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TEMPERATURE VARIATIONS WITH RESPECT TO THE SPECIFIC GRAVITY OF GLASS FRAGMENTS

Comments on Donald F. McCall's Paper*

Paul L. Kirk and A. Melville Dollar

Professor Paul L. Kirk, Department of Biochemistry, University of California Medical School, Berkeley, is recognized as an authority on the identification of glass fragments and their physical properties. Several of his studies on the subject have appeared in this Journal. The comments which he makes on Prof. McCall's paper are based not only on his extensive work in this field but also upon special research on questions raised by this recent paper. In accord with its policy of full discussion of police science questions the Journal considers it fortunate to be able to publish a further discussion of this important problem. A. Melville Dollar is a graduate student in Criminology at the University of Cali-

A. Melville Dollar is a graduate student in Criminology at the University of California who has carried out special research on the identification of glass fragments.— EDITOR.

In a recent number of this Journal (1) McCall has published a paper entitled "Temperature Variations with Respect to the Specific Gravity of Glass Fragments." Since this article is misleading and inaccurate, it seems worth while to comment on it and clarify some of the facts of the matter which may be misleading to the reader.

If there is a reason for studying the specific gravity of glass fragments, it lies in determining the degree to which variations in specific gravity are useful in determining identity or nonidentity of glass samples. The same may be said with respect to refractive index or any other physical property which is altered by changes in composition of the glass. If two samples of glass are identical chemically, it is a well recognized fact that all of the physical properties will be identical, regardless of temperature, provided both samples are measured under the same conditions and treated similarly (2). Since the coefficient of linear expansion of glass is such a factor, it might have been assumed that this was the property being studied by McCall. That such was not the case is indicated by the absence of any statement to this effect, or any comparison of the coefficients for different samples. Aside from this one logical purpose of the work, the present writers can think of no other reason for its preparation.

Apparently quoting Beeman (3) McCall states: "It has been noted that particle size may materially affect the specific gravity." It does not appear to have occurred to either author that this astounding statement is apparently a clear denial of the Archimedean principle, discovered about 300 B.C. and which remains unrefuted and unanimously accepted by all scientists

^{*} This paper appeared in the May-June (1948) issue of this Journal: 38 (1): 113.

today! By definition, the specific gravity of homogeneous material cannot vary with the size of particle. If it was implied that glass is not homogeneous to this extent. the burden of proof on the person making such a claim would be a serious one since it would require significant variations in composition over almost microscopic distances to affect the measurable specific gravity in small pieces. It is true that the data of Gamble, Burd, and Kirk (4) with 100 glass samples, apparently overlooked by Mc-Call, showed that out of twenty large glass objects, only one showed a slight but detectable difference in refractive index when the fragments were taken at opposite ends of the glass object. No differences in specific gravity could be found even in large objects (4) nor were they noted by Roche and Kirk (5) who studied the matter further on 50 similar bottle glasses. Certainly, no sharp variations would be expected in the composition of glass from point to point except in the case of an actual flaw.

If such rapid variations in composition of glass exist as implied by McCall, this would be the most significant point noted in his article. This possibility is supported by a statement of data from the work of Young et al. (6), that the differences in specific gravity in the same sample have varied as much as 0.065. Examination of the publication quoted (6) shows (a) that the largest difference listed by these investigators was 0.0069; (b) this difference was caused by different cooling procedures from the softening temperature (about 550° C.) and bore no relationship to variations from place to place in a given sample. Thus the author of the article in question has apparently both misinterpreted and misquoted the reference given. In fact Young et al. state "... the density of a specimen after treatment does not depend upon the size of the specimen, providing size, as such, is not a factor in determining the rate of cooling." Their study of cooling rate of molten glass has no possible relationship to a study of specific gravity measurements made at different tem--peratures.

In order to demonstrate once and for all that there are ordinarily no detectable variations in density of different pieces of glass from the same glass bottle, a study of 10 Coca Cola bottles, 1 "Dr. Pepper" bottle, 3 Pioneer Beverage bottles (1 Qt. size), 1 "Nehi" bottle (1 Qt. size) and 1 gal. cider container (same manufacturer as Pioneer Beverage bottles), was made. These were broken in such a way that a sample could be saved from the neck, from the base, and from three intermediate points so that five different large pieces of glass were available from each

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bottle, giving a distribution along the glass object. Five small chips were removed, one from each of the large pieces, for each bottle. They were dropped into a gradient tube which was made sensitive enough (0.00035g./ml./mm.) that it would distinguish density differences within less than the experimental error of the pycnometric flotation method (7) used by McCall. The five chips from each of the bottles tested fell at exactly the same level in the gradient. The results demonstrated quite definitely that there were no measurable specific gravity differences in the same bottle in any of the 16 samples tested.

The variation in the levels of different bottles is important, as it shows the general sensitivity of the gradient tube used. It was found rather surprisingly that Coca Cola bottles are much more uniform than is generally true of beverage bottles, both in comparison with the other bottles studied and with respect to 50 beer and other brown bottles (5) which have been studied previously in this laboratory. The total spread of fragments from Coco Cola bottles was only about 1 cm. and in that cm. there were distinguishable from ten bottles, only six distinct layers. This demonstrates that not all Coca Cola bottles could be distinguished from each other on the basis of specific gravity alone, which is in agreement with previous findings on beer bottles, though the proportion that is indistinguishable is considerably higher with the Coca Cola than with the beer bottles. The results with the other beverage bottles confirm previous findings, and in fact no two were found which were indistinguishable from each other. In view of this direct evidence that different beverage bottles do not show wide variations from point to point, or in fact any detectable variation, and the fact that many previous bottles and other glass specimens tested in this laboratory produced the same results, we feel that there is no doubt of the probable identity of different fragments of glass from the same glass object, such as a beverage bottle. Unless more definite evidence than that of McCall is produced to refute this result, we can assume that his values are without significance.

McCall further states "It is commonly understood that temperature changes materially affect the specific gravity of glasses." It would appear that the author may have confused the concepts of specific gravity and density by not realizing that specific gravity is actually the ratio of the density of the material to that of water at the same temperature, and that the effect of temperature change is almost exclusively on the density of the water. The coefficient of linear expansion of glass is given in handbooks as about (depending on the type of glass) $8 \ge 10^6$ expressed as the increase in unit length per degree C. A 10° change would then expand a unit length $8 \ge 10^{-5}$, which would correspond to a cubic volume increase of about $5 \ge 10^{-13}$. Since the analytical balance is reliable only to 10^{-4} g. it is clearly apparent that an increase in volume produced by a 10° change in temperature ($5 \ge 10^{-13}$) would change the glass density by an amount of only 0.000,000,005 part of the difference determinable on the analytical balance. On the other hand, the density of water changes quite significantly with every 10° change of temperature, and not linearly but at an accelerating rate as the temperature is raised, as shown in the table below.

| Temp. interval | Density of water | Change in density/10° |
|----------------|------------------|-----------------------|
| 4° | 1.00000 | |
| 14° | 0.99927 | 0.00073 |
| 24° | 0.99732 | 0.00195 |
| 34° | 0.99440 | 0.00292 |
| 44° | 0.99066 | 0.00374 |
| 54° | 0.98621 | 0.00445 |

The reported difference in specific gravity of glass with different temperatures is seen to be due *entirely* to the change in the density of water with temperature, though by inference attributed by the author to a change in the glass. Added to this is the complication of making the determination through the medium of organic suspension liquids which also have large density changes with temperature, but which are again different from that of water. It must be reluctantly concluded that not only has the author attributed to glass the properties of water, but possibly also those of the suspension liquid.

The above consideration is important also with respect to the statement, "It was noted that the specific gravity increased in all cases as the temperature increased." By definition, all substances with a positive coefficient of expansion will show a *lower density* as the temperature increases. Water shows a much greater lowering of density than does glass, therefore causing an increase in the density ratio, i. e. the specific gravity, due merely to a greater decrease in density of water than of glass. The further statement "There did not appear to be a ratio between the increase in temperature and the increase in specific gravity" presumably means that there was no direct proportionality since obviously there will always be a "ratio". Assuming this meaning, the statement can only be interpreted as an admission of uncontrolled factors in the determination, or as a demonstration that the density of water is not a linear function of the temperature, a fact that is implicit in every handbook table of water densities. This is also implicit in the further statement"... the increase in specific gravity from 20° (!. to 37.5° C. was small, and from 37.5° C. to 70° C. the increase was more rapid and approximated a straight line", since the change in density of water in the first range is much slower than in the second range mentioned as shown in the table above. The "straight line" is not followed however in any range and can only represent experimental inaccuracy.

Another interesting statement of McCall, "Since specific gravity changes due to composition of glass is seven times greater than corresponding refractivity changes" requires critical comment. The work on which this statement is based (8) was limited to soda-lime-silica glasses, and referred only to the *numerical differences* of the properties without respect to the sensitivity and reproducibility of measurements. The data of Gamble, Burd, and Kirk indicate a numerical factor of slightly over five for miscellaneous glass of all types which is not a serious discrepancy. However, due to the much greater sensitivity and reproducibility of the refractive index measurement as compared with the specific gravity determination, the former is actually more useful in separating similar glasses than the latter. This is well demonstrated by the investigation of Roche and Kirk in which specific gravity alone divided 50 similar glass samples into 40 distinct groups. Refractive index comparisons further subdivided the groups into 49, thus indicating again the better distinction that can be obtained by refractive index measurements.

One further statement requires comment, "If the criteria collected in these few samples may be used to base a conclusion. then it would appear that specific gravity comparisons would be of doubtful value unless some method is devised other than that which has been stated in the literature up to the present time." Certainly these writers would not care to base conclusions on the limited data reported here, nor do we feel that the fundamental principles of elementary physics were understood or properly interpreted. The very purpose of making measurements at varying temperatures appears pointless in that it contributes nothing to the determination of identity. It is unfortunate that the author has been misled about the existence of adequate methods for specific gravity comparisons which have been studied by several investigators mentioned above and by Morris (9) who studied 65 samples of glass. Much valuable information is also available in the extensive volume of Winchell

(10) and in publications by Sun, Safford, and Silverman (11), Wang and Turner (12), Donovan (13), and others.

It would be a serious misfortune if the article in question should be the cause of misunderstanding or error on the part of students, and particularly of witnesses, jurors, and court officials whose attitude would be at least partly conditioned by the appearance of the article in a reputable journal. It should be strongly emphasized that glass identities on the basis of physical properties have been demonstrated conclusively many times and that unequivocal testimony on this point has been offered and accepted by courts of law in numerous cases. To this end, it is here concluded that the article in question is irrelevant, inaccurate, and misleading and should be disregarded by students of glass identification by means of physical properties.

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