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Density Determination of Plastics by a Volumetric Titration Method

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SUMMARY:

A simple volumetric titration method is described for rapid and reliable routine determination of the density of plastics. The method is based on titrating a binary liquid of suitable composition, having the sample on the bottom, with the heavy liquid component until the sample is brought to a floating position.

ZUSAMMENFASSUNG:

Es wird eine einfache volumetrische Titrationsmethode für die schnelle und zuverlässige Bestimmung der Dichte von Kunststoffen beschrieben. Die Methode beruht auf der Titration einer binären Flüssigkeit geeigneter Zusammensetzung, wobei mit der schweren Komponente titriert wird, bis die sich auf dem Boden befindende Probe aufschwimmt.

Some current investigations in this laboratory are concerned with the radiation effects in plastics, particularly with physical-mechanical and morphological changes induced by radiation. An important physical parameter in the characterization of plastics is the density, and our investigations often required a considerable number of routine density determinations of various samples of plastics. The present paper describes a simple, rapid and reliable method for measuring densities of plastics. The method is based on matching the density of a suitable two-component liquid with the density of the solid sample. This is

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achieved by "volumetric titrations" with a burette, i. e. by successive addition of the heavy liquid component until the sample, initially on the bottom of the liquid, is floating. This simple technique is particularly suitable for plastics, either as a rapid routine procedure, or (with more precautions) as a precise analytical control.

Experimental

The set-up for density titration is shown in Fig. 1. It consists of a double-walled observation vessel (a) with a stopcock at the bottom (b) for draining the liquid content. The thermostated liquid (c), usually water, circulates in the outer mantel, and keeps the

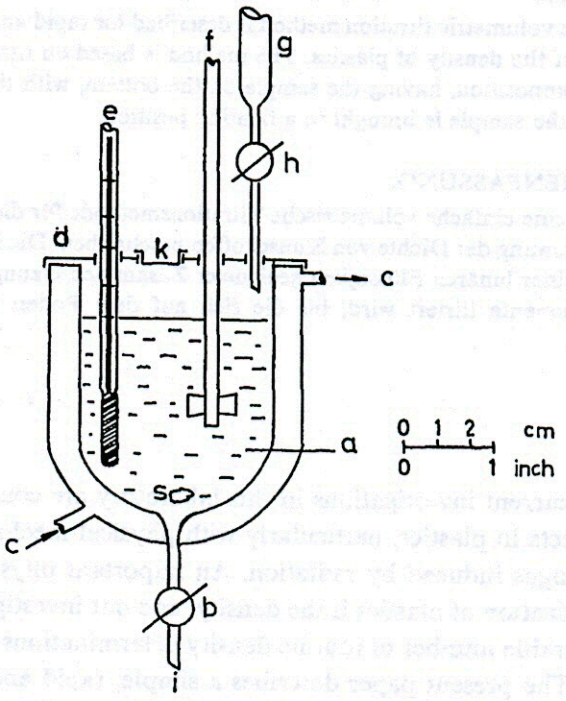

Fig. 1. Density determination by volumetric titration. (a) observation vessel, (b) stopcock, (c) thermostated fluid, (d) cover, (e) thermometer, (f) stirrer, (k) sample inlet, (g) burette, (i) drain.

temperature in the inner vessel within $\pm 0.05\,^{\circ}C$. At the top is a cover plate (d) with openings for the thermometer (e), the stirrer (f), the sample inlet (k) and the top of burette (g). The burette serves for precise addition of small volumes of the heavy liquid component.

The choice of two-component liquid systems is restricted by four requirements: (1) two components should be completely miscible in the composition range of interest, (2) the density of solid samples should be within the upper and lower limit of density of the liquid mixtures used, (3) the liquids should not react chemically with nor dissolve the samples and (4) at the temperature of density determination the loss of the liquid phase due to evaporation should be negligible.

To measure densities of plastics preferably binary liquids recommended by ASTM D-1505 for "columns with gradient" should be used. In Tab. 1 several useful binary systems are listed.

Tab. 1. Binary liquid systems.

System	Range of densities, (kg dm^{-3})
isopropanol — water	0.79–1.00
ethanol — carbon tetrachloride	0.79–1.59
toluene — carbon tetrachloride	0.87–1.59
carbon tetrachloride — trimethylene dibromide	1.60–1.99

Procedure

At the beginning of the procedure, the liquid mixture is of slightly lower density than the density of the sample, so that the later falls to the bottom of the observation vessel. To find out the proper composition (weight-fraction) of the liquid mixture at the beginning, one might determine the composition of the mixture in which the sample of lowest density still falls to the bottom. The weight fraction of the starting liquid mixture

$$x_1^0 = \frac{m_1}{m_1 + m_2}$$

must be known precisely and therefore the weights of the liquid components, m_1 and m_2, should be measured within ± 0.1 mg.

The plastic sample (a piece of several millimeter in size) is placed in the starting liquid mixture, thermostated, then a small volume of the heavy liquid component is added, the mixture is stirred, the temperature controlled, then again, a fresh increment of volume in the heavy liquid is dispensed, and so on, until the sample floats near an arbitrary placed line in the middle of the liquid bulk in the observation vessel. (The exact position of the "floating line" is not important). When the sample floats, its density is equal to the density of the li-

quid mixture. The composition of this "matched" liquid mixture, expressed in weight fraction, is

$$x_1 = \frac{m_1}{m_1 + m_2 + \Delta m_2} = \frac{m_1}{m_1 + m_2 + \varrho_2 \nu_2}$$

where m_1 and m_2 are the weights of the liquid components of the mixture at the beginning (starting mixture), Δm_2 is the weight of the added heavy liquid component from the burette, ϱ_2 the density and ν_2 the volume of the heavy liquid component. For precise determinations, the temperature of the liquid in the burette should be known, so that an accurate value of ϱ_2 can be adapted. If a weight-burette is used, Δm_2 is simply obtained from the loss of weight of the burette.

The density of the matched liquid mixture of composition x_1 is obtained by interpolation from standard tables or from a previously prepared plot of density vs weight fraction. Of course, the measurements should refer to the same temperature as in the table or plot.

The method can be used to determine rapidly and successively the density of several samples, or the average density of several samples. In that case, several samples are placed in the liquid of the observation vessel and one by one brought into floating position by incremental additions of the heavy component from the burette. At the beginning of measurements, it is advisable that the liquid has only a slightly lower-density than the samples, so that the volume of heavy liquid added from the burette is small compared with the bulk volume in the observation vessel.

Application

The application of the volumetric titration method to the density determination of various polyethylene (PE) samples is illustrated in Tab. 2 and Fig. 2. In the first column of Tab. 2, under numbers 1–12 are listed samples of different origins. The composition x_1 of the matched binary liquid (water-n-propanol), when the sample is in the floating position, is listed in the second column. The x_1 values are the most important and critical data, since they are used to "read" the densities directly from standard tables or plots. These density values are listed in the third column.

Tab. 2. Densities of polyethylene samples of various origins, measured by volumetric titration. Binary liquid used: n-propanol—water, temperature 25 °C.

Samples	"Matched" *n*-Propanol — Water Mixture		
	Composition x_1 (wt.-% n-Propanol)	Density (kg dm^{-3}) (Stand. Tab.)*	Density (kg dm^{-3}) (Pycnometrically)
1	43.86	0.9179	0.9178
2	43.70	0.9183	0.9183
3	43.45	0.9188	0.9186
4	27.75	0.9517	0.9521
5	36.10	0.9342	0.9342
6	37.00	0.9323	0.9327
7	23.40	0.9610	0.9609
8	43.15	0.9194	0.9198
9	41.70	0.9225	0.9228
10	37.55	0.9312	0.9316
11	39.68	0.9267	0.9270
12	44.40	0.9168	0.9175

* obtained with x_1 by interpolation of data from standard tables[2].

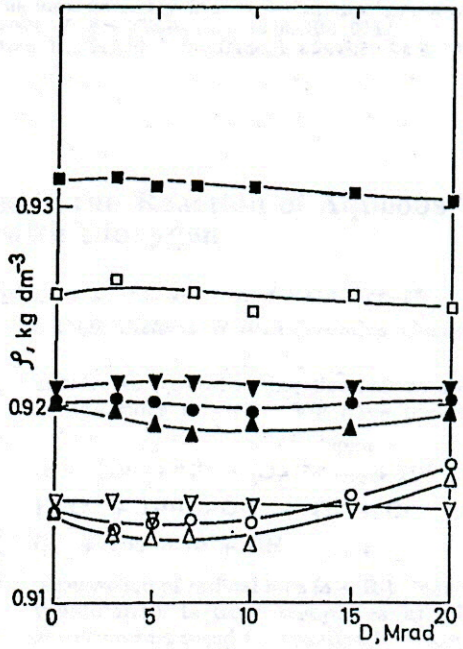

Fig. 2. Densities (25 °C) of irradiated polyethylene samples, measured by volumetric titration. Full marks: samples cooled slowly at ambient temperature; empty marks: samples cooled by quenching in ice-water mixture.
PE I (■, □); PE II (●, ○); PE III (▲, △); PE IV (▼, ▽).

After each experiment the "matched" liquid has been drained from the observation vessel and its density determined pycnometrically. Errors in the x_1 values are, of course, reflected in the densities of the third column, but as seen from the table, the later values are in good agreement with densities obtained pycnometrically. Fig. 2 illustrates how the density of polyethylene samples depend on γ-irradiation at low doses and on the mode of cooling after hot molding. The lower line refers to samples cooled quickly by quenching in an ice-water mixture, the upper line to samples cooled slowly at ambient temperature. After irradiating by appropriate doses, samples have been annealed. As expected, the densities of slowly cooled samples are appreciably higher, but the effect of irradiation up to 20 Mrads is negligible. All densities in Fig. 2 have been obtained routinely by the volumetric titration techniques, using again the binary liquid system n-propanol-water.

[1] ASTM D 1505

[2] R. H. Perry, C. H. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill Kogakusha, Ltd. 1973