Isotopic Method for the Determination of Density in Compressible Systems

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Densities of compressible systems may be determined apart from the viscosity of and without disturbing the system under study using a densitometer consisting of a sealed source containing thulium-170 and a scintillation detector connected to a preamplifier and pulse-height analyzer. The densities of a series of liquid systems whose values are in the region of those of the compressible systems under study are determined first using a Mohr-Westphal balance. The source and detector are immersed in each of these liquids, and corrected activities expressed as counts per minute are obtained. Three analytical methods as well as graphical methods are presented to relate density to activity in liquids of known density. The discussion includes the sensitivity of the method and its applicability to creams, ointments, and powders.

UNTIL THE advent of man-made radioisotopes, methods for measurement of the density or specific gravity of viscous liquids and creams which exhibit compressibility were dependent mainly on the principle of Archimedes. The displacement of a known amount of the substance was measured by the use of a liquid (or gas) in which the substance was insoluble, or methods involving the use of sinkers (*e.g.*, the Mohr-Westphal balance) were employed. Such techniques are limited by the viscosity of the system being measured. Methods employing capillary rise also have been employed, but the surface tension of the system must be known.

Methods involving soundings taken using electromagnetic radiations of various frequencies are generally useful within the framework of a given group of systems but are not always extrapolable to other systems whose chemical compositions are different.

Densitometers or density-thickness gauges utilizing radioisotopes have been used, for example, in the metals industries, to insure the uniform thickness of sheet metal and to locate imperfections in castings. These instruments involve the absorption of α-, β-, or γ-radiation and occasionally may utilize neutrons of appropriate velocities. The radioisotope approach (1–4) to the measurement of density eliminates the necessity for the direct measurement of the volume of the system, the quantity most troublesome to determine in density measurements of porous or compressible systems (5). Martin (6) suggests that three types of densities—true,

granule, and bulk—be applied to powders. The analogy between powders and systems of pasty or creamy consistency becomes apparent when certain creams are stirred, resulting in the incorporation of air, with consequent increase in volume and decrease in density.

THEORY

The attenuation of X- or γ-rays by matter may be considered a first-order reaction obeying the Beer-Lambert law, namely,

$$I = I_o e^{-\mu x} \qquad (Eq.\ 1)$$

where I is the radiant energy passing through the interfering substance of linear absorption coefficient, μ; I_o is the total incident energy; and x is the distance in centimeters through which the absorbed beam travels. For γ- or X-rays, Eq. 1 may be modified to

$$R_x = R_o e^{-k \rho_x x} \qquad (Eq.\ 2)$$

where R_x is the correct activity detected when incident activity R_o passes through a substance of density ρ_x and thickness x. K is a constant, although it no longer represents the linear absorption coefficient. For a standard, Eq. 2 becomes

$$R_s = R_o e^{-k \rho_s x} \qquad (Eq.\ 3)$$

if the distance x from source to detector remains unchanged. Solving Eqs. 2 and 3 for R_o and equating gives

$$R_x e^{k \rho_x x} = R_s e^{k \rho_s x} \qquad (Eq.\ 4)$$

so that with x constant

$$R_x = R_s e^{k(\rho_s - \rho_x)} \qquad (Eq.\ 5)$$

Thus

$$\ln R_x - \ln R_s = k(\rho_s - \rho_x) \qquad (Eq.\ 6)$$

and, converting to common logarithms

$$2.303(\log R_x - \log R_s) = k(\rho_s - \rho_x)$$

or

$$\log R_x - \log R_s = \frac{k}{2.303}(\rho_s - \rho_x)$$

Setting $k/2.303$ equal to K^1

$$\log R_x = K^1(\rho_s - \rho_x) + \log R_s \qquad \text{(Eq. 7)}$$

which is the equation of a straight line of slope K^1 obtained by plotting $\log R_x$ as ordinate and $(\rho_s - \rho_x)$ as abscissa and having $\log R_s$ as vertical intercept. If the standard is water and its density is assumed to be unity, Eq. 7 reduces to

$$\log R_x = K^1(1 - \rho_x) + \log R_w \qquad \text{(Eq. 8)}$$

where R_w corresponds to the activity of a water sample at $4°$.

If good linear fit is not obtained by a plot of log R_x versus $(\rho_s - \rho_x)$, a series of systems of known density, ρ, may be prepared and their corrected activities, R, determined. A plot of $\log R$ as ordinate against $\log 1/\rho_x$ or $(-\log \rho_x)$ as abscissa then may produce linearity. In this case, the equation of the curve would be

$$\log R = m \log 1/\rho_x + \log R_w \qquad \text{(Eq. 9)}$$

where m is the slope of the curve.

If it is merely necessary to compare systems, none of whose true densities are known, a density index may be computed, which may be defined as

$$D = \frac{R_w}{R_x} \qquad \text{(Eq. 10)}$$

Thus

$$\log R_x = \log \frac{1}{D} + \log R_s \qquad \text{(Eq. 11)}$$

It may be seen readily that a plot of $\log R_x$ versus $\log (1/D)$ has unit slope and vertical intercept equal to the log of the corrected activity of the standard or reference substance. If a density index has been calculated and if it is desired to relate it to system(s) of known density which exhibit corresponding activities, Eq. 9 may be equated to Eq. 11 to give

$$m \log(1/\rho) + \log R_w = \log(1/D) + \log R_s$$

so that

$$\log \rho = \frac{1}{m}\left(\log \frac{DR_w}{R_s}\right) \text{ and } \rho = \sqrt[m]{\frac{DR_w}{R_s}}$$
$$\text{(Eq. 12)}$$

If D is calculated on the basis of water at $4°$, Eq. 12 becomes

$$\rho = \sqrt[m]{D} \qquad \text{(Eq. 13)}$$

If experimental data are in agreement with Eqs. 7 or 8, they would of necessity produce linearity if plotted in the form of Eqs. 9 or 11.

MATERIALS AND METHODS

The source holder consists of a nylon cylinder into which a hole has been drilled to receive the radioactive source. The hole is threaded to receive a nylon bolt. The source volume within the container is approximately 25 μl. A 0.25-in. cylindrical lead shield is friction-fitted to the cylindrical nylon source holder. The thulium-170 source is sealed into the holder by inserting the nylon bolt and turning it down firmly. As a precaution against possible leakage, several coats of acrylic lacquer constitute

an external seal. The entire assembly is bolted to the bottom of an L bracket. The vertical member of the L bracket serves to support a scintillation detector.

The output of the scintillation detector (similar to Baird-Atomic model 812 scintillation probe) is fed into a pulse-height analyzer, adjusted to accept the thulium γ peak in the vicinity of 0.085 Mev. Discrimination reduces the observed background and scattered radiation and at the same time provides a high degree of sensitivity which renders unnecessary the use of a very active source.

The thulium-170 was purchased as the oxide in powdered form from the Atomic Energy Commission of Canada. For ease in transfer to the source holder the oxide was converted to the chloride by addition of hydrochloric acid. Repeated transfers of the chloride solution were made and evaporated to dryness in the source holder with the aid of an infrared lamp; the whole system was contained within a hood and behind a wall of lead brick. When the transfer was complete, the system was sealed as described above, and wipe tests were performed to assure that a tight seal had been made and that no external contamination had occurred. The holder containing the source was affixed to the L bracket and the spectrum from 0 to 2 Mev. was scanned to assure radiochemical purity of the sample of thulium. The spectrometer then was set at the 0.085 Mev. photopeak using a 3.0-v. window width. A series of 1-min. counts in air were made with the system, and the average counting rate was determined in counts per minute. This process
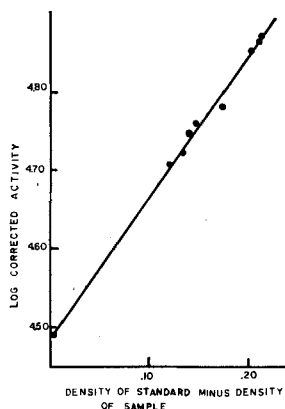

Fig. 1.—Plot demonstrating linearity of log of corrected activity as a function of $(\rho_s - \rho_x)$ for a series of aqueous methanol solutions.
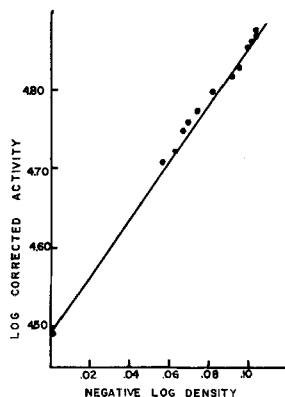

Fig. 2.—Plot of log corrected activity as a function of $\log (1/\rho_x)$, where ρ_x represents the densities of a series of aqueous methanol solutions.

TABLE I.—DATA RELATING CORRECTED ACTIVITY IN COUNTS PER MINUTE TO DENSITIES
OF AQUEOUS METHANOL SOLUTIONS

Density (ρ), Gm./ml.	$\rho_s - \rho_x$	$1/\rho$	Log($1/\rho$)	Corrected Activity $\times 10^{-4}$, counts/min.	Log Corrected Activity
0.787	0.211	1.270	0.1040	7.497	4.874
0.788	0.210	1.269	0.1035	7.322	0.864
0.791	0.207	1.264	0.1018	7.291	4.862
0.797	0.201	1.254	0.0985	7.091	4.850
0.803	0.195	1.245	0.0953	6.728	4.827
0.816	0.182	1.225	0.0883	6.578	4.818
0.828	0.170	1.207	0.0820	6.296	4.799
0.842	0.156	1.187	0.0747	6.022	4.779
0.852	0.146	1.173	0.0696	5.744	4.759
0.858	0.140	1.165	0.0665	5.604	4.748
0.864	0.134	1.157	0.0635	5.219	4.720
0.878	0.120	1.138	0.0565	5.114	4.707
0.998	0.002	1.002	0.0009	3.080	4.489

was repeated with the source, the L bracket, and the lower half of the scintillation detector immersed in water which was contained in a plastic bucket to minimize any counting errors due to scattering by a metal container. Solutions of varying concentrations of methanol in water, ranging from 100% methanol to 100% water were prepared. Their densities were measured using a Mohr-Westphal balance, and the activity of the thulium source was measured in air, in a standard water sample, and in each of the methanol–water systems of known density. A plot of log of corrected activity (R) as ordinate versus ($\rho_s - \rho_x$) as abscissa was made (Fig. 1) which proved to be linear. ($\rho_s = 0.998$ Gm./ml., the density of water at 21°, and $\rho_x =$ the known density of each of the methanol–water systems.) A plot of log$R$ as a function of log($1/\rho_x$) (Fig. 2) was made and also was linear. A plot of log$R$ *versus* log($1/D$) also proved to be linear ($D =$ density index). The plotted lines were determined by the method of least squares. Data relating known densities to known activities are given in Table I.

To determine the density of a compressible system, the apparatus is inserted into the container which contains, for example, a cream. Counts are made at different locations within the container and densities calculated as above. For systems whose densities are either higher or lower than those of the standard solutions, it is merely necessary to change standards and recalibrate the system.

RESULTS AND DISCUSSION

A series of 24 determinations of the densities of oil-in-water type emulsion creams were made at different stages during their manufacture and packaging. Data were obtained which were considered more reliable and significant than those obtained by other methods, since it is not necessary to disturb the cream matrix when measuring density by this method. The densities of creams are greatly affected by loss of water and by the incorporation of air into the cream during the various mixing processes in its manufacture. If the densitometer is inserted vertically downward into the cream, then moved horizontally about 6 in. before counts are taken, most consistent results are obtained with minimum disturbance to the cream matrix.

Repeated measurements and their mathematical analysis indicate that density data obtained by this method are significant to three figures and are reproducible readily at this level. Since the system under investigation need not be disturbed for a measurement to be made, terms such as apparent density or effective density need not be applied. A brief statement of temperature and packing conditions should suffice to describe the conditions of measurement adequately.

The sensitivity and reproducibility of density data obtained by this method might conceivably be affected by (*a*) electronic noise, (*b*) the effects of temperature on the scintillation detector, (*c*) geometry (position of probe relative to source, collimation, etc.), and (*d*) variations in voltage.

Although electronic safeguards (use of the scintillation spectrometer, especially stable amplifiers, etc.) may obviate certain of the above difficulties, it is recommended that during the course of a series of measurements the probe assembly be removed repeatedly from the system under study and placed in a similar container of a substance of known density (like water) at a temperature the same as that of the sample. Thus, activity values may be corrected for each of the above, and a continuous calibration and standardization may be run.

SUMMARY

The radioactive isotope thulium-170, which emits a γ-ray in the region of 0.085 Mev. may be used as a sealed source to determine the densities of compressible systems when a pulse-height analyzer is employed. Either relative or absolute values of density may be calculated which are considered to be more precise than those obtained by other methods, since the radioisotopic method requires a minimum of disturbance of the system.

REFERENCES

(1) Glander, F., *Kautschuk Gummi*, 14, WT 302(1961).
(2) Palegrin, P., and Buscarlet, L. A., *Bull. Inst. Agron. Sta. Rech. Gembloux*, Extra 2, 854(1960).
(3) Shumilovski, N. N., *Akad. Nauk S.S.S.R., Kiev: Tr. Conf. Elektr. Izmereniyam i Priborstr.*, 1959, 20.
(4) Volarovich, M. P., *Kolloid Zh.*, 22, 524(1960).
(5) Clark, G. L., and Liu, C. H., *Anal. Chem.*, 29, 1539(1957).
(6) Martin, A. N., "Physical Pharmacy," Lea and Febiger, Philadelphia, Pa., 1960, p. 586,