$ pellets of ~0.1 g in weight and ~9.55 g cm^{-3} in density were determined with an accuracy better than ±0.05 %.

Keywords : Floatation Method, Float, High-density Solids, Small Amounts, Accuracy, Volume, Degassing, $(Th,U)O_2$, Pellet

浮遊法による少量高密度試料の密度測定

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赤堀　光雄・柴　是行

（1984年8月22日受理）

少量の高密度試料に対する密度測定法として，浮子を使った浮遊法について検討を行い，浮子と適当な浮遊液を用いることにより，高密度物質の密度測定が少量の試料で可能となった。

密度3.0 g cm^{-3} の浮遊液と，1.5 g cm^{-3} の浮子を用いた場合，密度5，10および20 g cm^{-3} の試料0.1 gで，それぞれ±0.002，±0.01および±0.05 g cm^{-3} よりも高い精度で密度測定が可能であり，これは体積精度にして$\pm 1 \times 10^{-5}$ cm^3 以下に相当する。密度が約9.55 g cm^{-3} の（Th，U）O_2 ペレットを用いた測定では，適当な脱ガス処理をすることにより，約0.1 gの試料で±0.05％以下の精度で密度が測定できた。

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1. Introduction

Density measurements of nuclear fuels such as UO_2, $(Th,U)O_2$ and so on have been applied to estimation of the volume changes induced by irradiation [1-3]. However the irradiated fuels are so radioactive that the accurate measurement is very difficult. For this purpose it is advantageous to use small amounts of the fuels.

A floatation method allows the density of small amounts (a few mg) of solids to be measured to an accuracy better than ±0.1 % [4]. However the method is not capable of measuring the density of high-density (above 5 $g\,cm^{-3}$) solids for lack of high-density floatation liquids with densities above 4.76 $g\,cm^{-3}$, which is the density of thallium formate at 90 °C. The density of the high-density solid can be determined using an improved floatation method in which floats are used. Rose et al. [3] have measured the density of small fragments (~2 x 10^{-3} g) of unirradiated and irradiated UO_2 pellets to an accuracy of 0.6 % using a density-gradient column technique, where PTFE floats were used. The method requires a complicated apparatus, where the whole column is necessary to keep at a constant temperature all the time at measurement. Also, choice of transparent liquids used in the method is limited, since the range of the density of the PTFE float is very narrow, probably 2.1 ~ 2.5 $g\,cm^{-3}$.

In the present study, the densities of small amounts (~0.1 g) of ThO_2 and $(Th,U)O_2$ pellets were determined using a floatation method, where hollow glass spheres were used as floats. The glass floats have wide-range densities (0.2 ~ 2.5 $g\,cm^{-3}$), so that many floatation liquids with various densities such as benzene, water, carbon tetrachloride, methylene iodide and so on, can be used for determining densities.

2. Experimental

2.1 Apparatus

A float used in the floatation method requires the following properties

(a) smaller density than floatation liquids

(b) chemical stability to the floatation liquid

(c) thermal and mechanical stabilities to degassing at somewhat high temperature and handling

We developed the float to satisfy the above limitations, which was a hollow sphere made of glass and has a platinum wire of 0.1 mm in diameter to suspend solid sample. Fig.1 shows schematically the glass float. The floats were 0.3 ~ 1.0 g cm^{-3} in apparent density and 0.01 ~ 0.08 g in weight, and stable up to 500 °C in vacuum. Their densities were determined by a conventional floatation method using a mixed solution of distilled water ($\rho_{20°C}$=0.9982 g cm^{-3}) and acetone ($\rho_{20°C}$=0.7920 g cm^{-3}) as the floatation liquid. The float density was corrected by using a volume expansion coefficient of glass (1 x 10^{-5} K^{-5}) at each measurement.

Fig.2 illustrates an apparatus, which can heat solid samples and fill a sample container with the floatation liquid after cooling.

The pycnometer method was used for determining the density of the floatation liquid. The pycnometer, made of glass, was ~14 g in weight and ~10 cm^3 in inner volume, which was calibrated by weighing the pycnometer filled with distilled water at a series of temperatures. Thus the inner volume V_p was calculated from $V_p(T°C) = V_p(0°C) + \alpha T$, where α was a constant of 2 x 10^{-4} cm^3 and T the temperature of the floatation liquid at each measurement.

The solid sample and the float were weighed on a single-pan balance of 20 g capacity and reading to 5×10^{-6} g and the pycnometer on a balance of 200 g capacity and reading 1×10^{-4} g.

2.2 Procedure

After degassing at a temperature above 200 °C and weighing in air, a sample is suspended by the glass float. The joined sample is degassed for 1 hour and, if necessary, at elevated temperatures in the apparatus as shown in fig.2. After cooling, the floatation liquid is poured into the sample container through a stainless steel tube. The floatation is conducted in air by dropwise adding a mixed solution with proper densities and, at the same time, the liquid temperature is measured. After attaining the floatation equilibrium, where the density of the liquid is equal to the joined density of the sample and float, the liquid is transferred into the pycnometer. The pycnometer filled with the liquid is then weighed.

2.3 Floatation liquid and solid sample

A mixed solution of methylene iodide ($\rho_{20°C}$=3.325 g cm^{-3}) and benzene ($\rho_{20°C}$=0.8790 g cm^{-3}) was used as the floatation liquid. Both are miscible each other and not highly volatile.

The floatation method was applied to determinations of densities of non-porous and porous solids, which are several metals of above 99.99 % in purity (zinc, silver, tantalum and platinum) and oxide ceramics (ThO_2, and 0.5(No.1) and 7.1(No.2)mol% UO_2-ThO_2 solid solutions), respectively.

3. Theory

3.1 Basic formulation

In the floatation method, the density of the solid sample ρ_s, which is supported by the float weight W_f and density ρ_f at a measuring temperature, is calculated from the equation [3]

$$\rho_s = \frac{W_s \rho_L}{W_s + W_f(1-\rho_L/\rho_f)} = \frac{W_s}{V_s} \tag{1}$$

where W_s is the weight of the sample and ρ_L the density of the floatation liquid at floating equilibrium. From the previously measured W_p and calculated inner volume V_p of the pycnometer at the measuring temperature, the density can be calculated from the equation

$$\rho_L = \frac{W'_p - W_p}{V_p} = \frac{W_L}{V_p} \tag{2}$$

where W'_p is the weight of the pycnometer filled with the liquid and W_L the weight of the liquid necessary to fill the pycnometer.

3.2 Estimation of errors

In the floatation method, some errors come from the following experimental procedures and natural phenomena :

(a) weighing the sample, float and pycnometer with and without the liquid.

(b) measuring the temperature of the liquid at which the liquid attains the same density as the joined sample.

(c) the judgement whether or not the floating has attained equilibrium.

(d) the attachment of air bubbles to the sample, float and pycnometer.

(e) the evaporation of the liquid during weighing.

The errors in weighing W_1 and W_2 were estimated to be approximately 1×10^{-5} and 2×10^{-4} g, respectively, which are twice as much as minimum readings of the balances. The temperature change ΔT of the liquid during weighing was estimated to be within 0.5 K. The error which comes from an uncertainty of the judgement on the floating equilibrium may be negligible, since the sample and float appear to be easily changed from sinking to rising in the liquid by a little fall in temperature near the temperature of the floating equilibrium. The weight loss of the liquid by evaporation during weighing was found to be less than 5×10^{-4} g. This value is equivalent to about 1.7×10^{-3} % of the fractional error of the density of the sample $\Delta\rho_s/\rho_s$. The $\Delta\rho_s/\rho_s$ can be calculated from the equation

$$\frac{\Delta\rho_s}{\rho_s} = \{\left(\frac{\Delta W_1}{W_s}\right)^2 + \left(\frac{\Delta V_s}{V_s}\right)^2\}^{1/2} \tag{3}$$

with

$$\frac{\Delta V_s}{V_s} = \frac{\rho_s}{W_s}\left[\left(\frac{W_s+W_f}{\rho_L}\right)^2\{2\left(\frac{\Delta W_1}{W_s+W_f}\right)^2 + 2\left(\frac{\Delta W_2}{W_L}\right)^2 + \left(\frac{\Delta V_p}{V_p}\right)^2\} + \left(\frac{W_f}{\rho_f}\right)^2\{\left(\frac{\Delta W_1}{W_f}\right)^2 + 2\left(\frac{\Delta W_2}{W_L'}\right)^2 + \left(\frac{\Delta V_p}{V_p}\right)^2\}\right]^{1/2} \tag{4}$$

where W_L' is the weight of the mixed solution of distilled water and acetone necessary to fill the pycnometer in measuring the density of the float. The fractional error of the volume of the pycnometer $\Delta V_p/V_p$ may be calculated from the equation

$$\frac{\Delta V_p}{V_p} = \{2\left(\frac{\Delta W_2}{W_{H_2O}}\right)^2 + \left(\frac{\Delta\rho_{H_2O}}{\rho_{H_2O}}\right)^2\}^{1/2} \tag{5}$$

where W_{H_2O} is the weight of distilled water required to fill the pycnometer, ρ_{H_2O} the density of distilled water at T °C, $\Delta\rho_{H_2O}$ the sum of the errors come from the measurement of the temperature of water and the change of the temperature during weighing. The value of ρ_{H_2O} was calculated by taking account of the volume expansion of water. The value of $\Delta\rho_{H_2O}$ was estimated to be 2.1×10^{-4} g cm^{-3}K^{-1} near 20 °C.

Fig.3 shows ΔT (the error of the temperature of the floatation liquid) dependence of the fractional error $\Delta\rho_s/\rho_s$ ($\Delta V_s/V_s$), for W_s=0.1 g, ρ_s=10 g cm^{-3}, ρ_f=1.5 g cm^{-3}, W_L=34 g and ρ_L=3 g cm^{-3}. In the following estimation of errors, the ΔT was assumed to be 0.5 K.

Fig.4 shows the float density dependence of the $\Delta\rho_s/\rho_s$ for different sample weights, sample and liquid densities. The decrease of the error may be possible by increasing the density of the liquid and the weight of the sample and decreasing the density of the sample. The error appeares to be minimized at roughly the half of the density of the liquid.

Fig.5 shows the sample density dependence of the $\Delta\rho_s/\rho_s$ for several different sample weights. Using the sample weighing 0.1 g, the float of 1.5 g cm^{-3} in density and the liquid of 3.0 g cm^{-3} in density, the present floatation method allows the sample densities of 5, 10 and 20 g cm^{-3} to be measured to an accuracy better than ±0.0025, ±0.01 and ±0.05 g cm^{-3}, respectively that correspond to about $\pm 1 \times 10^{-5}$ cm^3 in volume.

4. Results and discussion

4.1 Densities of nonporous solids

The floatation method was applied to the measurement of the density of

several nonporous solids. Table 1 shows theoretical and measured densities of metal sample weighing about 0.1 g, indicating errors calculated from eq.(3) and lattice parameters used for calculating the theoretical density. The theoretical one was calculated from $\rho_{th}=MN/VA$, where M is the atomic number, N the number of metal atoms per unit cell, V the volume of unit cell and A the Avogadro's number (6.022045×10^{23}). The measured densities are in good agreement with the theoretical ones and support the essential validity of the present floatation method.

4.2 Comparison of the floatation density with the Archimedes one

An Archimedes method is frequently used for measuring the density of relatively large amounts (greater than about 1 g) of solids [6,7]. On the other hand, Cawthorne and Sinclair measured the density of stainless steel only 0.03 g with repeatability better than ±0.05 % using a micro electro-balance of reading to 1×10^{-7} g. However the applicability of the Archimedes method to porous solids such as ceramics, whose pore structures would require degassing procedures, is doubtful.

In the present study, the Archimedes density of porous solids such as ThO_2 and $(Th,U)O_2$ pellets was measured using water and a balance of 200 g capacity and reading to 1×10^{-4} g. Table 2 shows the weights of the sample, the Archimedes densities and the calculated errors of the ThO_2 and $(Th,U)O_2$ pellets. An accuracy better than ±0.05 % was obtained by using large amounts of the samples. Table 3 shows the floatation densities, and the experimental (3σ) and calculated errors. The sample was degassed at room temperature for 1 hour in the apparatus as shown in fig.2. The floatation density is higher than the Archimedes one, indicating that water, in the Archimedes method, would not penetrate well in open pores of the sample. In the floatation

method, the experimental errors are much higher than the calculated ones. This suggests that the degassing procedure would not be sufficient and that there may be a difference in density among samples taken from a batch.

4.3 Effects of degassing procedures at elevated temperature on the floatation density in porous solids

Following the suggestion of the previous section, we tried to make the degassing condition most suitable. The density of the $(Th,U)O_2$-2 pellets weighing about 0.1 g was measured after degassing at several temperatures : room temperature, 100, 200 and 300 °C for 1 hour each, as shown in table 4. The density tends to increase with degassing temperature up to 200 °C and remain constant above 300 °C, indicating that the degassing condition of about 200 °C is probably suitable. Under the degassing condition, an accuracy better than ±0.05 % was obtained.

5. Conclusions

A floatation method for determining the density of small amounts of high-density solids is described. In the method, hollow glass spheres with variable apparent densities are used as floats, so that many floatation liquids with various densities can be used for determining densities.

Using the float of 1.5 g cm^{-3} in apparent density and the floatation liquid of 3.0 g cm^{-3} in density, the method allows the sample densities of 5, 10 and 20 g cm^{-3} to be determined to an accuracy better than ±0,002, ±0.01 and ±0.05 g cm^{-3} for about 0,1 g specimens, respectively that correspond to about ±1 x 10^{-5} cm^3 in volume.

With mixed solutions of methylene iodidi and benzene as floatation liquid, the densities of $(Th,U)O_2$ pellets with density of approximately 9.55 g cm^{-3} were determined with an accuracy better than ±0.05 % for ~0.1 g specimens.

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Table 1 Comparison of theoretical and floatation densities of several metals

Sample	Weight	Density ρ_s (g cm^{-3})		
	W_s(g)	T.D.*1	meas.	$\Delta\rho_s$ ($\Delta\rho_s/\rho_s$)
Zn	0.15122_1	7.137_7	7.131_7	$\pm 0.006_4$ (0.089%)
Ag	0.12978_5	10.501_5	10.518_5	$\pm 0.016_8$ (0.160%)
Ta	0.10692_0	16.634_5	16.656_2	$\pm 0.051_1$ (0.307%)
Pt	0.10406_0	21.461_6	21.456_7	$\pm 0.087_0$ (0.406%)

*1 T.D.=theoretical density calculated from $\rho_{th}=MN/VA$, where M is the atomic number, N the number of metal atoms per unit cell, V the volume of unit cell and A the Avogadro's number.

Table 2 Archimedes densities of oxide ceramics using distilled water

Sample	Weight	Density	
	W_s(g)	ρ_s(g cm^{-3})	$\Delta\rho_s$ ($\Delta\rho_s/\rho_s$)
ThO_2	7.941_2	9.560_1	0.002_6 (0.027%)
$(Th,U)O_2$-1*1	8.413_2	9.801_2	0.002_5 (0.026%)
$(Th,U)O_2$-2*2	8.174_4	9.470_7	0.003_8 (0.040%)

*1 $Th_{0.929}U_{0.071}O_2$

*2 $Th_{0.995}U_{0.005}O_2$

Table 3 Floatation densities of oxide ceramics using methylene iodide-benzene mixtures

Sample	Number of samples	Density ρ_s (g cm^{-3})	$\Delta\rho_s$ ($\Delta\rho_s/\rho_s$)	
			3σ	cal.
ThO_2	2	9.603_8	0.039_4 (0.410%)	0.008_3 (0.086%)
$(Th,U)O_2$-1	6	9.833_4	0.043_0 (0.437%)	0.003_4 (0.035%)
$(Th,U)O_2$-2	23	9.533_7	0.037_1 (0.389%)	0.003_1 (0.033%)

Table 4 Effect of degassing on floatation densities of $(Th,U)O_2$-2 pellets

Degassing conditions	Measurement times	Density ρ_s (g cm^{-3})	$\Delta\rho_s$ ($\Delta\rho_s/\rho_s$)	
			3σ	cal.
Room temperature	3	9.539_1	0.008_4 (0.089%)	0.008_7 (0.091%)
100 °C	4	9.544_1	0.015_7 (0.165%)	0.007_5 (0.079%)
200 °C	4	9.550_1	0.002_9 (0.031%)	0.007_5 (0.079%)
300 °C	4	9.548_5	0.004_0 (0.042%)	0.007_5 (0.079%)

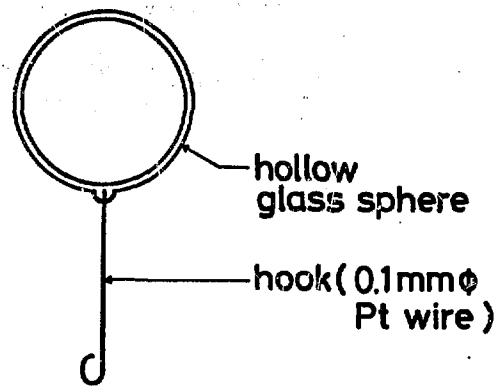

Fig.1 Hollow-sphered glass float with a platinum wire hook of 0.1 mm in diameter.

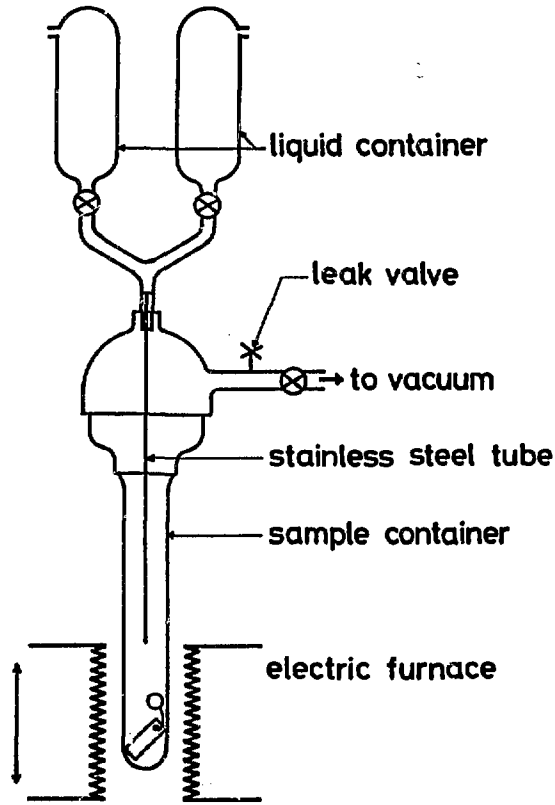

Fig.2 Apparatus for degassing samples and pouring floatation liquids into the sample container through the stainless tube.

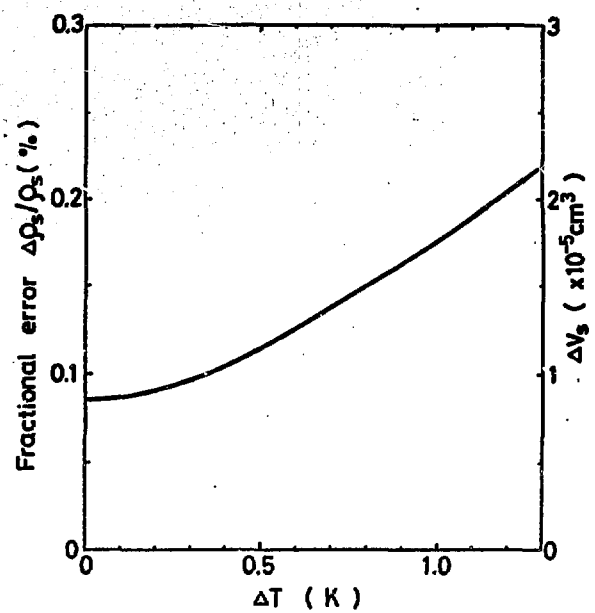

Fig.3 ΔT dependence of fractional errors of sample densities for W_s=0.1 g, ρ_s=10 g cm^{-3}, ρ_f=1.5 g cm^{-3}, W_L=34 g and ρ_L=3.0 g cm^{-3}.

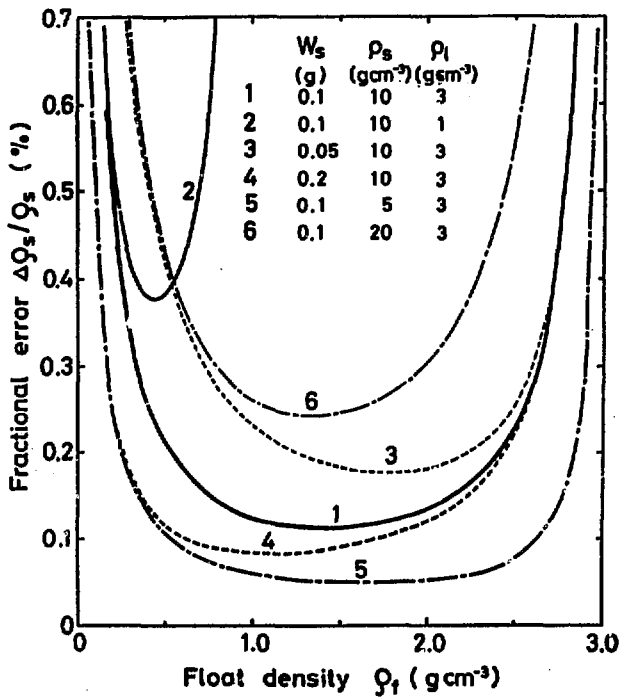

Fig.4 Float density dependence of $\Delta\rho_s/\rho_s$ for different sample weights, sample and liquid densities.

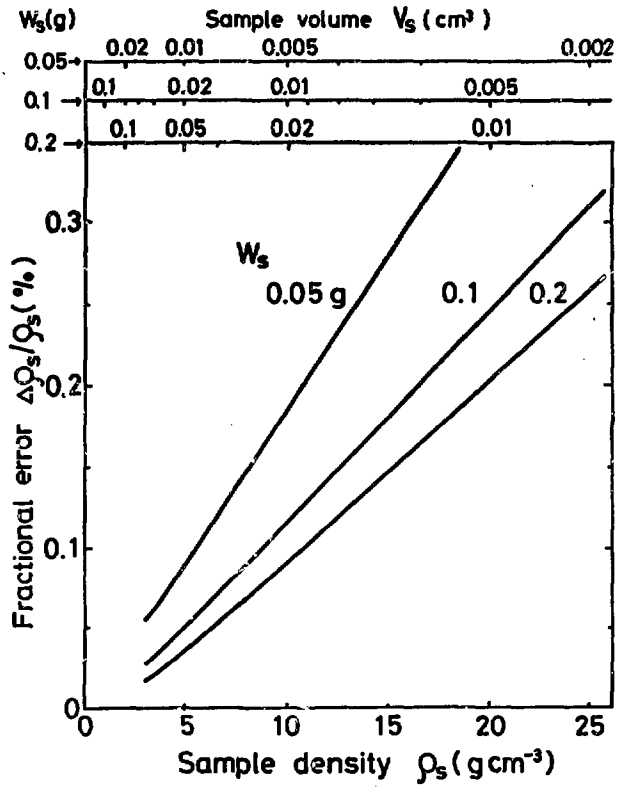

Fig.5 Sample density dependence of $\Delta\rho_s/\rho_s$ for several different sample weights.