

REVIEW ARTICLE

GLASS FOR PHARMACEUTICAL PURPOSES

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INTRODUCTION

To most of us the term "glass" implies a brilliant, brittle, amorphous substance, usually transparent but sometimes translucent, and capable of production in many colours. Specimens have come down to us through centuries without being seriously impaired in appearance as may be seen in the windows of cathedrals and churches, or in museums. The widespread use of glass at the present day, as for instance in windows, building blocks, mirrors, cooking vessels, optical and artistic ware and containers, testifies to its possession of some great advantages as compared with other materials. The survival of window glass through the centuries at once indicates resistance to the chemical action of atmospheric agents as well as mechanical strength. Some of these old glasses have, however, become dimmed or covered by a thin, whitish or iridescent film, due to surface decomposition. In nature many rocks slowly disintegrate, as instanced by the slow decomposition of feldspars into clays of much lower alkali content, so it is perhaps not surprising that the "silicate" glasses suffer slow change when exposed to all weathers over a long period.

But to-day, glasses are called upon to give good service under a great variety of conditions, some of which may involve exposure to chemical reagents, or to water and steam at temperatures well above the normal boiling point of water, or to the action of solutions over long periods, often in tropical climates. Again, some glasses are required to exercise selective absorption of radiations as for protection against ultra-violet or infra-red rays, or in the production of definite colours.

Under all these many and varied conditions it is essential that glasses retain their characteristic brilliance, but the pharmaceutical chemist makes even greater demands. In addition, he requires glass containers to preserve, without contamination, preparations differing considerably in chemical composition. This involves careful cleaning and sterilisation of the containers before use, and glass is satisfactory in all these respects. But commercial glasses, like many other materials, differ in chemical composition and as a result they differ in their properties, including absorption of radiation and chemical behaviour, two properties of paramount importance to the pharmaceutical chemist. Other factors such as mechanical strength, resistance to thermal shock, ease of moulding into pleasing yet functional shapes capable of secure and ready closure, and steady supply at a reasonable price are also of importance but not peculiarly to the pharmaceutical trade. In this review, therefore, attention will primarily be paid to the consideration of chemical resistance

and absorption of radiation, but it may be well to note here that, broadly speaking, glasses which exhibit the greatest all-round chemical resistance also have great thermal resistance and mechanical strength. They are not, however, as easy to melt and mould, nor are they as cheap to produce, as glasses of higher alkali content but resultant lower chemical stability.

TYPICAL CHEMICAL COMPOSITIONS AND COEFFICIENTS OF LINEAR EXPANSION OF GLASSES

Although several substances, when fused, can form glasses, the glasses of commerce are produced by fusing at 1300° C, or above, silica in the form of sand, with two or more other materials such as, for instance, limestone and soda ash in the production of containers, and red lead with potash for high quality artistic "crystal" ware. Other constituents may be barium oxide, alumina, zinc oxide, magnesia, boric oxide, lithia, arsenic or antimony oxides, with oxides of copper, cobalt, iron, manganese, chromium, and nickel, as colouring agents. Selenium and cadmium, gold, or copper are used in making ruby glasses. Optical glasses and glasses used in the electrical industry differ widely in composition but need not receive further notice here.

A few typical percentage compositions with some coefficients of linear expansion of glasses are given in Tables I and II, from which it will be seen that container glasses are generally of the simple soda-lime-magnesia-alumina-silica type, with relatively high expansion coefficients, whilst "neutral" tubing for ampoules may contain considerably more alumina, with boric oxide, and lower alkali content and somewhat lower expansion. "Lead crystal" is of an entirely different composition, whilst chemical or cooking ware generally contain several per cent. of boric oxide with low alkali but high silica content and much lower expansion coefficient. The resistant glass "Vycor" approaches the composition of fused silica, and the special conditions necessary to the production of these two glasses render them too expensive for general use as containers. Moreover, fused silica cannot be "worked" or moulded as easily as the more usual glasses. Of all the glasses which are commercially available it has the lowest coefficient of expansion and is famed for its thermal shock resistance.

THE CHEMICAL BEHAVIOUR OF GLASS

(1) *Historical Note.*

During the last 50 years much research work has been directed towards an understanding of the chemical behaviour of glass, in fact the literature of this subject is now vast. The superiority of glass over competing materials as containers for foods and pharmaceutical preparations, enabling the purchaser to see what he buys, and at the same time preserving the contents uncontaminated, testifies to the resistance offered by glass surfaces to decomposition when in contact with atmospheric agents (mainly moisture), as well as with solids and liquids differing widely in chemical composition, some solutions being neutral, others alkaline, or acidic. But, as has already been stated, some old glasses show a marked

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TABLE I
PERCENTAGE COMPOSITIONS OF TYPICAL CONTAINER GLASSES, TUBINGS FOR VARIOUS PURPOSES, AND SOME SPECIAL PURPOSE GLASSES

Constituent oxides	Colourless containers†		Soft soda tubings* and electric bulbs	Thermometer stem‡ tubing	Colourless "neutral" ampoules*	"Neutral" amber tubing*	Electric lamp tubing† and bulbs	High pressure mercury vapour lamp* (alkali-free)
	British	U.S.A.						
SiO ₂	73.4	73.3	70-12	55.7	67.0	64.1	56.6	54.25
B ₂ O ₃	—	—	0.78	—	7.5	7.1	0.2	7.5
TiO ₂	0.04	0.48	2.58	0.03	n.s.	n.s. } 7.1 }	0.8	22.0
Al ₂ O ₃	0.75			0.22	8.5		0.05	n.s.
Fe ₂ O ₃	0.045	—	—	0.016	n.s.	4.1	—	n.s.
MnO	—	—	—	—	n.s.	1.4	—	—
CaO	8.9	5.3	5.4	0.15	4.0	6.8	—	13.25
MgO	0.1	3.9	3.6	—	0.3	0.1	—	—
BaO	—	—	—	—	—	—	—	3.0
PbO	—	—	—	31.4	—	—	30.2	—
Na ₂ O	15.9	16.31	16.82	0.1	8.7	6.3	5.1	nil
K ₂ O	0.4		0.35	12.04	—	4.0	3.0	7.2
As ₂ O ₃	0.01	—	—	—	—	—	n.s.	—
SO ₂	n.d.	n.d.	0.20	—	n.s.	—	n.s.	—
Coefficient of linear expansion × 10 ⁶ ...	—	—	9.6	—	7.3	7.5	—	—

* "Glass, Ostram, G.E.C. Glass Works Products brochure, July 1950.
 † Turner, *Outline of the Properties of Glass*, 1942. Glass Manufacturers' Federation.
 ‡ This glass (or slight modifications of it) is the "English lead crystal" glass.
 n.s. = not stated. n.d. = not determined.

TABLE II
PERCENTAGE COMPOSITIONS OF SOME CHEMICAL AND HEAT RESISTANT GLASSES AND SOME COLOURED GLASSES

Constituent oxides	Fused silica	"Vycor" (U.S.A.)*	"Pyrex"†	"Flamorex"‡	Kimble Laboratory No. N51a†	Dark green (British)*	Amber		Cobalt blue*
							Fe-Mn*	C-S*	
SiO ₂	100	96.3	80.7	57.52	74.7	67.22	67.78	70.48	71.82
B ₂ O ₃	—	2.9	12.0-12.6	5.74	9.6	—	—	—	—
TiO ₂	—	—	0.05	—	—	0.09	0.1	—	0.03
Al ₂ O ₃	—	0.4	2.2-3.0	19.42	5.6	1.81	1.06	2.08	1.08
Fe ₂ O ₃	—	—	0.08	0.10	—	2.38	2.31	—	0.13
MnO	—	—	—	—	—	2.47	3.80	n.d.	0.03
CoO	—	—	—	0.01	—	—	—	—	0.29
CaO	—	—	0.20	6.53	0.9	8.14	8.58	8.85	12.54
MgO	—	—	—	9.20	—	1.47	1.32	1.38	1.13
BaO	—	—	—	—	2.2	—	—	—	—
ZnO	—	—	—	—	0.1	—	—	—	—
Na ₂ O	—	0.02	3.9-4.1	1.10	6.4	14.81	13.85	15.98	11.80
K ₂ O	—	<0.02	—	—	0.5	0.96	0.41	0.56	0.31
As ₂ O ₃	—	0.005	<0.01	—	0.03	—	—	n.d.	—
SO ₃	—	—	—	—	Sb ₂ O ₃ 0.009	0.37	0.42	0.25	0.43
Coefficient of linear expansion × 10 ⁶	0.5	0.8	3.3†	—	4	—	—	—	—

* Turner, *Outline of the Properties of Glass*, 1942.
 † Wichers, Finn and Clabaugh, *J. Res. Nat. Bur. Standards*, 1941, 26, 537.
 ‡ Typical results.

dimming or iridescence on the surface, and as far back as 1770, Lavoisier¹ reported that some material was extracted from glass vessels in which water was boiled for long periods. Sir Humphry Davy found that alkaline matter was extracted from glass by water, whilst later, the contamination of precipitates by matter derived from glass vessels was noted by Dumas and Berzelius. Towards the end of the nineteenth century several empirical formulæ were proposed for controlling the composition of glasses to achieve resistance to the action of aqueous solutions but now, thanks to recent researches, the atomic structure of alkali-silica glasses has been revealed and it is possible to assess, at least approximately, the nature and strength of the chemical bonds existing between the various constituents, and hence to choose that composition most likely to yield any result desired in the properties of a glass. It was not until the closing years of the last century that the boron-containing glasses were developed commercially, particularly at Jena, whilst Pyrex glass was produced at Corning, U.S.A. in 1915. A number of other new types of laboratory apparatus glass, including some of the alumina-zinc oxide-borosilicate type, appeared in Europe and in America at this period and considerable activity centred around investigations into the respective merits of these glasses and into the whole subject of the chemical properties of glasses in general.

The replacement during the last 50 years of the centuries-old "hand" methods of common glass container fashioning by automatic mechanical methods has meant modification of chemical compositions and stringent control, not only of chemical homogeneity but also of viscosity. Thus, careful technical supervision of raw materials and of every operation of manufacture is essential to satisfactory production, and not least among such controls is that of chemical properties.

(2) *Factors Influencing the Chemical Properties of Glass.*

The resistance which a glass offers to the action of any attacking agent in contact with it is generally termed the chemical durability of the glass, or precisely, its durability towards the particular agent. Methods of measuring this property will be dealt with later (page 981). Several factors influence this chemical resistance and these may be listed as:—

- (A) Chemical composition.
- (B) Temperature of attacking agent.
- (C) Length of period of contact.
- (D) Previous history of the glass, e.g., mode of production, annealing, special treatments and storage.

(A) *The Influence of Chemical Composition.*

(i) *Theoretical Considerations.* The most important factor controlling the chemical durability of glass towards any agent is its chemical composition, and in order to obtain some idea of the influence of the various constituents it is useful to consider briefly the atomic structure of glasses. Starting with the simple vitreous silica, this is now regarded as being a

random, three dimensional network, in which each small silicon cation is bonded tetrahedrally to 4 larger oxygen ions, each oxygen being linked to two silicon ions. Such a bonding is predominantly covalent and is strong. If, now, a flux such as sodium oxide be introduced, some of the oxygen-silicon links are broken, resulting in a weaker bonding, the alkali-oxygen bond being much more electrovalent or ionic. It is to be expected, therefore, that the greater the proportion of alkali in such a glass the less will be its resistance to chemical attack. Further, if some of the alkali be replaced by another oxide, for example, BaO, CaO, MgO, PbO, Al₂O₃, ZnO, TiO₂, the bond strengths will be altered, and, from known data which cannot be given here, in every case, the replacement of the monovalent alkali by a divalent, trivalent, or quadrivalent element results in a stronger bonding with resultant increase in chemical resistance. The acidic oxides SiO₂, P₂O₅ and B₂O₃ are network-formers, whilst the amphoteric oxides such as Al₂O₃ contain cations which can either enter the silica network or modify it. The alkali cations, and those of the basic oxides do not generally enter the network, and are termed "modifiers." From theoretical considerations it is expected, therefore, that fused silica will resist the attack of water and acids, except hydrofluoric acid, and that, of all the other constituents of silicate glasses the alkalis will be most potent in reducing chemical durability, whilst alumina, titania, zirconia and zinc oxide should be less potent in this respect than the alkaline earths, provided that comparison be made on a molecular basis. Boric oxide presents an anomaly, for if it be present beyond some 12 to 14 per cent. it reduces the chemical resistance of glasses so far studied. The reason for this is still not fully agreed. Alkalis disrupt the silica network, forming alkali silicates so all silica-containing glasses, including fused silica itself, are attacked by alkaline solutions. For a full consideration of the atomic structure of glasses and assessment of "chemical stability" reference may be made to the works of Zachariasen², Warren³, Warren *et al.*^{4,5}, Fajans⁶, Barber and Fajans⁷, Weyl⁸, Cole⁹, Stanworth¹⁰ and Stevels¹¹.

(ii) *The Action of Water, Acids and Alkalis (Including "Weathering")*. The ease with which the alkali ions can be extracted from a glass can result in chemical decomposition of the surface at relatively low temperatures, in fact, free alkali can be detected on the surface of some freshly-made glasses immediately on exposure to atmospheric moisture. When glasses are stored, especially if in damp atmosphere with alternate rise and fall in temperature, as in the tropics, the wetting of the surface by condensed moisture results in extraction of alkali and when the surface dries again, a whitish deposit can be seen. On subsequent condensation an alkaline solution is at once formed which then dissolves out some of the surface silica. This decomposition may seriously impair the brilliance of the surface and water, or even acid, washing will not restore the original appearance, but acid washing of the soluble products of decomposition can expose a whitish film of silica.

This slow surface decomposition of a glass exposed to the action of atmospheric agents only, is known as "weathering" and is manifest in the

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early stages by the appearance on the glass surface of fine crystals, mainly of sodium carbonate (carbonation due to carbon dioxide from the air) which can at this stage be removed by water or acid washing. The removal of this alkali leaves the glass surface poorer in alkali and the decomposition process will, in commercial glasses, be slowed up. In some cases, due to prolonged, undisturbed storage in damp atmosphere, crystals of calcium carbonate have been detected along with the sodium carbonate on the surface of soda-lime-silica glass. Sulphates may be produced if sulphur-containing gases be present in the atmosphere. "Weathering" proceeds most rapidly, of course, with glasses of high alkali content. No "weathering" occurs in an atmosphere free from moisture, as demonstrated by Dimpleby and Turner¹².

When water is in contact with a glass the alkali in the surface reacts, but to preserve the electrical balance something must enter the glass in return. Thus, hydrogen ions replace the alkali, some water accompanying the hydrogen. If the glass has an appreciable alkali content its surface will swell and may become cracked and broken on subsequent drying due to expulsion of this water. This exchange of H^+ for Na^+ occurs in the preparation of glass electrodes.

The action of water, of acids and of aqueous solutions upon glass is primarily a preferential extraction of alkali and to a much less extent, of the other most basic constituents and if by this action the reagent becomes alkaline then the silica "framework" of the glass is decomposed thus exposing fresh glass to attack and decomposition will proceed. If, however, the reagent be continuously removed and replenished, or if it remain acidic, the attack will slow down due to the formation of a surface film, richer in silica than the original surface, and this film may be indicated by faint iridescence.

The rate of decomposition of glasses by alkaline solutions is much greater than by water or acids, and the glass may, in prolonged contact with hot caustic alkali solutions, appear to be unaffected but may be dissolving as a whole. The alkali silicates formed by the reaction of the glass silica and alkali of the reagent are soluble in water and diffuse away, thus in no way producing a protective coating. But, if the solution becomes loaded with salts extracted, or if certain salts be added the reaction can be slowed down, as found by Geffkin and Berger¹³. Silicates, aluminates and salts of zinc exert this influence and are used to decrease the attack of alkaline cleaning solutions upon glass as in the patent of Cooper¹⁴. On the other hand, phosphates were reported by Brown and Watts¹⁵ to be corrosive towards glass.

(iii) *Experimental Data (a) Behaviour of Fused Silica, Simple Soda Silica Glasses, and Three Component Glasses based on a Parent $6 SiO_2$, $2 Na_2O$* . Fused silica is practically unattacked by water or by acids except hydrofluoric, but is attacked by alkalis, by caustic solutions more than by the carbonates, as proved by Mylius and Mäusser¹⁶. Dimpleby and Turner¹⁷ prepared series of glasses to include molecular compositions ranging from $2 SiO_2$, Na_2O to $4 SiO_2$, Na_2O , and 3-component series based on $6 SiO_2$, $2 Na_2O$ in which Na_2O was systematically replaced in

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steps of 0.1 molecule by the other oxides BaO, CaO, MgO, PbO, ZnO, Al₂O₃ or Fe₂O₃, TiO₂ or ZrO₂.

In the soda-silica series a decrease in the soda content resulted in increased resistance to the action of boiling water, hydrochloric acid (constant boiling strength) and sodium carbonate (2N) as measured by percentage losses in the weight of the glasses. The results for the 3-component glasses showed that replacement of Na₂O by any of the other oxides, even in very small proportions, resulted in great improvement in resistance towards boiling water, hydrochloric acid and sodium carbonate (2N). With greater substitutions the improvement continued but the rate fell off until, in many cases an almost constant value was reached at compositions approximately 6 SiO₂, (R₂O₃) (RO) (RO₂), Na₂O where (R₂O₃) (RO) (RO₂) represents the substituted oxide. Figures 1 and 2 show the results of the water tests, and Figure 3 shows those of the sodium carbonate tests. The zirconia glasses exhibited marked resistance to all the reagents and to caustic soda.

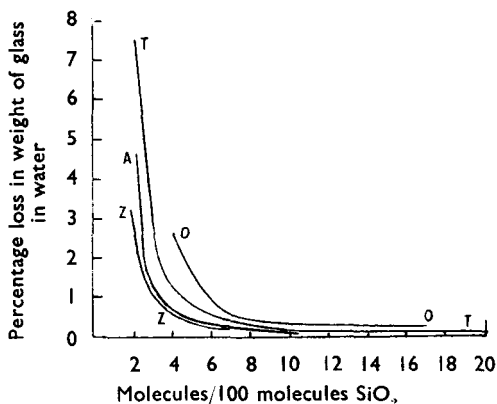


FIG. 1. Glass series based on 6SiO₂2Na₂O. Other oxides substituted for Na₂O in 0.1 mol. steps.

O.	Substituting CaO
A.	.. Al ₂ O ₃
T.	.. TiO ₂
Z.	.. ZrO ₂

(Dimbleby and Turner.)

and alkaline solutions. A faint maximum durability was indicated at about 9 to 11 per cent. of B₂O₃ in the 20 Na₂O series and Enss¹⁸ obtained a maximum towards water at about 7 per cent. of B₂O₃ in a similar series. Winks and Turner¹⁹ reported no maximum when they systematically substituted B₂O₃ for SiO₂ in a mixed alkali-lime-silica glass (the old Kavalier resistance glass) but they reported a fall in durability when B₂O₃ exceeded some 11 to 12 per cent. In these glasses, as in those of Dimbleby and Turner containing more than about 15 per cent. of B₂O₃, digestion with hydrochloric acid extracted all constituents but SiO₂. This fact is utilised in the production of "Vycor" glass. (See Table II).

Towards acid and water the order of decreasing effectiveness of oxides, was Fe₂O₃, ZrO₂; Al₂O₃, TiO₂; ZnO; MgO, PbO, CaO, and BaO thus agreeing with theoretical expectations as described above.

(b) *Boric Oxide-containing Glasses.* In 2 series of glasses developed by substituting B₂O₃ for SiO₂ on a percentage basis in parent glasses of respective percentage compositions 80 SiO₂, 20 Na₂O and 90 SiO₂, 10 Na₂O, Dimbleby and Turner found that when the B₂O₃ exceeded some 14 per cent. the glasses were seriously attacked by water, hydrochloric acid

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From Table III in which are quoted some results of Dimpleby and Turner using a "grain" method, and from Table IV, giving some results of Wichers, Finn and Clabaugh²⁰, the comparative actions of water, acids and alkaline solutions are evident. Hydrochloric acid has proved to be the most corrosive of the common acids excluding hydrofluoric, concentrated sulphuric and nitric acids having little action on most glasses. Nitric acid readily decomposes some special high lead or phosphate glasses.

TABLE III

VARIOUS GLASSES TESTED IN GRAIN FORM (LIMITS 25 TO 26 B.S.I. SIEVES). BOILED 1 HOUR IN WATER, OR IN THE REAGENT STATED
(Dimpleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, T. 304)

Glass type	Na ₂ O extracted by water per cent.	Percentage loss in weight in			
		Water	20 to 24 per cent. hydro- chloric acid	2N sodium carbonate	2N sodium hydroxide
Bottle	0.04	0.09	0.08	0.53	1.42
Machine drawn sheet	0.008	0.01	—	—	—
Resistant boiler gauge	0.014	0.019	—	—	—
Chemical Resistant No. 1	0.002	5 hours* boiling 0.01	—	—	—
No. 2	0.001	0.009	—	—	—

TABLE IV

CHEMICAL GLASSWARE (AMERICAN) IN FORM OF 250-ML. FLASKS TREATED WITH 200 ML. OF GENTLY BOILING REAGENTS FOR 6 HOURS
(Wichers, Finn and Clabaugh²⁰)

Reagent	Losses in weight. Average of 3 successive treatments			
	Pyrex mg.	Vycor mg.	Kimble mg.	Glasbake mg.
Water	0.2	0.1	0.1	0.3
N sulphuric acid	0.4	0.1	0.5	0.8
N phosphoric acid	0.5	—	0.5	0.7
Hydrochloric acid, 20.24 per cent.	2.2	0.4	2.6	4.6
Sulphuric acid 95 per cent.	1.6	1.3	1.5	2.1
Perchloric acid	0.1	0.02	—	0.3
Sodium chloride, 5 per cent. unbuffered	2.2	0.5	0.7	12.8
Sodium chloride, 5 per cent. in 0.001N HCl	0.1	—	0.03	0.4
Sodium chloride, 5 per cent. buffered at pH 6.2	4.0	—	1.9	6.3
" " " 8.4	10.2	7.4	4.7	22.1
Buffer solution at pH 6.8, 10.85 g. Na ₂ HPO ₄ ·12H ₂ O + 4.55 g. KH ₂ PO ₄ per l.	2.6	—	0.8	4.9
0.05N sodium hydroxide	90.9	43.3	55.3	94.1
0.5N "	287	—	173	251
0.5N potassium hydroxide	166	—	93.6	156
0.5N sodium hydroxide	84.1	—	53.2	94.2

(B) *The Influence of Temperature of Reagent.*

As might be expected, the temperature at which glass is exposed to any reagent has a great influence upon the extent of attack especially above some 60° C. for all types of reagent. This was investigated (20° to 100°C.) for caustic soda (2N) by Cauwood, Way and Turner²¹; for water (80° to 102° C.) by Rexer²², and for water (25° and 90° C.) sulphuric acid (0.02N) and caustic soda (0.02N) by Taylor²³. This effect is more pronounced

above 100° C. and whenever such treatments must be given to glass, as in sterilisation in an autoclave, precise control should be maintained upon temperature and time.

(C) *The Influence of Period of Contact.*

Generally speaking, in service, glass is very slowly decomposed on the surface in contact with any reagent, the extraction being preferential and at first involves only the alkali ions. Later, the decomposition will

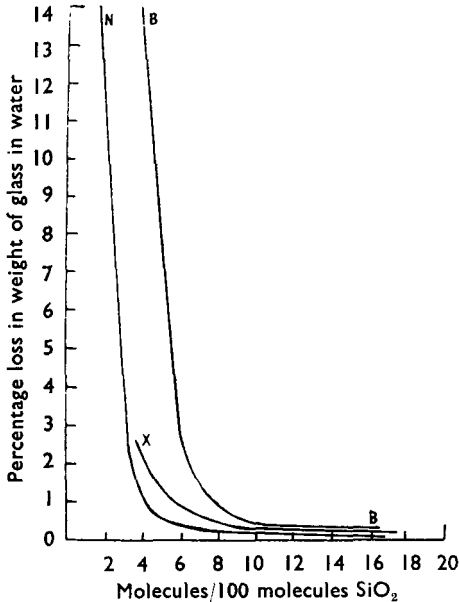


FIG. 2. Glass series based on $6\text{SiO}_2\cdot 2\text{Na}_2\text{O}$. Other oxides substituted for Na_2O in 0.1 mol. steps.

B. Substituting BaO
N. ,, ZnO
X. ,, MgO

(Dimbleby and Turner.)

depend upon whether the reagent is replenished, and whether the new compounds formed by the decomposition can readily diffuse away from the surface. The reactions may in some cases become complex, but, Turner *et al.*²⁴, Rexer²², and Douglas and Isard²⁵ have shown that, for good, commercial, soda-lime- (or lime-magnesia)-silica glasses, the relationship between extent of attack by water, and time, was parabolic, resembling that for the passage of an electrolyte through a gel. At first the extraction proceeds most rapidly, the rate falling off gradually, until after some 10 to 30 hours a constant and much lower rate is attained. Rexer found that at 80° C. the extraction in 3½ hours was equal to 80 per cent. of a 7 hour extraction. For a

less durable glass the decrease in rate may not be so great.

In this connection it is interesting to note the work of Hinson, Smith and Greene²⁶ who investigated the storage of distilled water in 5 types of glass ampoules autoclaved and un-autoclaved before storage which extended to 24 months. They found (1) differences in total extracted matter and in pH of the water in the different glasses, (2) that pH values were unreliable for following the course of the attack during storage after autoclaving, due to the buffering effect of dissolved matter, (3) that, except in one case, the total matter extracted into the water after 24 months was the same whether samples were autoclaved at 121° C. for half an hour or not before storage, (4) that the storage times at room temperature at which the pH increase and total dissolved matter were the same as after autoclaving differed for the different glasses and there was

no general rule for predicting storage results from those of autoclaving.

Turner *et al.*²⁴ and Rexer²² have also shown that water in contact with bottle glass changes in composition as time progresses, At first the solution contains alkali only but later calcium and even silica appear; the total extracted matter differs considerably in percentage composition from the glass itself, usually being much richer in alkali and much poorer in silica and lime.

(D) *The Influence of the Previous History of the Glass.*

Any treatment which can alter the condition of a glass surface will affect its surface reactions, and it is known that furnace atmosphere, fire-finishing, mechanical or acid-polishing, acid or water-washing, atmosphere during annealing, conditions and length of storage, as well as special surface treatments such as coating with water-repellent substances or "sulphuring" can all affect the chemical activity of a finished glass surface. Unannealed glasses have been found to be more "reactive" than well annealed, but it is difficult to eliminate other influences in such investigations. Gehlhoff and Schmidt²⁷ found that well annealed bulbs resisted weathering two or three times as well as unannealed samples.

The effects of damp storage conditions upon glass and general "weathering" have already been considered (page 973). Dimbleby and Turner¹² have shown that moisture is the cause of this slow decomposition and, further, that bottle glasses which have been stored and then washed so as to remove the alkaline debris, yielded

less alkali to boiling water than the glasses when new, but in one case after 9 months' storage the glass tended to produce insoluble flakes more readily. Water or acid-washing of glasses followed by drying, renders the glass more resistant to weathering and is sometimes used when glasses must be packed and stored for long periods. Gehlhoff and

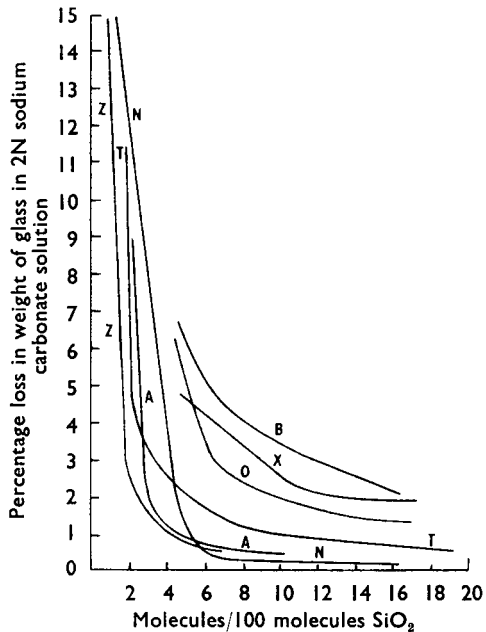


FIG. 3. Glass series based on $6\text{SiO}_2 \cdot 2\text{Na}_2\text{O}$ as in Figures 1 and 2.

B.	Substituting BaO
X.	„ MgO
O.	„ CaO
A.	„ Al_2O_3
T.	„ TiO_2
N.	„ ZnO
Z.	„ ZrO_2

(Dimbleby and Turner.)

Schmidt recommend open, dry storing, with good ventilation rather than wrapping in any paper.

The fire-polished "skin" of a glass is more resistant, generally, than the inner layers of a glass, hence mechanical abrasion or chipping of bottle surfaces should be avoided, particularly when the bottles must be sterilised.

The Effect of Sulphuring. It is now well established that exposure of a glass to an atmosphere containing water vapour and acidic gases, particularly sulphur dioxide as in the old type of direct-fired lehr, or in "sulphuring," results in reaction between the gases and some of the surface alkali and, therefore, the surface becomes more resistant for a period, to attack by water. The following values for 5-hour extractions by boiling water from washed wide-mouth jars quite alike except for annealing atmosphere, show this.

	Extraction as mg. Na ₂ O
Annealed in absence of SO ₂ = ..	2.9
Annealed in presence of SO ₂ = ..	0.9

Unless the ware be wide-mouthed so that the gases can readily penetrate, steps must be taken to ensure entry of the SO₂, to produce this effect, as found by Cousen²⁸. Douglas and Isard proved that this "sulphuring" treatment in gas saturated with water vapour at 20° to 100° C. produced a white deposit of sodium sulphate on a soda-lime glass, the amount of sodium removed from the glass varying as the square root of time as for a water-leaching (page 978), the two processes as also the electrical conductivity depending upon the diffusion of sodium ions in the glass. They suggested that the production of a layer of "H⁺ glass" as in this action of sulphur dioxide in presence of water vapour, resulted in the formation of a "compacted" layer on drying and expulsion of the water. The diffusion of sodium through this layer was greatly retarded, hence extraction by water would be considerably reduced. Heating at temperatures above 500° C. could aid diffusion and restore the rate of extraction. It must be remembered that this reaction generally proceeds to but a slight depth in the glass surface, and that, in long term usage the resulting silica-rich layer may be penetrated or removed. (See also effect of cream of magnesia, page 983.)

Holland, some years ago in the Department of Glass Technology at Sheffield, found that long term heating of flat glasses at 500° to 550° C. caused sodium to diffuse to the surface whence it could be removed by washing, leaving a more water-resistant layer. The present writer has observed that the surfaces of bottles annealed in an atmosphere of sulphur dioxide were difficult to scratch with a diamond and had a different texture from that of untreated bottles, whilst Boow and Turner²⁹ reported that sulphur dioxide treatment above 500° C. increased the mechanical strength of soda-lime-silica glass surfaces.

The Effect of Water-Repellent Coatings.

The coating of a glass surface with a water-repellent substance such as a silicone appears attractive on first thoughts but the writer does not feel

competent to reach definite conclusions without further experience. She has seen some coatings which were streaky and patchy, certainly not enhancing the beauty of the glass, and likely to arouse suspicion. Questions that immediately arise concern the preparation of the glass, the uniformity of the coating, its freedom from pin-holes; its behaviour towards alkaline solutions, to cleaning agents (acid and alkaline), and towards dry sterilisation; its impermeability, and its resistance to aqueous solutions in presence of any type of closure at temperatures above 100° C. If under any service conditions the coating be liable to peel off then its remnants may appear as "flakes" which may be more harmful than alkali extracted from the glass and the glass will become exposed. It is to be hoped that all these points will be investigated before putting such treated glasses into use.

An interesting paper upon silicones was published in 1950 by Tod³⁰, who dealt with their early application to glass for electrical purposes.

(3) *Methods Used for Measuring the Chemical "Durability" of Glass.*

From what has already been written it will be obvious that there is no actual value of the "durability" of any glass as there is for some of its properties, for at temperatures ordinarily employed glasses have no true solubility but are very slowly decomposing on the surface. The rate of this decomposition is influenced by all conditions, in fact, an increase of temperature alone, can alter the order of merit of glasses under test. The best way to test a glass is, of course, to subject it to the conditions it will meet in service but this often involves too long a time and is impracticable. Recourse must be had, therefore, to accelerated methods. These should as nearly as possible simulate service conditions but give a reasonable "safety margin."

Acceleration can be achieved by increasing temperature, or by increasing the surface area of contact of reagent and glass by using small cubes or plates or even grains of definitely controlled size rather than a glass vessel. But such increase in area involves the use of a different type of surface and one which does not represent truly the ware as it would be used. Further, if the glass be strained it fractures irregularly, giving grains of rougher surface than an annealed glass thereby enhancing attack. So, if the behaviour of finished ware is in question the test pieces should preferably be that ware, not grains, but if, for research purposes, glass is being studied as a substance only, then the grain test is most useful as the effects of surface peculiarities are eliminated.

Test methods are exceedingly numerous and standardisation has not progressed far in any one country, and far less internationally, though there are moves in this direction now. Generally, the attacking media are water or water and steam at temperatures above 100° C., or acid or alkaline solutions of definite strength at various specified temperatures. In all tests all conditions, including temperature, time, and ratio of volume of attacking medium to surface area exposed, should be precisely specified and maintained.

Measurement of the extent of attack demands sensitive methods and is made in various ways such, for example, by:—

- (i) Change in appearance of the glass coupled with production of flakes. This is not reliable as the only measurement.
- (ii) Change in pH or electrical conductivity of water. pH determinations may be affected by a “buffering” effect as found by Hinson *et al.*²⁶.
- (iii) Rate of formation of a precipitate in an alkaloid solution, as in the narcotine hydrochloride test used in Germany but not to any extent elsewhere. (See Kroeber³¹, and Blackmore, Dimbleby, and Turner³².)
- (iv) The determination of the total alkalinity of water by titration. Bases may be mixed alkalis, lime, magnesia, but are generally reported as mg. of Na₂O, as in the Standard 5-hour boiling test for medicine bottles, adopted by the Society of Glass Technology³³ and in the Tentative Standards of the American Society for Testing Materials³⁴. Limits were proposed in these Standards.
- (v) The determination of total solids extracted. Usually the solution is made acid with sulphuric acid then evaporated in platinum, the residue finally ignited at 500° C. or so. This is similar to the British Pharmacopœia test upon water for injection.
- (vi) The loss in weight of the glass, but high-alkali-containing glasses can gain in weight due to absorption of water.
- (vii) Combination of (i) with (iv)–(vi) but this is not often practicable.
- (viii) Rate of neutralisation of an acid solution, as in the B.P. ampoule test, or in the Tentative Standards of the American Society for Testing Materials³⁴.

It is beyond the scope of this paper to discuss in detail the methods of test which have been adopted as standards in the various countries but emphasis should be given to the following points:—

- (a) The rates of reaction of glass are highly susceptible to slight differences in experimental conditions.
- (b) No one test can safely be chosen for application to all types of glass.
- (c) The choice of test should be governed by service requirements, and before its adoption comprehensive experimental work should be carried out to establish that the method does distinguish between glasses which are known to be satisfactory, and those which are unsatisfactory in service.
- (d) Test procedures should be as simple as possible to facilitate wide application and they should be specified precisely to ensure faithful reproduction.* Any procedure should include the careful preparation of the glass for test. Since glass can become weathered on storage the surface should be cleansed of all alkaline weathering

* In the British Pharmacopœia whole ampoule test no instructions are given as to the orientation of the ampoules in the autoclave yet, if the acid test solution gets into the necks it can become yellow, whereas it remains pink if the samples be kept upright.

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debris before test, and before use—a fact rarely recognised, yet of great importance as in the storage of distilled water for injection.

THE EXTRACTION OF ARSENIC AND LEAD FROM CONTAINER GLASS

Some years ago there was considerable concern lest arsenic, which was introduced into glass as a decolourising aid, or lead, was extracted in such quantity as to render medicinal preparations poisonous. The bonding of arsenic and of lead in commercial glasses would not be expected to be weak like that of the alkalis, but if the silica framework were attacked as by an alkaline reagent then all constituents would be involved. Very little work on this matter has been published but at one glass-making firm at least, the question of arsenic was investigated and I am indebted to Mr. Hodkin of Messrs. Bagley and Co. Limited for permission to quote the results of this work which included the use of bottles "sulphured" and "unsulphured," some containing arsenic, others not. The results are summarised briefly in Table V. It is obvious that cream

TABLE V
EXTRACTION OF ARSENIC FROM GLASS

(From a note read by S. Chaplin, B.Sc., A.R.I.C., at a meeting of the Yorkshire Section of the Society of Glass Technology, on November 4th, 1944.)

Bottle No.	Contents	As ₂ O ₃ extracted p.p.m. as by B.P. method
<i>Test No. 1, 4 oz. medicine bottles kept at 60 to 70° C. for 8 hours daily for over 2 months</i>		
1	Cream of magnesia (1) As ₂ O ₃ 0.1 p.p.m.	1.0
2	do.	0.9
3	Cream of magnesia (2)	0.4
4	Cream of magnesia (1) + 0.1 per cent. of sodium hydroxide	2.0
5	Cream of magnesia (1) + 1.0 per cent. of sodium hydroxide	2.0
6	Cream of magnesia (1) + 2.0 per cent. of sodium hydroxide	2.0
7	Sodium hydroxide solution (0.1 per cent.)	0.1
8	Sodium hydroxide solution (1.0 per cent.)	0.1
9	Sodium hydroxide solution (2.0 per cent.)	0.1
<i>Test No. 2, 4 oz. medicine bottles sulphured (S) and unsulphured* (U) kept at 85 to 90° C. daily for about 2 months.</i>		
1 (U)	Cream of magnesia (1)	3.0
2 (U)	" " "	3.5
3 (U)	" " "	3.0
4 (S)	" " "	3.5
5 (S)	" " "	3.0
6 (S)	" " "	3.0
<i>Test No. 3. Using blue and white bottles of two different makes (B or C) and some arsenic-free "medicals" stored for 7½ months, with some heating, probably 35 to 40° C. for a quarter of the time.</i>		
1, 2, 3 (4 oz. B. white)	Cream of magnesia (1)	0.3, 0.4, 0.5 (glass inner surfaces iridescent).
4, 5, 6 (B. pale blue)	" " "	1.1, 0.5, 0.5 (surfaces iridescent)
7, 8, 9 (4 oz. Win. dark blue less resistant)	" " "	2.5, 2.0/2.5; 2.0/2.5
10, 11, 12 (4 oz. As-free)	" " "	0.1, 0.1, 0.1 (surfaces iridescent)
13, 14, 15 (4 oz. C. As-free)	" " "	0.1, 0.2, 0.1 (surfaces iridescent)

* Sulphured and unsulphured bottles, subjected to the Standard 5-hour boiling water test of the Society of Glass Technology, yielded average values for Na₂O extracted, U = 2.45 mg. S = 0.74 mg. Limit = 5.0 mg.

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of magnesia did attack the glasses tested during long storage periods or if heated to 85° to 90° C. for about 400 hours, with 900 hours at room temperature, and if the glass contained arsenic this could be removed in appreciable quantity. Sulphuring the inner surfaces of the bottles does not prevent this extraction. Under normal storage during 7½ months it is unlikely that many glasses would yield arsenic in excess of the British Pharmacopœia limit (1 p.p.m. of As_2O_3), but the use of arsenic-free glass is advisable for storing all alkaline reagents. The extraction of arsenic by the caustic soda solutions used was not as great as that of the cream of magnesia, which fact raises an interesting query.

Most colourless container glasses on the British market to-day contain very low proportions of arsenic if any, and extraction by neutral or acidic contents would be considerably less than by alkaline solutions or hygroscopic, alkaline solids. Dry solids generally do not attack glass, although some vapours, e.g., iodine can be absorbed into a glass surface, particularly into a ground one.

With regard to the extraction of lead, this is not likely to occur now that container glasses in this country, rarely, if ever, contain lead except as a trace impurity.

THE PRODUCTION OF INSOLUBLE MATTER (FLAKES) IN SOLUTIONS STORED IN GLASS

Insoluble flakes sometimes "appear" when solutions are stored in glass and these may arise from several causes such as (i) decomposition of the contents due to oxidation or under the influence of radiation; (ii) the formation of a precipitate due to reaction between the contents and closure, or between contents and glass; (iii) the presence of minute glass splinters which were not noticed in the contents when filled into the glass, or which were produced in handling or closing.

Particles due to cause (iii) are proof of careless or wrong operations in filling and should never get beyond inspection in the filling department, whilst those due to (i) could be avoided by study of the character of the preparation and correct choice of container and closure. Cause (ii) involves reaction with closure or container, and careful investigation may be necessary to decide which. The writer has encountered closures which were adequate so long as the preparation did not wet them for some time but the bottles had been stored horizontally, with disastrous results. Again, thin protecting layers on closures may become loosened or pin-holed, with resultant trouble if a liquid reaches the closure. As stated previously, water and aqueous solutions can react very slowly with glass, alkali being preferentially extracted from the glass leaving a minute decomposed layer richer in silica than the body of the glass. This layer may, under suitable conditions, develop until it falls away and is seen as "flakes" in the solution. If a glass has suffered to this extent its surface often shows iridescent or whitish patches after rinsing and drying. Analysis of the separated flakes reveals their origin. Some samples investigated by the writer, resulting from the storage of neutral aqueous solutions or water, have contained quite 80 per cent. of SiO_2 with CaO, MgO, and

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Al_2O_3 , the flakes differing in composition from the glass, as expected after removal of alkali. When these flakes were washed with hot hydrochloric acid nothing but SiO_2 remained, again showing that they were not of the glass itself. Flakes examined from acidic solutions in glass have been found to consist almost entirely of SiO_2 , and they have appeared as minute, thin, iridescent, glistening particles which settled slowly. Quite different in appearance and settling tendency are precipitates produced by reaction of a liquid with the matter extracted from glass as in the precipitation of alkaloid solutions by alkali.

Sodium phosphate and citrate, and caustic alkali solutions relatively quickly produce flakes from some glasses. In some cases decomposition of the glass may be proceeding without visible sign, as the writer has known of some boric oxide-containing glasses being dissolved slowly but completely in boiling strong caustic soda solution, remaining bright until final collapse on reaching wafer thickness. This susceptibility of glass to alkaline solutions can be reduced by choice of composition as will be shown in a paper soon to be published by the writer and others, and as indicated by the results represented in Figure 3, but when it is known that interaction is likely it might be helpful if a warning be issued to keep the packages cool. It is not generally realised that temperatures inside containers exhibited in windows may rise to 30°C . in this country.

THE PROTECTION OF LIGHT-SENSITIVE PREPARATIONS

The solar radiation transmissions of glasses can be controlled by adjustment of chemical composition and conditions of production, hence, by the choice of the right glass as container adequate protection can be given to sensitive materials. The famous "Crookes" glass and those of the "Noviol" type³⁵ absorb ultra-violet radiation; common "colourless" glass transmits throughout the visible range but absorbs in the ultra-violet, whilst glasses have been developed to absorb infra-red rays. Recently, attempts have been made to produce glasses transmitting well in the visible whilst absorbing in the ultra-violet, as reported, for instance, by Čtyroky³⁶. Amber, blue and green glasses are often used in the pharmaceutical industry and in Figures 4 and 5 are given the transmission curves (determined by Mr. D. K. Hill in this Department) for such glasses, for a colourless glass, and a medium-green bottle glass, taken from recent trade supplies.

These curves show clearly that, quite unlike the colourless glass (Fig. 5, curve 9) each of the others exerts considerable selective absorption, the "actinic" or yellow green (curves 5 and 6) "cutting off" completely at $400\text{ m}\mu$, the amber (Fe-Mn) (curves 1 and 2) transmitting slightly at this wavelength, with increasing transmission until the infra-red region is reached, the medium-green bottle glass (curves 3 and 4) transmitting to some extent throughout the visible range but absorbing somewhat in the infra-red, whilst the blue (curves 7 and 8) transmits over 80 per cent. at $400\text{ m}\mu$ with a rapid drop in transmission to about $540\text{ m}\mu$ and again at 600 to 650 , but with considerable transmission in the infra-red.

Thus, for protection against ultra-violet radiation the yellow-green glass

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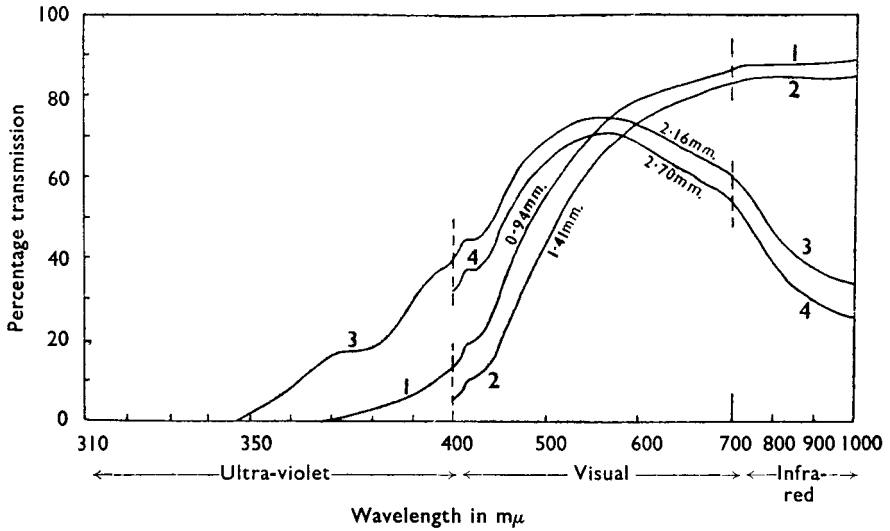


FIG. 4. Transmission curves.

- | | | | | | |
|----|--|----|----|-----------|----------|
| 1. | Amber vial (Fe-Mn) | .. | .. | thickness | 0.94 mm. |
| 2. | " | " | " | " | 1.41 mm. |
| 3. | Medium green bottle (Fe ⁺⁺ -Fe ⁺⁺⁺) | | | thickness | 2.16 mm. |
| 4. | " | " | " | " | 2.70 mm. |
- (Hill.)

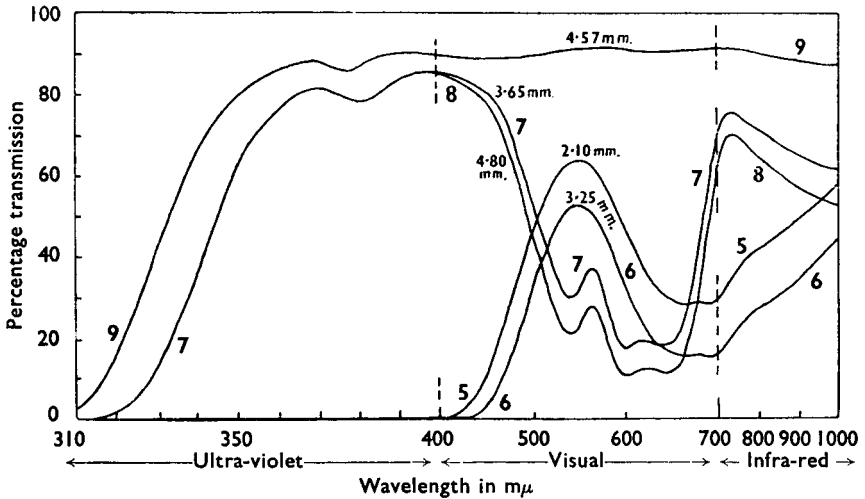


FIG. 5. Transmission curves

- | | | | | |
|----|-----------------------------|-----------|----|----------|
| 5. | "Actinic" green bottle (Cr) | thickness | .. | 2.10 mm. |
| 6. | Blue "bottle" (Co) | " | .. | 3.25 mm. |
| 7. | Blue "bottle" (Co) | " | .. | 3.65 mm. |
| 8. | "Actinic" green bottle | " | .. | 4.80 mm. |
| 9. | Colourless medicine bottle, | thickness | .. | 4.57 mm. |
- (Hill.)

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is the best tested here, followed by the iron-manganese amber. The green glasses would give the greatest protection from infra-red rays. Of course, an increase in the thickness of a glass specimen increases its absorption.

In order to facilitate the comparison of the absorbing powers per unit (1 mm.) thickness of the glasses studied, the extinction coefficients (k) have been calculated from the curves given in Figures 4 and 5, and the coefficients have been plotted against wavelength in Figure 6. The equation relating k with the percentage transmission (T) is, $T = (1-R)^2 \times 10^{-kt}$ where t is the glass thickness in mm. and R is the reflection loss from one glass surface.

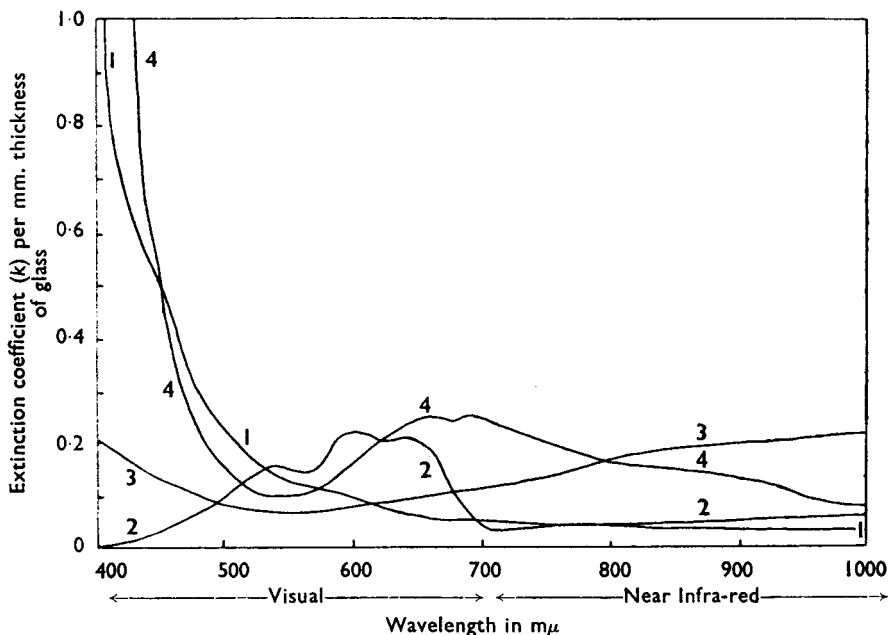


FIG. 6. Extinction coefficients

1. Amber vial (Fe-Mn)
2. Blue bottle (Co)
3. Medium green bottle (Fe⁺⁺-Fe⁺⁺⁺)
4. Actinic green bottle (Cr)

(Hill.)

A high value of k at any wavelength indicates high absorption, or low transmission. Thus, the actinic green and the amber glasses have high values for k at 400 m μ . (Fig. 6, curves 1 and 4.)

Comprehensive, recent publications dealing with coloured glasses, giving transmission curves for a wide range of glasses, are due to Weyl³⁷, and to Moore *et al.*^{38,39,40}

THE CLEANING OF GLASS

For cleaning of unused glassware for testing it should be sufficient to use tap water followed by 3 washes with acetic acid (0.1N) being sure to

treat all the surface, then finally rinsing thoroughly, once with tap water then 4 times with distilled water, draining for 1 minute between washes. The vessels should be cleaned immediately before use. If used glass is to be cleaned for re-use some special reagent may be necessary, such as one of the proprietary detergents or even "chromic acid." The writer has limited experience of the latest types of synthetic detergents but remarks already made upon the action of alkaline solutions upon glass should be kept in mind. Rounsfel⁴¹ discussed the relative efficiency of caustic soda, sodium carbonate and solutions containing these in addition to phosphates including sodium hexametaphosphate and favoured the inclusion of the last named for exerting a satisfactory softening effect upon hard waters without producing scaling. The germicidal character of caustic soda is well known but it cannot be readily rinsed from glass, neither can potassium chromate in sulphuric acid, and the use of "chromic acid" is to be discouraged except in those rare cases where a strong oxidant is necessary to remove residues from previous use. Abrasion or chipping of the glass should be avoided.

CONCLUSION

In concluding I would say that glass possesses just those properties required of containers for the pharmaceutical industry. It is robust, transparent, or coloured to give any radiation-absorption desired; it can be moulded to please the eye and yet to provide a neck which can readily be closed to prevent ingress of gas and dust or leakage from within, or it can be sealed in a flame; it has a smooth, brilliant surface which can readily be cleaned, and when the type is correctly chosen it does not contaminate preparations stored in it, under normal conditions.

If close co-education and co-operation between the pharmaceutical and glass industries be attained there should be very few, if any, problems which defy solution.

I wish to express my thanks to Mr. D. K. Hill for the curves in Figures 4 to 6, and to Professor H. Moore for allowing the work to be done in the Department, to Mr. F. W. Hodkin for the data upon the extraction of arsenic from glass, and for permission to publish, and to Dr. J. Boow, Editor of the *Journal of the Society of Glass Technology*, for permission to reproduce the data in Figures 1 to 3.

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